Microstructural Characterization of Plasticized Starch-Based Films

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Edible films were developed using different starch sources (corn starch and amylomaize). Starch suspensions were cold gelatinized with NaOH; either glycerol or sorbitol were used as plasticizer. Films were characterized by Differential Scanning Calorimetry (DSC), X-ray diffraction, Scanning Electron Microscopy (SEM) and gas (CO_2 and O_2) permeabilities. SEM observations showed that plasticizer addition was necessary for film integrity. The evaluation of film formation by DSC indicated that cold gelatinization was the main factor of thermal transitions. Film crystallinity was analyzed by DSC and X-ray diffraction during storage. For all tested formulations, film crystallinity increased while gas permeability decreased during storage. Films containing glycerol or sorbitol showed a lower crystalline/amorphous ratio by X-ray diffraction and DSC than unplasticized films. Amylomaize films with higher crystalline/amorphous ratio gave lower gas permeabilities than the corresponding corn starch films; films containing sorbitol showed lower permeability values than those containing glycerol.

Keywords: Starch films, edible films, plasticizers, X-ray diffraction, differential scanning calorimetry, microstructure.

1 Introduction

Since the 1970s, polar biopolymers such as polysaccharides and proteins have been studied as prospective replacers of synthetic polymers in the film and plastic industries. The potential benefits of these films are both environmental and cost-related. Traditional techniques for processing thermoplastic polymers have been adapted to hydrophilic polymers such as starch and gelatin [1, 2]. However, the main disadvantages of biopolymer materials are their poor mechanical properties. In several patents this drawback was overcome by blending starches with synthetic polymers obtaining biofragmentable materials with improved mechanical properties [2]. Another application is the use of biopolymers as coatings of certain foods; while the coating film acts as a protective barrier, the food provides the necessary support.

The use of edible films and coatings is constantly increasing in the food industry. Coatings can help to meet the many challenges involved in the storage and marketing of foods that are nutritious, safe, of high quality, stable and economic [3–5]. Several types of composite films and coatings reported in the food literature over the last ten years contain a polysaccharide base. For these films the advantages are more in the area of decreasing gas exchange rather than retardation of water loss due to their hydrophilic nature [6]. In the case of vegetables the application of polysaccharide-based coatings positively affect fruit physiology by delaying senescence, extending storage life [7–9].

The functional, organoleptic, nutritional and mechanical properties of an edible film can be modified by the addition of various chemicals in minor amounts. Plasticizers, such as glycerol, sorbitol and polyethylene glycol are often used to modify the mechanical properties of the film. These compounds decrease intermolecular attractions between adjacent polymeric chains, thus increasing film flexibility [10]. Incorporation of these additives may, however, cause significant changes in the barrier properties of the film.

Mechanical and barrier properties of films and coatings depend on their microstructure and determine the applications [11]. Thus, the study of microstructure and the interaction of film components is important, both for the fundamental aspects of material science and from a practical point of view. Most methods used in the characterization of the solid state are based on the detection of structural properties such as the crystalline structure. The methods used to study crystallinity are microscopy and X-ray diffraction. X-ray diffraction is probably the most important technique in observing properties of crystalline solid materials, polymers, and foods [12, 13]. Besides, changes in physical state are observed by analyzing changes in the thermodynamic quantities, which can be measured with calorimetric techniques and thermal analysis. In addition to the changes in thermodynamic quantities and molecular mobility, phase transitions affect physicochemical properties, mainly the barrier properties.

The objectives of the present work were to characterize physicochemically the microstructure of edible starch-based films by DSC, X-ray diffraction, SEM and determination of barrier properties.

2 Materials and Methods

Two starches were used for film formulations: commercial corn starch (Molinos Río de la Plata, Argentina) with 250 g/kg amylose and high-amylose corn starch, i.e. amylomaize (Amylomaize VII, Amaizo, USA) with 650 g/kg amylose.

2.1 Film preparation

In all cases, 20 g/L starch aqueous solutions were cold gelatinized with 10 g/L aqueous NaOH to obtain the films [14, 15]. These suspensions were then neutralized with 7 M H_3PO_4. Either glycerol or sorbitol (Merck, USA) were added as plasticizers after neutralization, at a concentration of 20 g/L in the formulation. Starch suspensions were cast on polyethylene films 6 cm in diameter and placed in an electrical oven with leveled stages. Samples were dried at 60 °C until constant weight (approximately 8 h). Films were stored in a room at 20 °C and 63.8% relative humidity.

