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Physicochemical, Water Vapor Barrier and Mechanical Properties of Corn Starch and Chitosan Composite Films

Biodegradable flexible films were developed from corn starch (CS) and chitosan (CH); their microstructure, mechanical and barrier properties were evaluated. Chitosan and starch blend filmogenic suspensions showed a pseudoplastic behavior, similar to that of chitosan solutions. Smooth surfaces, homogeneous and compact film structures were observed from microstructure studies using scanning electron microscopy (SEM). The addition of glycerol reduced film opacity and increased film solubility of both CS and composite CS-CH films. Water vapor permeability values of composite CS-CH films plasticized with glycerol ranged between 3.76 and $4.54 \times 10^{-11} \text{ g s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1}$, lower than those of the single component films. CS-CH films were resistant and their flexibility increased with glycerol addition. Tensile strength values of CS-CH films were comparable to those of low-density and high-density polyethylenes but lower than that obtained for cellophane, however, composite biodegradable films showed lower elongation at break values than the synthetic commercial ones. In conclusion, CS-CH films can be described as biofilms with a homogeneous matrix, stable structure and interesting water barrier and mechanical properties, with great possibilities of utilization, and with the advantage of biodegradability.

Keywords: Biodegradable composite films; Corn starch; Chitosan; Physicochemical properties; Water vapor permeability; Mechanical properties

1 Introduction

Biological recycling of polymers must be considered as an alternative to more traditional recycling procedures and this has stimulated researchers to synthesize new polymers that can be returned to the biological cycle after use. Therefore the use of agricultural biopolymers that are easily biodegradable not only would solve these problems, but would also provide a potential new use for surplus farm production [1].

Over the last few years, the interest in biodegradable films and films made from renewable and natural polymers has increased. Water-soluble polysaccharides such as starch, chitosan, cellulose derivatives, alginate, carrageenan and pectin can form biodegradable and edible films [2–6]. Numerous studies have been carried out to analyze the properties of starch-based films [7–12].

In absence of additives, films made from starch or amylose are brittle and sensitive to water (hygroscopic). The addition of plasticizers overcomes starch film brittleness

and improves flexibility and extensibility. Occasionally the plasticizers are used only to facilitate the polymer processing. Water, oligosaccharides, polyols and lipids are different types of plasticizers widely used in hydrocolloid-based films [13].

On the other hand, chitosan [β -(1–4)-2-amino-2-deoxy-D-glucopyranose] is a natural polymer formed by deacetylation of chitin, which is the second most abundant biopolymer in the nature after cellulose [14]. The production of chitosan from crustacean shells, wastes of the seafood industry, is economically feasible [15]. Compared with other polysaccharides, chitosan has several important advantages, including biocompatibility, biodegradability and no toxicity. Moreover, several studies have indicated the bacteriostatic and fungistatic action of chitosan [16–19].

Starch and chitosan are hydrocolloids with well-known good film-forming capacities. Both have been reported as potential materials for food packaging, especially as edible films and coatings [11, 20, 21]. However, the use of a mixture of chitosan and corn starch to obtain biodegradable films has not been extensively studied [5, 22, 23].

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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 efficiency of packaged foods conservation. The study of the microstructure and interactions of the film components also provide some insight into possible relationships between different physical properties.

The aim of this study was to develop flexible composite films based on corn starch and chitosan, to characterize them physicochemically and to evaluate their mechanical and water vapor barrier properties in comparison to the single component films.

2 Materials and Methods

2.1 Filmogenic suspensions

2.1.1 Preparation

Commercial corn starch was provided by Molinos Río de La Plata (Buenos Aires, Argentina) with 25% amylose. Commercial chitosan from crab shells with a minimum deacetylation degree of 85% was purchased from Sigma (St. Louis, MO, USA). Aqueous suspensions of 3.5, 5 and 6% (w/w) of corn starch were prepared and gelatinized at 95°C during 30 min in a Haake (Karlsruhe, Germany) thermostatic bath under continuous agitation.

After gelatinization, suspensions were cooled to 50°C and then glycerol (J.T. Baker, Xalostoc, México) was added as plasticizer. Glycerol concentration was 0.2856 g plasticizer per gram of corn starch in the suspension (dry basis).

A chitosan (CH) solution of 1% (w/w) was prepared by solubilizing it in 1% (v/v) aqueous acetic acid solution as described in a previous work [6], followed by vacuum filtration to eliminate insolubles [24].

