Microstructural characterization of yam starch films

Suzana Mali[a], Maria Victória E. Grossmann[a,*], Maria A. Garcia[b], Miriam N. Martino[b,c],
Noemi E. Zaritzky[b,c]

[a]*Departamento de Tecnologia de Alimentos e Medicamentos, Centro de Ciências Agrárias, Universidade Estadual de Londrina, Caixa Postal 6001, CEP 86051-990 Londrina, PR, Brazil*
[b]*Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), CONICET, Fac. Cs Exactas, Universidad Nacional de La Plata, La Plata, Argentina*
[c]*Depto. de Ingeniería Química, Facultad de Ingeniería (UNLP), 47 y 116, La Plata (1900), Buenos Aires, Argentina*

Abstract

Yam starch films were produced by thermal gelatinization of starch suspensions using different starch and glycerol concentrations and were compared to control samples without glycerol. Films were characterized by polarized light microscopy, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), X-ray diffraction, water vapor permeability (WVP) and water sorption isotherms. The polarized light microscopy and DSC data showed that starch gelatinization for film formation was complete. Plasticized films have a homogeneous structure as observed by SEM. At water activities > 0.43, glycerol increased the equilibrium moisture content of the films due to its hydrophilic character. X-ray pattern of the yam films could be assigned to a B-type starch; during storage this pattern remained almost the same, however a slight recrystallization process could be observed. Amylopectin retrogradation was not observed by DSC with storage time of the films. Glass transition temperatures of films with glycerol were lower than those of control films as measured by DSC and TMA. WVP of yam starch films increased with the presence of glycerol. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Biodegradable films; Microstructure; Plasticizer

1. Introduction

Most widely used polymeric materials for packaging purposes, developed in the past 50–60 years, are durable and inert in the presence of microorganisms, leading to a long-term performance. However, in view of the current emphasis on environmental pollution problems and the shortage of land for solid waste management, the need for environmentally degradable polymers has increased (Albertsson & Karlsson, 1995; Wool, 1995).

Over the last few years, there has been a renewed interest in biodegradable films and films made from renewable and natural polymers such as starch (Lawton, 1996). Several studies have been done to analyze the properties of starch-based films (Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1998; Garcia, Martino, & Zaritzky, 1999, 2000; Lawton & Fanta, 1994; Lourdin, Della Valle, & Colonna, 1995).

Edible and/or biodegradable films are not meant to totally replace synthetic packaging films, however they do have the potential to replace the conventional packaging in some applications. The use of a biopolymer such as starch can be an interesting solution because this polymer is quite cheap, abundant, biodegradable and edible. Yam tubers (*Dioscorea* sp.) are a good source of starch for film production, because native yam starch contains about 30% of amylose (Alves, Grossmann, & Silva, 1999), and amylose is responsible for the film forming capacity of starches.

In the absence of additives, films made from starch or amylose are brittle. The addition of plasticizers overcomes starch film brittleness and improves flexibility and extensibility. Plasticizers must be compatible with the film-forming polymer. They reduce intermolecular forces and increase the mobility of polymer chains. Hydrophilic compounds such as polyols (glycerol, sorbitol and polyethylene glycol) are commonly used as plasticizers in hydrophilic film formulations (Gontard, Guilbert, & Cuq, 1993).

As with synthetic polymers, the mechanical properties of starch biofilms depend on the crystallinity of the constituent polymers (Lai & Kokini, 1991; Van Soest, Bezemer, de Wit, & Vliegenhart, 1995). The study of microstructure and the interaction of the film components also provide some insight into possible relationships between different physical

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* Corresponding author. Tel.: +55-43-3714565; fax: +55-43-3714080.
  E-mail address: victoria@uel.br (M.V.E. Grossmann).

properties. Several methods can be used to analyze the effects of native starch processing on microstructure such as polarized light microscopy, X-ray diffraction, scanning electron microscopy (SEM) and differential scanning calorimetry (DSC).