2.2 X-ray diffraction

Samples were analyzed between 2 θ = 3 to 2 θ = 40° in an X-ray diffractometer Philips PW 1390 (The Netherlands) using Cu K$_\alpha$ radiation (λ = 1.5418 Å), 40 kV and 20 mA. Modifications of crystalline structure of films during storage at 20 °C and 63.8% relative humidity were evaluated.

2.3 Differential scanning calorimetry

Film samples were tested in a Polymer Laboratories DSC (Rheometric Scientific, Surrey, UK) working under a PL-V5.41 software. Indium was used to calibrate temperature and heat flux. Samples of 1.5–2 mg were weighed in aluminum pans and were hermetically sealed; an empty pan was used as reference. Samples were heated from 0 to 130 °C with 10 °C/min heating rate; then, the pans were punctured and dried until constant weight at 100 °C to obtain the dry weight of the sample. Gelatinization enthalpies ΔH (mJ/mg), onset and peak transition temperatures were obtained from the thermograms.

Starch edible films prepared by cold gelatinization as previously described were compared with films formulated with 70 g/L corn starch gelatinized by thermal treatment (15 min at 90 °C). To analyze the effect of neutralization, cold-gelatinized films were prepared with 20 g/L corn starch and 10 g/L NaOH without neutralization and with neutralization, using either 7 M H_3PO_4, 9 M H_2SO_4 or 6 M HCl. To analyze the effect of water content of films, samples (cold-gelatinized and neutralized with 7 M H_3PO_4) were stored in dissectors containing saturated salts of constant relative humidity: silica gel (0% relative humidity), $MgCl_2 \cdot 6\,H_2O$ (33.3%), NaCl (75%) and $K_2Cr_2O_7$ (98.2%).

2.4 Determination of degree of polymerization

Polymerization degrees (PD) of starch suspensions treated with NaOH, neutralized and non-neutralized, were determined by a colorimetric technique. The anthrone-sulfuric acid method was applied to determine starch concentration as glucose and then the reducing residues of the starch were measured using a modification of the Park-Johnson method [16]. The polymerization degree was calculated dividing the total number of glucose units (anthrone-sulfuric acid method) by the reducing residue data (Park-Johnson method). Assays were performed in duplicates.

2.5 Film characterization

2.5.1 Thickness determination

Thickness of films was determined using a digital coating thickness gauge Elcometer A 300 FNP 23 (UK) for non-conductive materials on non-ferrous substrates as described in a previous work [17].

2.5.2 Scanning electron microscopy

A JEOL JSMP 100 (Japan) electron microscope was used. Film pieces were mounted on aluminum stubs using a double-sided tape and then coated with a layer of gold (40–50 nm), allowing surface and cross-section visualization. All samples were examined using an accelerating voltage of 5 kV.

2.5.3 Gas permeability

CO_2 and O_2 permeabilities of the films were assessed by the accumulation method in a specially designed stainless steel cell as described in [17]. Gas concentration was measured in a gas chromatograph Varian Star 3400 cx (USA) with a Porapack Q column to determine CO_2 concentration and a molecular sieve column to determine O_2 concentration, using He as carrier. Gas permeability of films was calculated and expressed in [$cm^3\ m^{-1}\ s^{-1}\ Pa^{-1}$] at standard temperature and pressure conditions (20 °C and 101.3 kPa). Gas permeability assays were performed at 20 °C and 63.8% relative humidity (RH).
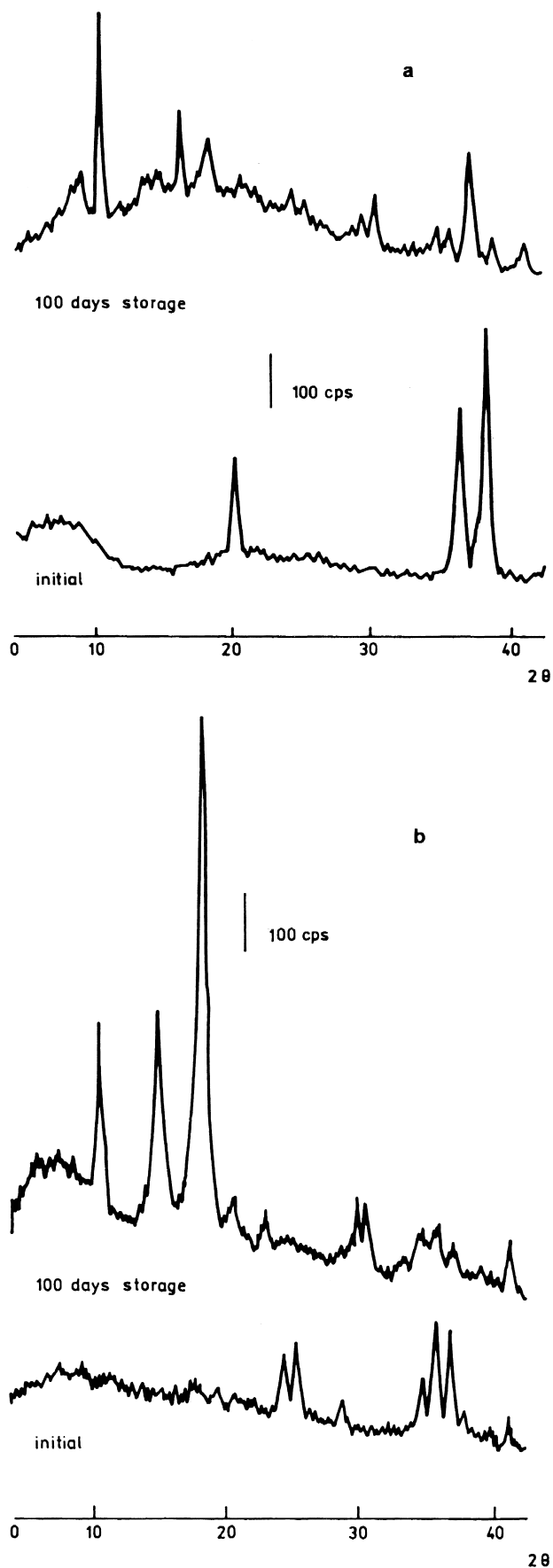