Gelatinized corn starch suspensions without plasticizer (CS 3.5, 5 and 6%, w/w) or with plasticizer (CS+G) and chitosan solution (CH) were mixed in equal weight proportions to obtain the composite filmogenic suspensions. Thus 100 g of the blends CS+CH and CS+G+CH were obtained by mixing 50 g of CS or CS+G suspension with 50 g of CH solution.

2.1.2 Characterization

Filmogenic suspensions were characterized by polarized light microscopy using a Leica DMLB microscope

(Leitz, Wetzlar, Germany) to analyze starch gelatinization process.

Rheological characterization of the filmogenic suspensions was performed with a Rheo Stress 600 Thermo-Haake (Haake, Karlsruhe, Germany) rotational and dynamic rheometer using a plate-plate sensor system PP35 at controlled temperature (25°C). Shear stress was determined as a function of shear rate between 0 and 500 s⁻¹. The Ostwald-de Waele model ($\sigma = k \dot{\gamma}^n$) was applied to determine consistency index (k) and flow behavior index (n). Apparent viscosities were calculated at 500 s⁻¹.

2.3 Film preparation

All the films were obtained by casting of 40 g filmogenic suspensions previously described onto rectangular acrylic plates (10 × 20 cm). The suspensions were dried (60°C) in a ventilated oven to constant weight (about 6 h). Translucent films which could be easily removed from the plate were obtained. Films were stored at 20°C and a relative humidity (RH) of 65% in a controlled temperature and humidity room.

2.4 Physicochemical characterization of films

2.4.1 Optical properties

Film opacity was determined using a procedure described by Gontard *et al.* [25]. A film sample was cut into a rectangle and placed on the internal side of a spectrophotometer cell. The absorbance spectrum (400–800 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 and determined by integration. The opacity was expressed as absorbance units × nanometers (AU × nm).

Film color was determined by a Minolta colorimeter CR 300 Series (Tokyo, Japan) calibrated with a standard ($Y = 93.2, x = 0.3133, y = 0.3192$). The CIELab scale was used, lightness (L) and chromaticity parameters a^* (red – green) and b^* (yellow – blue) were measured. Measurements were performed placing the film sample over the standard. Samples were analyzed in triplicates, recording four measurements for each sample.

Color differences (ΔE) were also calculated by the following equation:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where:

$$\Delta L^* = L^* - L_0^*$$

$$\Delta a^* = a^* - a_0^*$$

$$\Delta b^* = b^* - b_0^*$$

being: L_0^* , a_0^* , b_0^* , the color parameter values of the standard and L^* , a^* , b^* , the color parameter values of the sample.

2.4.2 Equilibrium moisture content

Equilibrium moisture content 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 triplicates and results were expressed as (%) of moisture content of samples.

2.4.3 Film thickness

Film thickness was determined using a digital coating thickness gauge Elcometer A 300 FNP 23 (Manchester, England) for non-conductive materials on non-ferrous substrates. In order to compare biodegradable and synthetic films commercial cellophane, low-density polyethylene (LDPE) and high-density polyethylene (HDPE) films were also tested. Fifteen values were randomly taken at different locations for each specimen and the mean value was reported. Thickness was also measured by scanning electron microscopy (SEM).

2.4.4 Film solubility in water

Pieces of film of 2 × 3 cm were cut from each film and were stored in a desiccator with silica gel (0% RH) during 7 days. Samples were weighed to the nearest 0.0001 g and placed into test beakers with 80 mL deionized 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:

$$\% \text{ Solubility} = \left[\frac{(\text{Initial dry weight} - \text{Final dry weight})}{\text{Initial dry weight}} \right] \times 100 \quad (2)$$

Samples were analyzed at least in duplicate.

2.5 SEM observations

Films were observed by SEM using a JEOL JSM 6360 electron microscope (Tokyo, Japan). For cross-section observations films were cryofractured by immersion of

the sample in liquid nitrogen. Previous drying of the films was not necessary due to their low moisture content. 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. SEM observations of the cross-sections also allowed to evaluate film thickness. All samples were examined using an accelerating voltage of 10 kV.

2.6 Water vapor permeability (WVP)

Water vapor permeability tests were conducted using ASTM method E96 with several modifications as described in a previous work [26]. Each film sample was sealed over a circular opening of 0.00181 m² in a permeation cell that was stored at 20°C in a desiccator. 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 desiccator. After steady state conditions were reached (about 2 h), eight weight measurements were made over 10 h.

2.7 Mechanical properties

Tensile tests were performed in a texturometer TA.XT2i – Stable Micro Systems (Hasleware, Surrey, England) using a tension grip system A/TG. Probes of 6 × 0.7 cm were used; at least four probes were used for each film formulation. Synthetic commercial cellophane, LDPE and HDPE films were also tested.