The objectives of the present work were to develop biodegradable and edible yam starch films, to characterize their microstructure and to determine water vapor permeability (WVP) and water sorption isotherms.

2. Materials and methods

2.1. Raw materials

Fresh tubers of yam (*Dioscorea alata*), with uniform size and shape, without any mechanical and pathological injuries, were obtained in a local farm (Londrina, PR, Brazil). Yam starch was extracted according to Alves et al. (1999). Amylose and amylopectin content of yam starch were determined simultaneously by the Landers, Gbur, and Sharp (1991) method; ash, protein, fat and starch were determined according to the standard AOAC (1995) methods.

2.2. Film preparation

Films were obtained using different yam starch concentrations (3.30, 3.65 and 4.00% w/w d.b.) and glycerol contents (1.30, 1.65 and 2.00% w/w d.b). The levels of starch and glycerol were selected after preliminary tests. Yam starch and glycerol were directly mixed with distilled water to make batches with a total weight of 500 g. The film-forming solutions were transferred quantitatively to the viscograph cup of a Brabender Viscograph Pt 100 (OHG, Duisburg, Germany), they were heated from 30 to 95 °C and maintained at 95 °C for 10 min, with regular shaking (75 rpm) and constant heating rate (3 °C/min). The films were prepared by casting; gelatinized suspensions were immediately poured on rectangular acrylic plates ($10 \times 20 \text{ cm}^2$). For each experiment, the quantity of starch suspension poured onto the plate was calculated to obtain a constant weight of dried matter of approximately 12.25 mg/cm^2 for 0.11 mm films and 11.00 mg/cm^2 for 0.09 mm films. The starch suspensions were dried (65 °C) in a ventilated oven, model TE-394-3 (Tecnal, Piracicaba, SP, Brazil) to constant weight (about 3 h); translucent films which can be easily removed from the plate were obtained. Films were stored at 20 °C and a relative humidity (RH) of 65%. DSC and thermomechanical analysis (TMA) thermograms, X-ray diffractograms and WVP of the starch films were monitored at the beginning and during storage time.

2.3. Thickness measurements

Thickness of the films was determined using a manual micrometer (Mitutoyo, São Paulo, Brazil) at 10 random positions of the film. The mean standard deviation within the film was about 5% of the average thickness.

2.4. Microscope observations

Polarized light microscopy observations of starch films were performed with a Leica DMLB microscope (Heerbrugg, Germany).

SEM analysis were performed with a JEOL JSPM 100 electron microscope (Japan). Film pieces were mounted on bronze 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. Water sorption isotherms

Sorption isotherms of native yam starch, yam starch films with glycerol (plasticized films) and yam starch films without glycerol (control films) were determined according to the procedure described by Spiess and Wolf (1983), with some modifications. Samples were dried in a forced air convection oven with P_2O_5 for 7 days. The dried samples were weighed to the nearest 0.0001 g into pre-weighed bottles and were equilibrated in desiccators containing different saturated salt solutions of known equilibrium relative humidities (water activities) ranging from 0.11 to 0.97, at 25 °C. Equilibrium moisture content (% db) was calculated from the gain in weight. Measurements were made in triplicate.

2.6. X-ray diffraction

Samples were analyzed between $2\theta = 2°$ and $2\theta = 60°$ with a step size $2\theta = 0.02°$ in a X-ray diffractometer Philips PW 1710 (The Netherlands) using a Cu Kα radiation ($\lambda = 1.543$), 50 kV and 30 mA. The diffractometer was equipped with 1° divergence slit and a 0.1 mm receiving slit.