Fig. 1. Effect of starch type and storage time on X-ray diffraction pattern of a) corn starch and b) amylomaize starch films stored at 20 °C and 63.8% relative humidity at initial time and 100 d of storage (cps = counts per second).
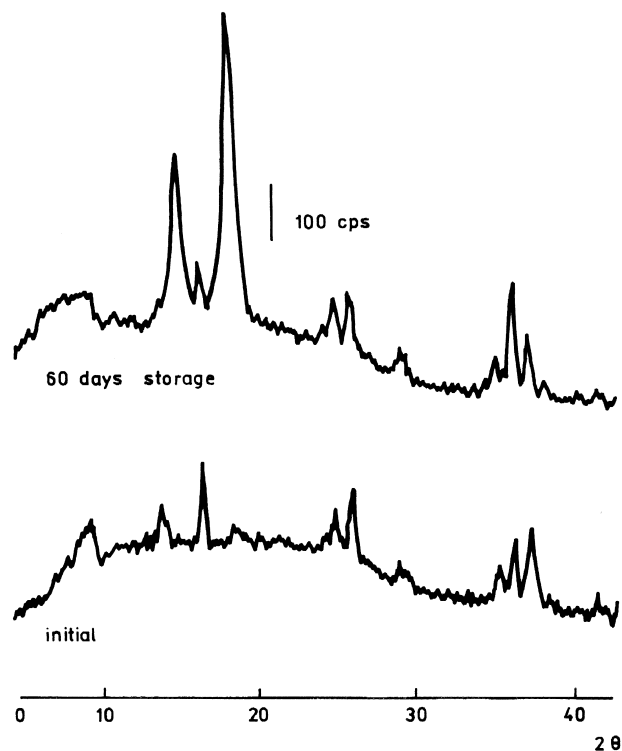
2.6 Statistical analysis

Systat-software (SYSTAT, Inc. USA, 1990) version 5.0 was used for all statistical analyses. Analysis of variance (ANOVA), Fisher LSD means comparison test and regression analysis were applied. The significance levels used were 0.05 and 0.01.

3 Results and Discussion

3.1 X-ray diffraction

X-ray diffraction patterns of starch composites are characterized by absorption peaks and an amorphous zone; the higher the amorphous zone the lower the crystallinity of the sample. At initial storage time, peak patterns for corn and amylomaize films were different, but at 100 d storage time both patterns coincided in position, the peaks of amylomaize films having the highest intensities (Fig. 1 a and b). This result showed that both types of films reached a common crystalline structure of higher stability with increasing storage time. The crystallinity of the films was associated with the amylose content of the starch source, because corn starch films showed larger amorphous zones than amylomaize ones. The peak pattern observed at 100 d of storage corresponds to that reported by *Bader* and *Göritz* [18] for 20 g/L amylomaize films obtained by autoclaving. These authors attributed their findings to an A-type starch pattern and stated that the crystalline structure of amylomaize films only depends on drying temperature [18, 19].