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/μm), deformation at break (extension at the moment of rupture, mm), percent elongation at break (deformation divided by initial probe length and multiplied by 100,%) and elastic modulus (slope of the force-deformation curve, N/mm) were obtained from force vs. deformation curves according to the ASTM D882–91 method [27]. Tensile strength (MPa) was calculated by dividing maximum force by film cross section (thickness × width).

2.8 Statistical analysis

All experiments were performed at least in duplicates, with individually prepared and cast 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 Suspension characterization

Microscope observations under polarized light of the corn starch films with and without plasticizer showed that starch was totally gelatinized during the production of fil-

mogenic suspensions, regardless the starch concentration. Chitosan suspensions were homogeneous, and insoluble matter was not observed indicating the efficiency of the filtration process. Mixed suspensions of both hydrocolloids were homogeneous.

With regard to the rheological measurements, chitosan suspensions showed a pseudoplastic slightly thixotropic behavior, (Fig. 1a). However, starch suspensions showed a typical viscoelastic response, given by the presence of the characteristic overshoot peak that indicates the damage of the system structure (Fig. 1b); the presence of the plasticizer reduced the height of the overshoot peak.

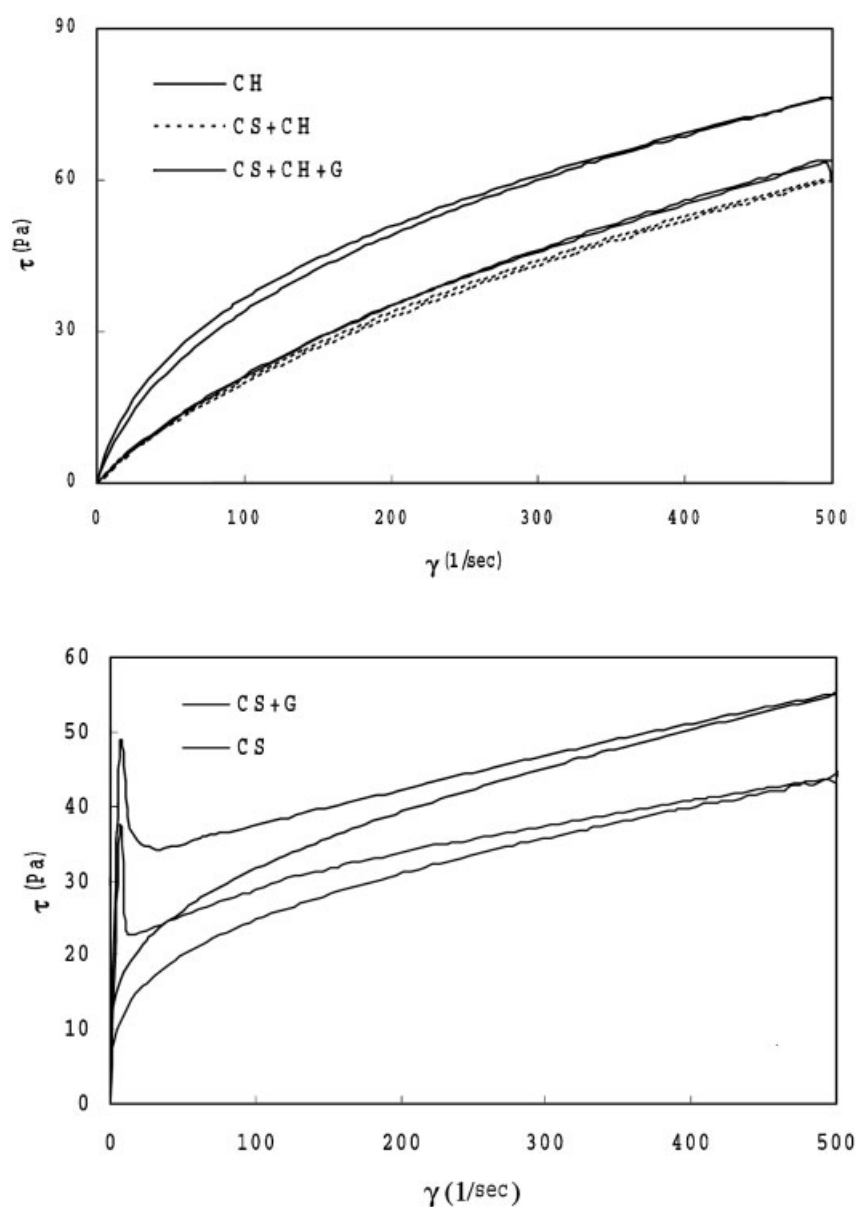


Fig. 1. Rheological behavior of the different filmogenic suspensions formulated with a) chitosan (CH), corn starch-chitosan (CS+CH) and corn starch-chitosan-glycerol (CS+G+CH); b) corn starch (CS) and corn starch with glycerol (CS+G). Filmogenic suspensions were formulated with 5% corn starch.