2.7. Thermal analysis

2.7.1. Differential scanning calorimetry

Film samples were tested in a Polymer Laboratories DSC (Rheometric Scientific, Surrey, UK) working under a PL-V5.41 software. Samples of 6–7 mg were weighed in aluminum pans and were hermetically sealed; an empty pan was used as reference. Samples were heated from −40 to 120 °C with 10 °C/min heating rate. The pans were punctured and dried until constant weight at 105 °C to obtain the dry weight of the sample. Samples were analyzed at initial time and during storage time at 20°C and 65% RH to evaluated thermal transitions (enthalpic changes and
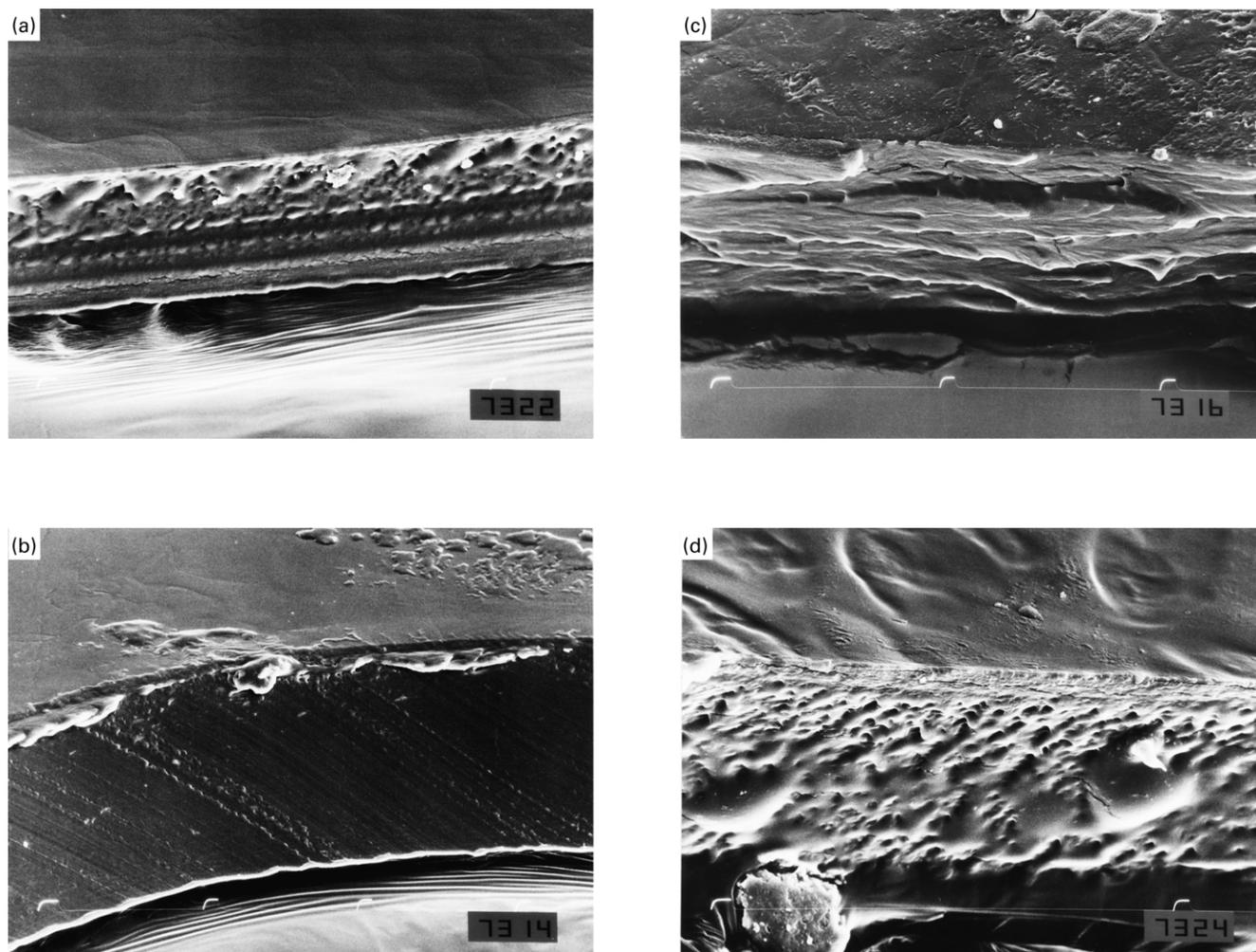
Fig. 1. SEM micrographs of cross-section of yam starch films formulated as: (a) 3.3% yam starch and 1.3% glycerol, (b) 4.0% yam starch and 1.3% glycerol, (c) 3.3% yam starch and 2.0% glycerol, and (d) 4.0% yam starch and 2.0% glycerol. Magnification: 100 μm between marks.

glass transition temperature, T_g), (Lund, 1983). All measurements were performed in duplicate.