Films without plasticizer showed higher crystallinity (higher peaks) than films containing plasticizer which showed a larger amorphous zone and lower peaks (Fig. 1b and 2). Films with glycerol did not modify their initial pattern with storage time; peaks only increased in intensity, maintaining t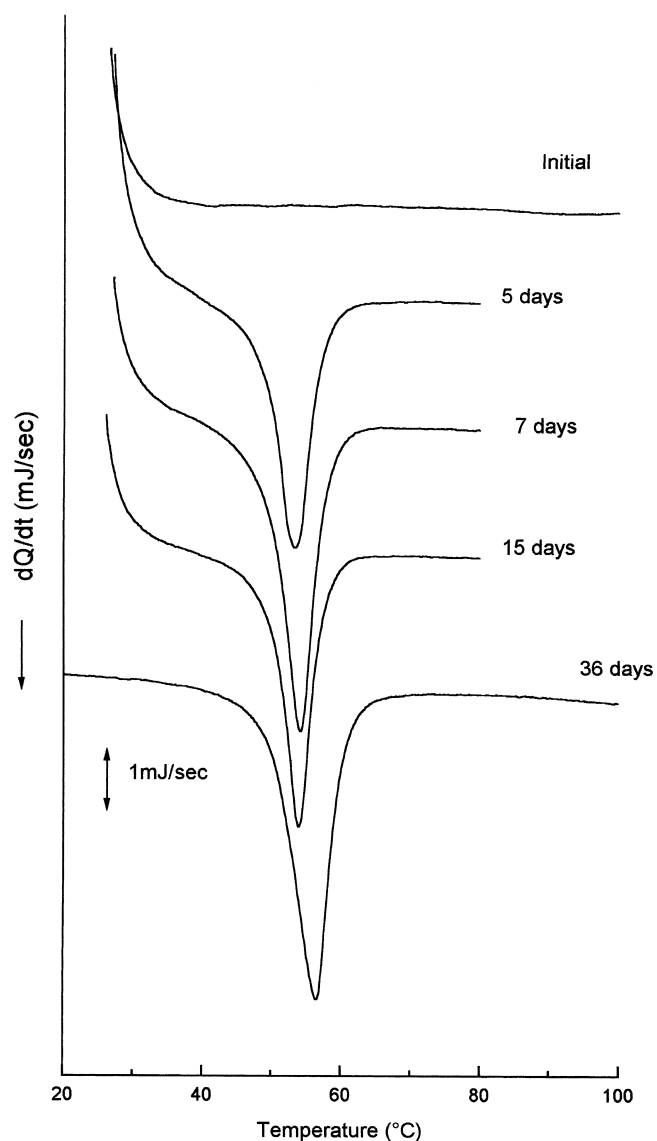he initial positions (Fig. 2). Sorbitol showed a similar trend as glycerol; sorbitol films only showed a slight increase in peak intensities with storage time. Films with plasticizer showed the stable pattern at initial storage time while control starch films without plasticizer required more time to reach that pattern.

Plasticizer presence in film formulations did not alter the X-ray pattern of the most stable structure developed in stored control films. Plasticizers probably decrease the activation energy of the formation of the most stable crystalline structure, facilitating polymeric chain mobility and allowing a rapid development of the most stable structure. However, since plasticizer limits polymer chain alignment, the degree of crystallinity of plasticized films is lower than in the control group.

3.2 Differential scanning calorimetry

Corn starch and amylomaize films did not show any peak on DSC thermograms at the beginning of storage, indicating that starch gelatinization with NaOH was complete (Fig. 3). With storage time, films showed increasing endothermic transitions, with peak temperatures between 50 to 54 °C and enthalpy values above 100 mJ/mg. The origin of this enthalpy change and its relationship with alkaline gelatiniza-

Fig. 2. Effect of storage time on X-ray diffraction pattern of amylomaize starch films with glycerol as plasticizer stored at 20 °C and 63.8% relative humidity at initial time and 60 d of storage (cps = counts per second).

Fig. 3. Effect of storage time on thermograms of corn starch films stored at 20 °C and 63.8% relative humidity.

tion of starch, neutralization of the formulation and storage conditions of the films were analyzed. It was concluded that gelatinization with NaOH was one of the main causes of this endothermic peak. The following observations supported this assumption:

a) when films were prepared with thermally gelatinized starch no peak was detected by DSC, neither at the beginning of storage nor with increasing storage time,

b) the thermal transition was observed with non-neutralized films and also with films neutralized with different acids (H_3PO_4, H_2SO_4 and HCl).