The Ostwald-de Waele model was fitted to the experimental data: a) in the cases of pseudoplastic behavior during all the range of deformation rates and b) after the peak of structural damage was overpassed for viscoelastic suspensions. The obtained rheological parameters (consistency index and behavior coefficient) are shown in Tab. 1. Glycerol addition decreased the consistency index of the filmogenic suspensions and increased their flow behavior index (Tab. 1). Chitosan-starch suspensions showed a pseudoplastic behavior, similar to those obtained with chitosan suspensions (Tab. 1). Thus, the presence of chitosan in the filmogenic suspension decreased the viscoelastic behavior leading to the absence of the overshoot peak.

Apparent viscosities at 500 s^{-1} were $150\pm 1.15\text{ mPa s}$ for chitosan and $87\pm 0.35\text{ mPa s}$ for the 5% corn starch suspensions and $120\pm 1.15\text{ mPa s}$ for the mixture, regardless the plasticizer addition (Tab. 1). A similar trend was observed for the suspensions with different corn starch concentrations.

3.2 Film characterization

Homogeneous, thin, flexible and transparent films were obtained from CS, CH and combined suspensions. All the films were easily removed from the cast plate. CS films

were colorless and CH ones had a slightly yellow appearance. Even though, the intensity of the yellowness was negligible when compared to values reported for whey protein based films [28]. Polysaccharide films are free of the problems associated with protein (such as Maillard reactions) and lipid films [29].

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. Tab. 2 shows that CH films were the most transparent and CS ones the most opaque, the opacity increasing with starch concentration. Even though, these values were lower than those reported by Gontard and coworkers [25] for wheat gluten films obtained under different solubilization conditions. Glycerol addition reduced film opacity. Blending CS with CH allowed to reduce opacity but increased the yellowness.

Lightness (L) values did not differ significantly ($P>0.05$), regardless of film formulation, and exhibited a value around 96.3 ± 0.6 . Tab. 2 shows the b^* values of CH films were significantly ($P<0.05$) higher than those of CS films. Plasticizer addition did not modify b^* values while the blending of CS with CH increased b^* values. Since b^* was the parameter with the highest contribution to color difference, ΔE showed a similar trend.

Tab. 1. Rheological characterization of composite corn starch and chitosan suspensions.

Suspension composition	Rheological characterization			
	Consistency index (k)	Flow behaviour index (n)	r^2	Apparent viscosity at 500 s^{-1} [$\text{mPa}\cdot\text{s}$]
Corn starch ^a (CS)	11.94 ± 3.72^b	0.254 ± 0.021^b	0.9783	109.8 ± 0.35
CS + G	8.86 ± 3.73	0.295 ± 0.050	0.9606	87.5 ± 0.65
CS + CH	0.963 ± 0.11	0.666 ± 0.02	0.9994	121.0 ± 1.0
CS + G + CH	0.854 ± 0.12	0.682 ± 0.004	0.9995	126.0 ± 1.2
Chitosan (CH)	3.776 ± 0.19	0.484 ± 0.15	0.9985	150.0 ± 1.2

^a CS concentration: 5 g/100 g filmogenic suspension and G: glycerol.

^b value \pm standard deviation.

Tab. 2. Optical properties of corn starch, chitosan and composite films.

Film composition	Film opacity ($\text{Au}\times\text{nm}$)	Film color	
		Color differences (ΔE)	Chromaticity parameter b^*
Corn starch ^a (CS)	138.0 ± 0.8^b	0.83 ± 0.16^b	2.20 ± 0.25
CS with glycerol (CS + G)	109.6 ± 0.9	0.60 ± 0.10	2.23 ± 0.08
CS with chitosan (CS + CH)	95.9 ± 1.05	1.74 ± 0.15	2.94 ± 0.15
CS with glycerol and chitosan (CS + G + CH)	88.7 ± 0.7	2.16 ± 0.19	3.68 ± 0.21
Chitosan (CH)	18.9 ± 1.1	3.79 ± 0.50	5.04 ± 0.32

^a CS concentration: 5 g/100 g filmogenic suspension.

^b value \pm standard deviation.