2.7.2. Thermomechanical analysis

Film samples were tested in Polymer Laboratories TMA 500 (Rheometric Scientific, Surrey, UK) working under a PLus-V5.40 software with a liquid nitrogen Dewar attachment. Samples of 20–40 mg and 2–3 mm in diameter were placed in open aluminum pans. A penetration standard probe of quartz was used and the applied force was 980 mN (10 g). Samples were heated from −80 to 90 °C with 10 °C/min heating rate. The temperature of glass transition (T_g) was determined by the change in the slope of the obtained curves. All measurements were performed in duplicate.

2.8. Water vapor permeability

WVP tests were conducted using ASTM (1995) method E96 with some modifications. Each film sample was sealed over a circular opening of 0.00181 m^2 in a permeation cell

that was stored at 25 °C in a dessicator. To maintain a 75% RH gradient across the film, anhydrous calcium chloride (0% RH) was placed inside the cell and a sodium chloride saturated solution (75% RH) was used in the dessicator. The RH inside the cell was always lower than the outside, and water vapor transport was determined from the weight gain of the permeation cell. After steady state conditions were reached (about 2 h), eight weight measurements were made over 24 h. Changes in the weight of the cell were recorded to the nearest 0.0001 g and plotted as a function of time. The slope of each line was calculated by linear regression ($r^2 > 0.99$) and the water vapor transmission rate (WVTR) was calculated from the slope of the straight line (g/s) divided by the cell area (m^2). After the permeation tests, film thickness was measured and WVP ($g\ Pa^{-1}\ s^{-1}\ m^{-1}$) was calculated as WVP = [WVTR/$S(R_1 - R_2)$]d, where S is the saturation vapor pressure of water (Pa) at the test temperature (25 °C), R_1, the RH in the dessicator, R_2, the RH in the permeation cell and d is the film thickness (m). Under these conditions, the driving force [$S(R_1 - R_2)$] was 1753.55 Pa.
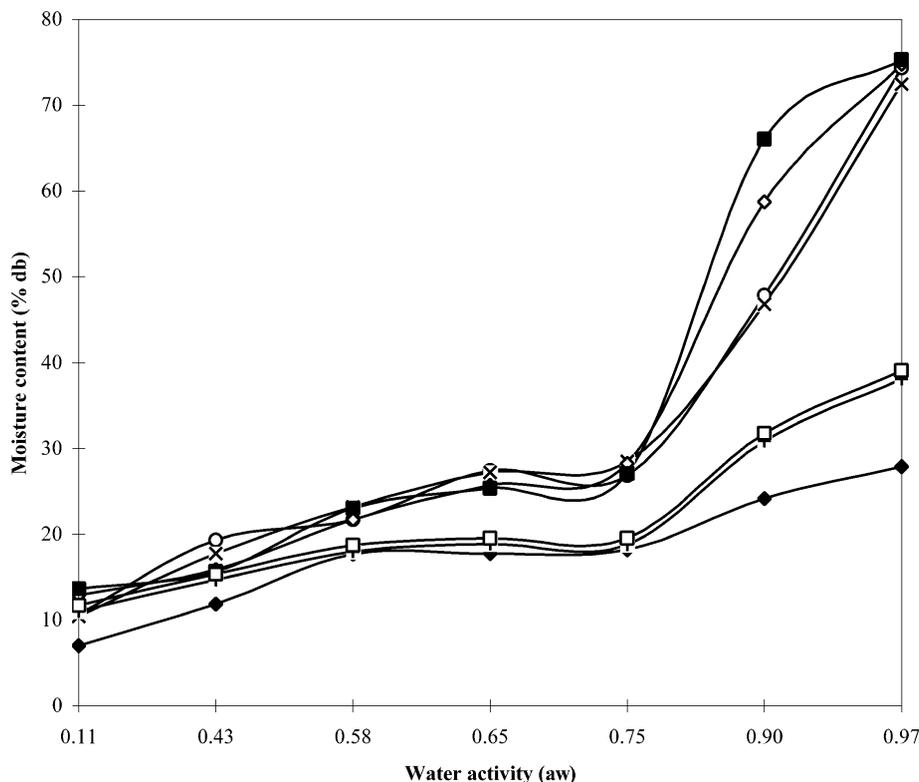
Fig. 2. Water sorption isotherms of yam starch films and native yam starch at 25 °C. (◆) yam starch. Film formulation: (—) 3.3% yam starch without glycerol, (□) 4.0% yam starch without glycerol, (○) 3.3% yam starch and 1.3% glycerol, (✕) 4.0% yam starch and 1.3% glycerol, (◇) 3.3% yam starch and 2.0% glycerol and (■) 4.0% yam starch and 2.0% glycerol.