It can be considered that during NaOH treatment not only cold gelatinization was produced but also hydrolysis of amylose and amylopectin chains did take place. According to *Hizukuri* and coworkers [16] PD of amylopectin is ≈ 2000 and that of amylose is ≈ 200. Taking into account the amylopectin/amylose ratio of the starches used, the estimated PD should be 1550 for corn starch and 830 for amylomaize. Our experimental results showed that PD of starch suspensions treated with NaOH was 147 for corn and 130 for amylomaize. PD of neutralized and non-neutralized suspensions were not significantly different ($P < 0.05$). The estimated values in untreated starch were higher than those of NaOH treated suspensions indicating that a significant hydrolysis occurred during cold gelatinization. As a consequence of hydrolysis processes, the starch suspension was enriched in short chains derived from amylose and amylopectin [14, 20]. Thus, the obtained high DSC transition values would correspond mainly to the fusion of the crystals formed from the products of alkaline hydrolysis of starch during storage (Tab. 1). Also, the crystallization process was evidenced by the shift of the peak temperature to higher values and the decrease of the DSC peak width with increasing storage time (Fig. 3, Tab. 1). These results are also supported by X-ray diffraction observations. This method showed that as storage time increased a higher crystallinity degree of the films was observed and the diffraction pattern shifted toward the most stable crystalline structure (Fig. 2). *Roos* [13] and *Knutson* [21] by reviewing literature, reported that A-type crystals are thermodynamically the most stable form and are found in systems with high crystallization temperatures, high polymer concentrations and short chain lengths. This report, that

Tab. 1. Effect of plasticizer on DSC thermal parameters of amylomaize films stored at 20 °C and 63.8% relative humidity.

| Time [d]	Plasticizer [20 g/L]	Enthalpy [mJ/mg]	Peak temperature [°C]	Melting range [°C]
0	WP[a]	–	–	–
	Glycerol	–	–	–
	Sorbitol	–	–	–
15	WP	139.24	54.08	6.03
	Glycerol	54.27	50.69	10.52
	Sorbitol	10.31	50.93	4.36
36	WP	189.25	54.51	4.58
	Glycerol	99.05	51.88	5.68
	Sorbitol	57.76	52.17	4.62

[a] WP = without plasticizer

attributes the formation of a stable crystal configuration to the presence of short chain length, can be related to our findings of X-ray diffraction and DSC observations.

Lower enthalpy (ΔH) and peak temperatures of gelatinization were observed with stored plasticized films compared to unplasticized ones for both starch types (Tab. 1 and Fig. 3). Experimental ΔH values were modeled using Avrami's equation, which predicts the increment of crystalline fraction (θ) as a function of time (t) according to the following expression:

$$\theta = (\Delta H_t / \Delta H_\infty) = 1 - \exp(-k\, t^n) \qquad (1)$$

where ΔH_t is the enthalpy at storage time t, ΔH_∞ is the limit enthalpy value obtained at long storage times, k is a kinetic parameter and n is a parameter related to nucleus formation and its morphology [22, 23]. According to *Colwell* et al. [24], when working on starch systems $n = 1$ led to the best fit, thus this n value was utilized in the present study. Fig. 4 shows Avrami model curves and experimental data; a satisfactory fit with a minimum $r^2 = 0.885$ for all curves was obtained, although a better fit (minimum $r^2 = 0.988$) was obtained in the case of unplasticized films. Amylomaize films with higher amylose content showed higher ΔH values (Fig. 4b) compared to those of corn starch films at the same
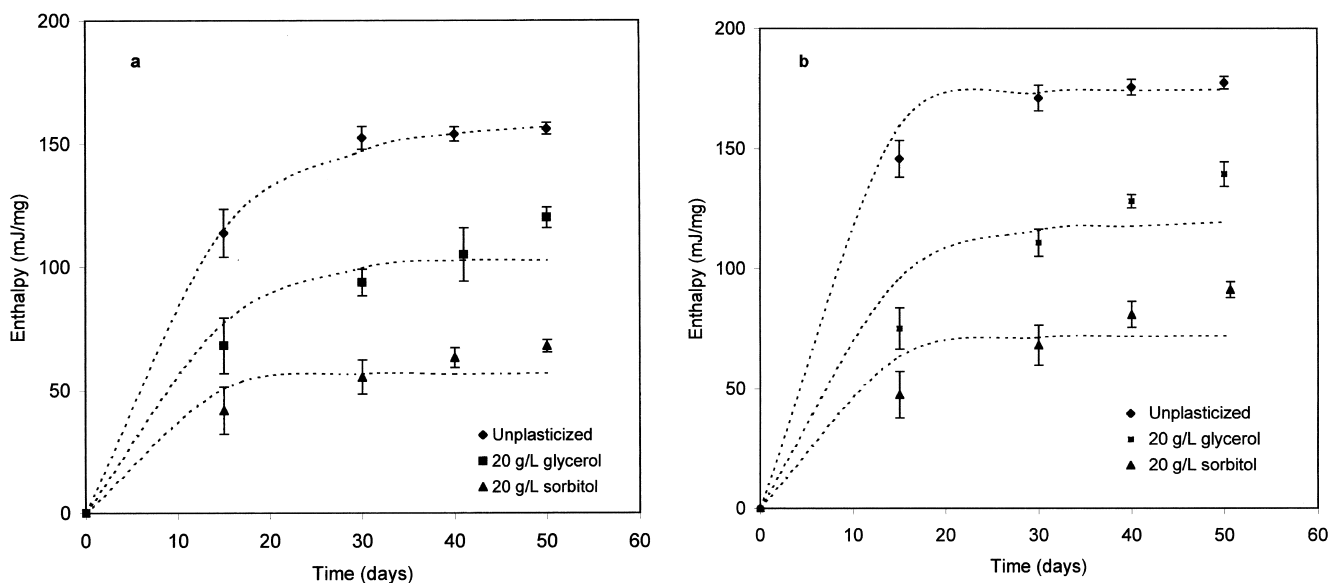
Fig. 4. Effect of storage time on thermal transitions of films of a) corn starch and b) amylomaize starch with 20 g/L glycerol or sorbitol or without plasticizer. Lines correspond to Avrami model fitting to experimental data represented by dots.
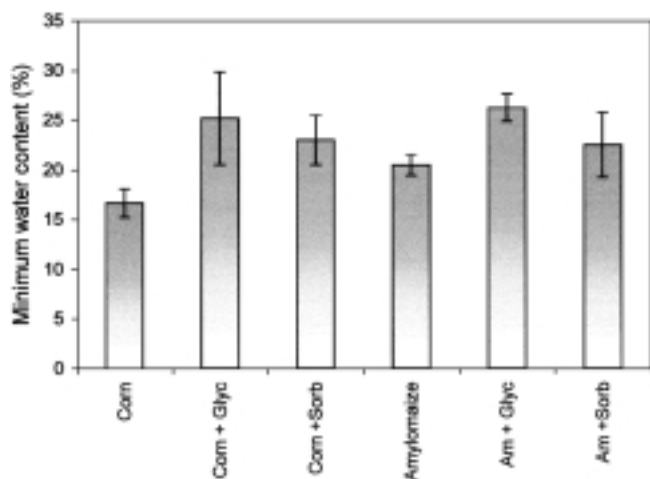
Fig. 5. Minimum amount of water at which thermal transitions of starch films were detected by DSC. Glyc = 20 g/L glycerol; Sorb = 20 g/L sorbitol; Am = Amylomaize.

storage time (Fig. 4a). Higher ΔH values in DSC tests correlate with higher peak intensities in X-ray diffraction analysis. The increase in the DSC peak with storage time in plasticized films correlates well with the trend observed with X-ray diffraction, because in this case the structure is slightly modified with storage time and the crystallinity degree was lower than that of unplasticized films.

Both plasticizers, glycerol and sorbitol, seemed to limit crystal growth and recrystallization due to the interaction with the polymeric chains. Corn starch films with sorbitol showed lower crystallinity, characterized by lower ΔH values (Fig. 4 a) as compared to films plasticized with glycerol. Since sorbitol is more similar to the molecular structure of glucose units than glycerol, the chances of sorbitol to interact with polymeric chains are higher. Thus, film crystallinity of plasticized films was lower than that of control films because plasticizers interfere with polymeric chain association. Another factor that modified thermal transitions during storage was the water content of the films [1]. During storage water content of films increased, reaching a maximum of $\approx 34\%$ for all the storage conditions above 33.3% (MgCl$_2$ · 6 H$_2$O). Similar results were obtained by *Bader* and *Göritz* [25] working on sorption isotherms of amylomaize films.

DSC thermal transitions were detected above a minimum water content which depended on both starch type and film plasticizer (Fig. 5). At water contents below 15% no DSC peak was detected. Similarly, films stored at 0% relative humidity did not modify the initial X-ray diffraction pattern. With higher water contents the probability of polymer chains alignment is higher, because water acting as a plasticizer increases polymer chain mobility, favoring chain interactions and thus, crystallization. Water could have an additional

role; according to *Even* and *Carr* [26] in amylose films water is incorporated into the structure through inter- and intramolecular hydrogen bonds. Besides, several authors reported that water takes part of the unit cell of B type crystals of amylose.