Tab. 3 summarized the physicochemical characterization of films. With regard to film solubility one-component films exhibited low values, CH ones being the most insoluble in water (Tab. 3). Although all films became rubbery when they were dipped in water, they maintained their integrity. At 100°C film solubility increased; plasticized films showed, as expected by the hydrophilicity of glycerol, the highest values. Similar results were obtained by *Laohakunjit* and *Noomhorm* [30] working on rice starch films plasticized with 20–45% (w/w) of glycerol and sorbitol which are in agreement with those used in the present work.

After drying, CS films exhibited the lowest equilibrium moisture content while the highest value was observed for CS+G films, due to the hydrophilic properties of the glycerol. All films showed smooth surfaces as observed by SEM (Fig. 2). No pores or cracks were detected by SEM observations even in those formulations that did not include glycerol as plasticizer. SEM observations of films with different CS concentrations did not show structural differences. Cross-sections of films showed homogeneous surfaces, without separation of phases between the two polymers, and a compact structure in the composite formulations (Fig. 2c). The homogeneous matrix of CS-CH films is an indicator of the structural integrity of the observed films, and consequently adequate mechanical properties (high resistance and elongation at break) are expected.

Cross-section observations of the films allowed to evaluate film thickness; the obtained results are also shown in Tab. 3. They are in agreement with those obtained using a digital coating thickness gauge. A mean thickness of 13.9 μm was observed for CH films; in the case of CS films, thickness ranged between 69.2 and 111 μm , increasing with CS concentration. Intermediate values were exhibited by the composite films (Tab. 3) and a similar trend was observed with CS concentration.

3.3 Water vapor permeability

Fig. 3 shows the effect of corn starch concentration (3.5, 5 and 6%, w/w) on the WVP of the CS-CH films. WVP values ranged between 13.2 and $21.2 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ for CS films and for CH films the WVP was $4.5 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$.

With regard to the effect of CS concentration ANOVA test indicated that films formulated with 5 or 6% CS did not differ significantly although 3.5% CS exhibited the lowest WVP values.

For all the tested starch concentrations, the addition of glycerol at a proportion of 0.2856 g plasticizer per gram of corn starch in the suspension, decreased WVP of CS films (Fig. 3). In previous works, we found that the addition of plasticizers improved water vapor barrier properties of starch based films and coatings [21]. *McHugh* and *Krochta* [31] found similar results for alginate and pectin films.

Blending CS with CH decreased WVP of composite films (Fig. 3). Plasticized composite CS-CH films had WVP values of 3.8 – $4.5 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$, which were lower than those of the individual component films. This result could be attributed to the development of a more compact and dense structure as observed by SEM, indicating hydrocolloids compatibility as well. This interaction is based on the similar chemical and geometrical linear structure of both polymers and could be reinforced by the different charge density of the substituents. Accordingly, *Chen* et al. [32] also stressed that physical properties highly depend on the interaction between polymer chains whose molecules are chemically or geometrically regular in structure.

Films developed in the present study showed lower WVP, with an order of magnitude below some protein films and even lower than other polysaccharide based films

Tab. 3. Physicochemical properties of corn starch, chitosan and composite films.

Film composition	Film solubility [%]		Moisture content [g water/ 100 g film]	Film thickness [μm]	
	At 25°C	At 100°C		Digital coating thickness gauge	SEM
Corn starch ^a (CS)	13.48±0.03	14.8±0.8	9.1±0.3	63.1±1.7	69.2±1.9
CS with glycerol (CS + G)	30.3±1.2	30.5±1.6	25.2±1.1	44.4±0.9	47.3±1.9
CS with chitosan (CS + CH)	15.5±0.5	17.2±0.4	10.1±0.5	51.5±7.8	56.1±11.3
CS with glycerol and chitosan (CS + G + CH)	24.2±2.5	27.6±0.5	13.9±0.5	52.2±1.4	57.0±2.1
Chitosan (CH)	8.6±1.6	11.0±0.8	15.0±0.9	15.2±1.8	13.9±2.9

^a CS concentration: 5 g/100 g filmogenic suspension.

^b value \pm standard deviation.