2.9. Statistical analysis

Different formulations of plasticized yam starch films were compared to each other, and control samples without glycerol were tested to evaluate the effect of this plasticizer on some studied characteristics. Statistica software (Oklahoma, USA, 1996) version 5.0 was used for all statistical analysis. Analysis of variance (ANOVA), Tukey test for means comparison and regression analysis were applied. The significance level used was 0.05.

3. Results and discussion

3.1. Chemical composition of yam starch

On dry basis, the chemical composition of yam starch was: ash ($0.17 \pm 0.01\%$), protein ($0.20 \pm 0.01\%$), lipids ($0.27 \pm 0.02\%$) and starch ($98.30 \pm 0.05\%$). The amylose and amylopectin contents of native yam starch were 30 and 70%, respectively. This amylose content is relevant for the film forming capacity of the starch and was higher than the values obtained by other authors (Ciacco, 1978; Emiola & Delarosa, 1981) being similar to those obtained by Alves et al. (1999). The differences could be explained by the different plantation conditions of yam tubers and by the method used in this analysis.

3.2. Microscopy observations

Polarized light microscopy observations of the yam starch unplasticized (control samples) and plasticized films showed that starch was totally gelatinized before the formation of the film.

SEM observations did not show differences among the samples containing different concentrations of plasticizer and starch (Fig. 1a–d). Plasticized films showed smooth surfaces without pores or cracks, and a compact structure. The homogeneous matrix of films is a good indicator of their structural integrity, and consequently good mechanical properties would be expected.

3.3. Water sorption isotherms

The sorption isotherms at 25 °C of yam starch films with and without glycerol (control samples) and native yam starch were compared (Fig. 2). All isotherms showed a similar sigmoid shape (isotherm type II). When the samples were conditioned at water activities, $a_w > 0.43$, the plasticized films showed higher equilibrium moisture content (% db) than the native yam starch and the control film. This could be explained by the presence of glycerol in the formulation of these films, that due to its hydrophilic character increased the hygroscopic characteristics of yam starch films.
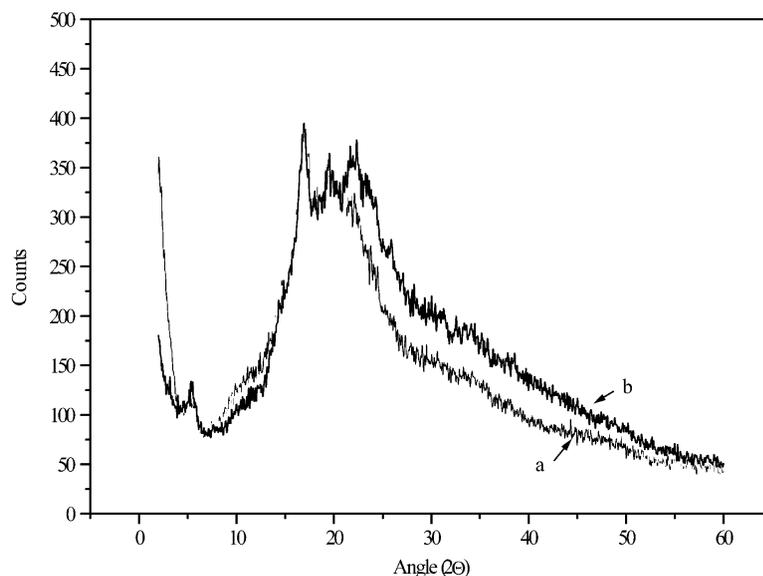
Fig. 3. X-ray diffraction pattern of yam starch films containing 3.65% yam starch and 1.65% glycerol (a) at initial storage time and (b) stored 90 days at 20 °C and 65% RH.