As water content increases in an amorphous system, the glass transition temperature (T_g) decreases. Thus, at the same storage temperature a matrix with low water content is stable (in the glassy state), while a matrix with higher water content (above the minimum water content that correspond to the T_g curve) can be in the rubbery state, thus becoming unstable. In the rubbery state polymer chains have enough mobility to allow crystal growth. In the present work, the minimum water content for crystal growth detection in films with glycerol or sorbitol was higher than that of control films (Fig. 5). When plasticizers such as glycerol or sorbitol are added to the matrix, maintaining the same water content and the same storage temperature, the system will modify its T_g value. Considering that T_g of these plasticizers (–65 °C for glycerol and –43.5 °C for sorbitol) are higher than the T_g of water (–135 °C) the plasticized system will have a higher T_g [27]. This explains why starch systems including glycerol or sorbitol are more stable than unplasticized ones; the plasticized films needed higher amounts of water to be in the rubbery state at the same storage temperature.

3.3 Film characterization

Plasticized films showed homogeneous surfaces without pores or cracks compared with unplasticized films as visualized by SEM (Fig. 6 a and c). *Donhowe* and *Fennema* [10] also reported that amylose molecules without plasticizer produced brittle films. Cross-sections of unplasticized films showed a multi-laminar structure while films containing a plasticizer showed a more compact structure (Fig. 6 b and d). SEM observations did not show differences due to plasticizer type.

Thickness of the films measured by coating thickness gauge are shown in Tab. 2. ANOVA showed a significant ($P < 0.05$) effect of starch type on films, amylomaize films were thicker than corn starch ones. Films with plasticizer were thinner than unplasticized films. A similar trend between thickness measurements by SEM and digital film thickness gauge was observed [17].

3.4 Gas permeability

ANOVA showed significantly higher ($P < 0.05$) CO$_2$ permeabilities of films without plasticizer (Tab. 2). Based on SEM observations, these high permeability and wide dispersion of values can be attributed to the presence of pores in unplasticized films (Tab. 2).

Edible starch-based films have much lower O$_2$ permeabilities than CO$_2$ permeabilities, indicating a selective action of these films on gas permeabilities [17]. These effects can be

Tab. 2. Effect of plasticizer and starch type on thickness and gas permeabilities of starch-based films.

Starch base	Plasticizer [20 g/L]	Film thickness [μm]	CO$_2$ permeability $\times 10^9$ [cm^3 m^{-1} s^{-1} Pa^{-1}][a]	
			Initial permeability	Stored samples[b]
Corn	–	119.92 ± 32.52[c]	29.21 ± 13.89	8.90 ± 1.28
	glycerol	104.34 ± 24.24	5.69 ± 0.97	2.76 ± 0.55
	sorbitol	110.71 ± 23.11	4.19 ± 0.81	2.42 ± 0.46
Amylomaize	–	157.45 ± 35.48	28.05 ± 7.37	7.71 ± 1.40
	glycerol	128.70 ± 20.82	3.85 ± 1.28	2.28 ± 0.33
	sorbitol	134.34 ± 25.13	2.96 ± 0.46	1.82 ± 0.15