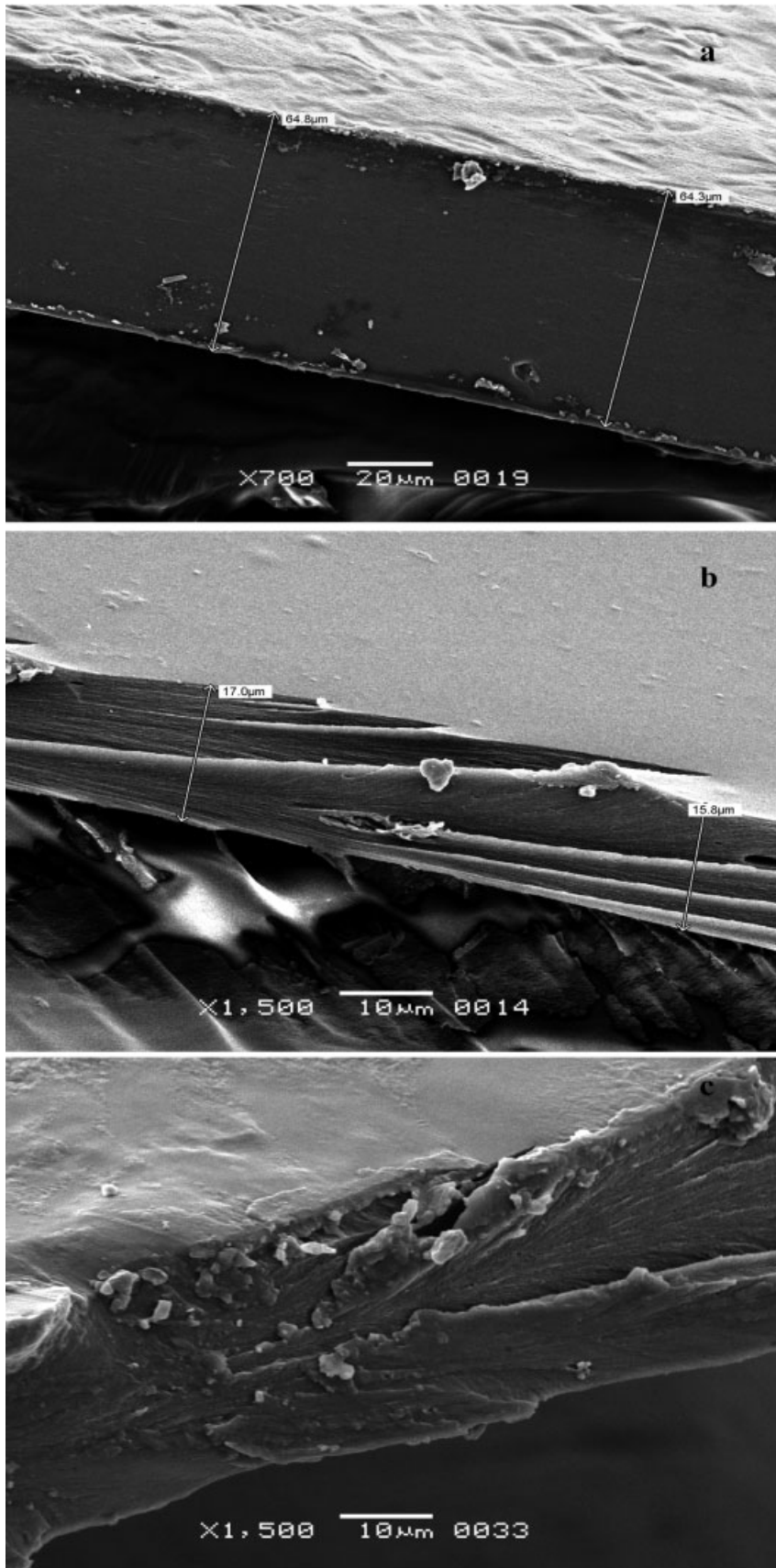


Fig. 2. Cross-section micrographs of different films formulated with a) corn starch (CS), b) chitosan (CH) and c) corn starch-chitosan plasticized with glycerol (CS+G+CH). Films were formulated with 5% corn starch. Magnification is indicated in the micrographs.

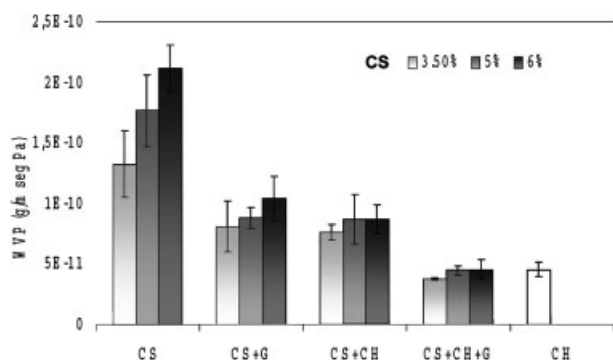


Fig. 3. Effect of corn starch concentration on water vapor permeability (WVP) of films formulated with corn starch (CS), chitosan (CH), corn starch plasticized with glycerol (CS+G), corn starch and chitosan (CS+CH) and corn starch and chitosan plasticized with glycerol (CS+G+CH).

reported in literature [4, 10, 11, 13, 26, 33–35]. With regard to synthetic polymers, CS-CH films have WVP values lower than those reported for cellophane (Tab. 3). However, they are higher than for LDPE, the most commonly polymer used in the food packaging industry (Tab. 4).