[a] At standard pressure and temperature conditions.　　[b] Stored 20 d at 20 °C and 63.8% relative humidity.　　[c] Value ± standard deviation.
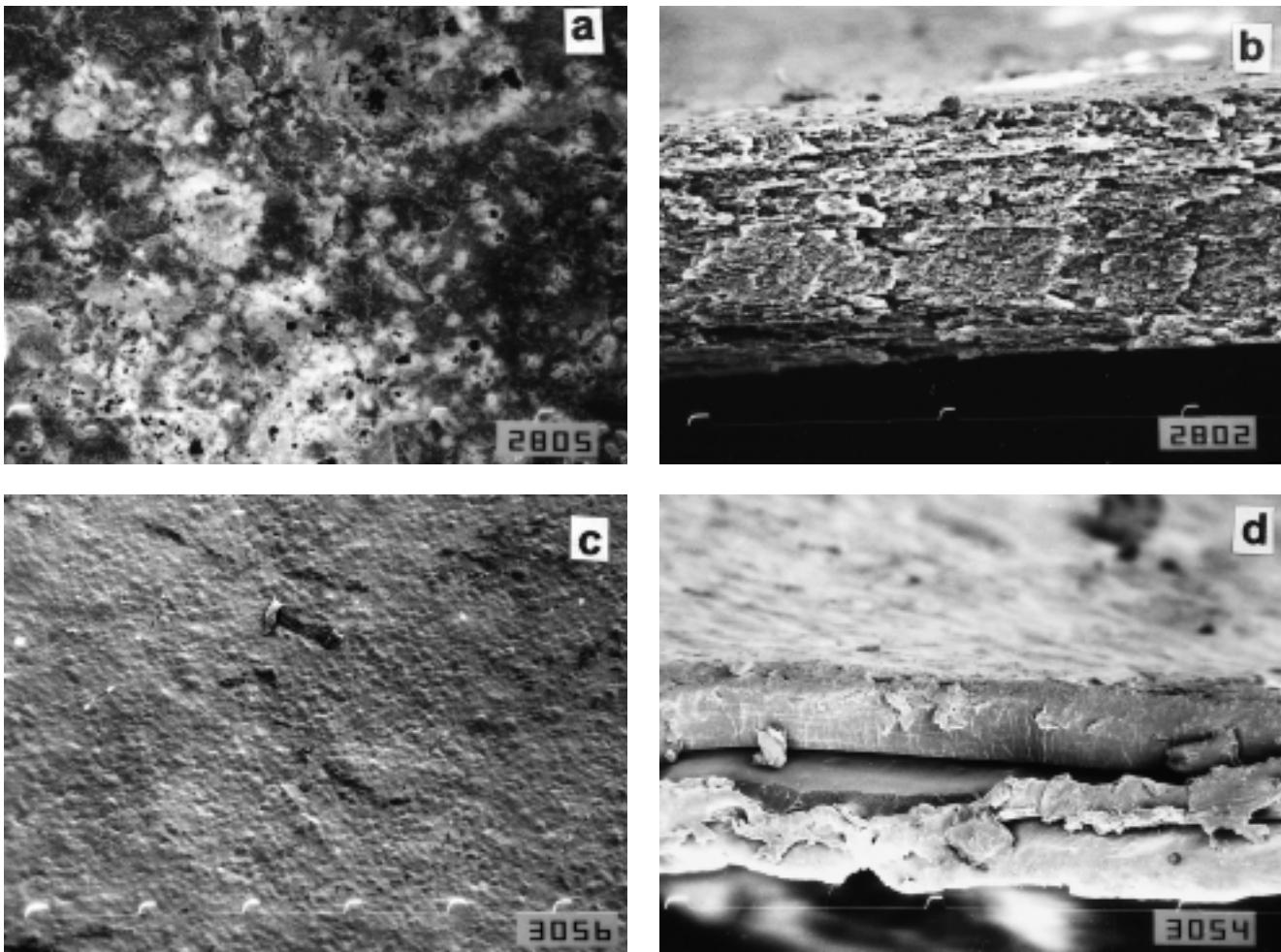
Fig. 6. SEM micrographs of starch-based films a) surface of films without plasticizer, b) cross-section of films without plasticizer, c) surface of films plasticized with 20 g/L glycerol and d) cross-sections of plasticized films with 20 g/L glycerol. Magnification: 100 μm between marks.

attributed to a higher solubility of CO_2 in the starch films [28]. Films with sorbitol exhibited statistically lower ($P < 0.05$) oxygen permeability values than films with glycerol. The type of both plasticizer and starch used in film formulations significantly influenced ($P < 0.05$) gas permeabilities. Sorbitol combined with the amylomaize film matrix gave the lowest gas permeabilities.

Tab. 2 shows that CO_2 permeability decreased significantly ($P < 0.05$) with storage time. As for synthetic materials, gas and vapor permeabilities depend on several factors such as the ratio between crystalline and amorphous zones, polymeric chain mobility and specific interactions between the functional groups of the polymers and the gases in the amorphous zones. According to *Donhowe* and *Fennema* [29] permeability increases with decreasing crystalline/amorphous ratio because permeation occurs through the amorphous zones of the film.

Permeability measurements of the stored films correlate with the previously described results because the degree of crystallinity of the stored films increased as was demonstrated by DSC analysis and X-ray diffraction.

4 Conclusion

Starch-based films showed partial crystalline microstructure evidenced by X-ray diffraction. DSC rsults showed that crystal formation and recrystallization could be mainly attributed to the alignment of short chains of starch polymers produced during NaOH treatment of the suspensions. Depending on film formulation, starch films required different minimum water contents to favor chain mobility and to allow the development of the crystalline structure.

The crystallinity of the films was associated with the amylose content of the starch source. Amylomaize films had higher crystalline/amorphous ratio than corn starch films. Both types of films had different X-ray diffraction patterns at the beginning of the storage, however they reached a common crystalline structure with time. Films with plasticizer showed lower crystallinity than films without plasticizer. Plasticizers favored chain mobility allowing the development of the more stable structure at shorter storage times. However, plasticizers limited crystalline growth because they interfere with polymer chain alignment due to steric hindrances. SEM analysis showed that plasticizer addition avoid the formation of pores and cracks. Lack of film integrity limits the application of films without plasticizers. Starch films including sorbitol as plasticizer showed lower gaseous permeability than films with glycerol. CO_2 permeability of starch-based films was higher than O_2 one, acting as a selective barrier. During storage time gas permeability of films decreased due to the increase of film crystallinity; a good agreement between crystalline structure and gas permeability results were observed.

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