3.4 Mechanical properties

The stress-strain curves of chitosan and starch films without plasticizer show the typical pattern of brittle materials, because they exhibited high values of tensile stress at break, breaking force and elastic modulus and low values of strain at maximum breaking force, i.e. low elongation values [12, 36, 37] (Fig. 4). Blends of chitosan and corn starch were not significantly different from one-

component films. Plasticized films exhibit the stress-strain behavior of ductile polymers. In these systems, the expected effect of plasticizer addition on mechanical properties was observed, since strain at break increased and stress decreased compared with unplasticized films (Fig. 4). A similar trend was obtained by *Mali et al.* [12] working with cassava starch films plasticized with glycerol or sorbitol, regardless the plasticizer used.

CH films were brittle and rigid, because they showed high elastic modulus and tensile strength values and low elongations at break (Fig. 5). There is a broad range of reported data in literature of mechanical properties of CH films; differences may be attributed to CH composition and suppliers, as well as film preparation techniques [32, 38, 39].

CH films exhibited a more brittle behavior (higher maximum breaking force and elastic modulus values) than CS films, although when tensile strength was evaluated significant differences ($P < 0.05$) were detected only with films formulated with 3.5 and 5% CS (Fig. 5a). A similar trend for maximum breaking force and tensile strength was observed in films formulated with different starch sources. *Mali et al.* [12] working on cassava starch films reported similar tensile strength values to those obtained in the present work.

Flexibility can be related with the higher elongation values at breaking point. The addition of plasticizer improved the flexibility of films; corn starch films plasticized with glycerol showed the most flexible behavior since they exhibited higher deformations and elongations than films from starch-chitosan blend. Similar results were obtained

Tab. 4. Comparison of water vapor permeability and mechanical properties of corn starch, chitosan and composite films with and commercial synthetic films.

Film type		Water vapor permeability $\times 10^{11}$ [g s ⁻¹ m ⁻¹ Pa ⁻¹]	Mechanical properties	
			Tensile strength [MPa]	Elongation at break [%]
Biodegradable	CS ^a	17.7±2.9	47.4±1.5	3.6±0.5
	CS + G	8.7±0.2	7.1±0.4	22.5±4.2
	CS + CH	8.8±0.9	24.7±4.0	3.0±0.2
	CS + CH + G	4.5±0.4	28.7±6.8	11.7±4.0
	CH	4.5±0.6	60.7±5.8	3.3±0.4
Synthetic	Cellophane	8.4 ^b	85.8±8.9	14.4±2.4
	LDPE	0.0914 ^c	16.2±4.0	68.7±14.9
	HDPE	0.023 ^c	27.8±3.2	150.0±18.5

^a CS: corn starch at a concentration of 5%.

^b *Shellhammer & Krochta* [41].

^c *Smith* [42].

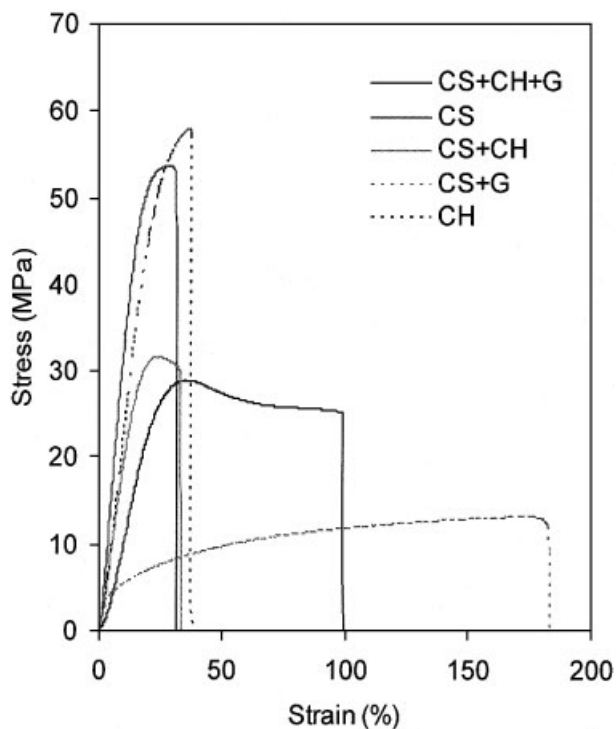


Fig. 4. Tensile mechanical behavior (stress vs strain curves) of films formulated with: corn starch (CS), chitosan (CH), corn starch plasticized with glycerol (CS+G), corn starch with chitosan (CS+CH) and corn starch with chitosan and glycerol (CS+G+CH). Films were formulated with 5% corn starch.

by *Laohakunjit and Noomhorm* [30]. 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 chain movements.

Glycerol can interact strongly with the CS matrix because both molecules are chemically similar and thus CS+G films exhibit a particular behavior compared with those of CS+CH+G films. When glycerol is added to a composite CS-CH matrix the interactions are not as extensive and strong as in the CS film, although both hydrocolloids are compatible.

Linear amylose molecules can readily aligned closely or associate with similar linear chitosan molecules to form the intermolecular hydrogen bonds [23].

No significant differences ($P > 0.05$) were detected between elongation values of films formulated with different corn starch concentrations (Fig. 5); in the case of tensile strength significant differences between the extreme CS

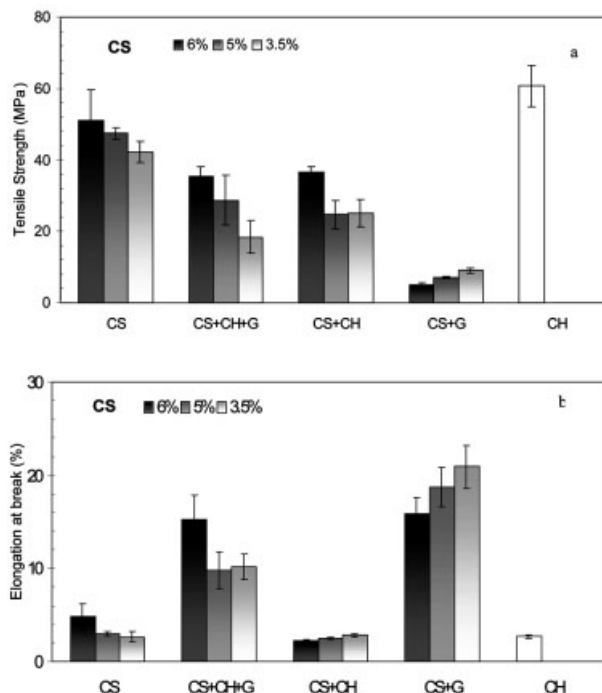


Fig. 5. Effect of corn starch concentration on the mechanical properties of films formulated with corn starch (CS), chitosan (CH), corn starch plasticized with glycerol (CS+G), corn starch and chitosan (CS+CH) and corn starch and chitosan plasticized with glycerol (CS+G+CH). a) Tensile strength and b) elongation at break.

concentrations (6 and 3.5%) were observed. Composite films exhibited higher deformation values and lower elastic modulus than those of CH.

Tab. 4 summarizes the results of the mechanical properties measured in biodegradable and synthetic films. Tensile strength values of CS-CH films were in the range of those of LDPE and HDPE but lower than that obtained for cellophane (Tab. 4). However, synthetic polymers such as LDPE and HDPE exhibited the highest elongation at break values (Tab. 4). Similar results were reported for synthetic films by *Cunningham et al.* [40].

4 Conclusions

Chitosan-starch blend suspensions showed a pseudo-plastic behavior, similar to that obtained with chitosan suspensions. Glycerol addition decreased the consistency index of the filmogenic suspensions.

Corn starch (CS), chitosan (CH) and combined suspensions led to homogeneous, thin and flexible films. CS films were colorless and opaque whereas CH films had a

slightly yellow appearance and were transparent; the addition of glycerol reduced film opacity of both CS films and composite ones.

After drying, CS films showed the lowest equilibrium moisture content while the highest values were observed for CS films plasticized with glycerol.

All films maintained their integrity when they were dipped in water even at 100°C; plasticized films showed the highest solubility values. The lowest values were observed for CH films.

An homogeneous matrix without phase separation was observed by SEM in CS-CH films; this structural integrity should evidence the compatibility of the hydrocolloids.

Chitosan addition improved markedly the water vapor barrier properties of starch films increasing the potential applications of composite starch-chitosan films.

CS-CH films were resistant and their flexibility increased when glycerol was added. Tensile strength values of CS-CH films were comparable to those of low-density and high-density polyethylenes but lower than that obtained for cellophane, however, composite biodegradable films showed lower elongation at break values than the synthetic commercial films.

In conclusion, CS-CH films can be described as biofilms with a homogeneous matrix, stable structure and interesting water barrier and mechanical properties with great possibilities of utilization, and with the advantage of biodegradability.

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