Control films showed higher equilibrium moisture content than the native yam starch at $a_w > 0.75$. This result could be attributed to the fact that during film production, gelatinization led to a starch molecule reorganization that increased the water absorption capacity of the unplasticized film compared to native starch. Unplasticized films showed similar behavior than those reported by other researchers working with high amylose starch films (Bader & Göritz, 1994) and tapioca starch films (Chang, Cheah, & Seow, 2000)

3.4. X-ray diffraction

X-ray diffraction patterns of the semicrystalline yam starch films with and without glycerol were characterized by absorption peaks and a high contribution of an amorphous
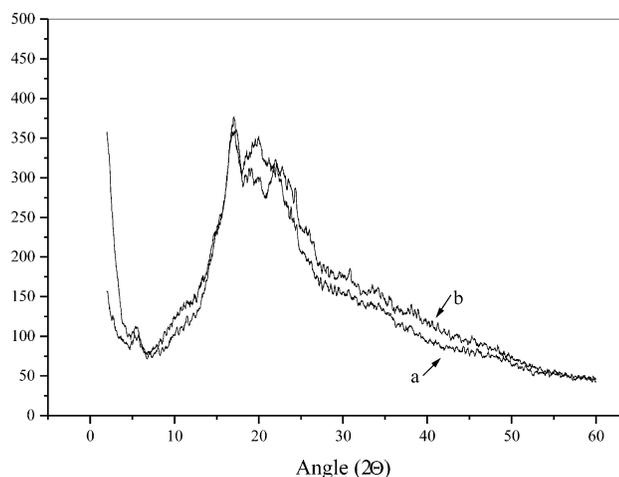

Fig. 4. X-ray diffraction pattern of yam starch films at 90 days of storage at 20 °C and 65% RH. Film formulation: (a) 3.65% yam starch without glycerol and (b) 3.65% yam starch and 1.65% glycerol.

zone (Figs. 3 and 4). The crystallinity of starch films is dependent on the processing conditions such as: (i) the completeness of dissolution of amylose in water, (ii) the conditions of drying process (rate and temperature), (iii) starch source, and (iv) the final moisture content of the samples (Van Soest & Vliegenthart, 1997; Van Soest, Hulleman, de Wit, & Vliegenthart, 1996).

The pattern of the starch films could be assigned to a B-type, characteristic of starch tubers (Roos, 1995). As an example Table 1 shows the crystallographic parameters of a plasticized yam starch film and literature data of B-type starch crystals. During 90 days storage, this pattern remained almost the same (Fig. 3). The shape and width of the diffraction profile are determined both by the mean crystalline size or distribution of sizes of the specimen and by the particular imperfections of the crystalline lattice (Klug & Alexander, 1974). With storage time peak width slightly decreased and peak intensities increased (Fig. 3)

Table 1
X-ray diffraction parameters of experimental data of 3.65% yam starch and 1.65% glycerol films and literature data

Literature data[a]		Experimental data	
Angle (deg, 2θ)	Intensity	Angle (deg, 2θ)	Intensity
5.590	50	5.675	12.4
9.930	10	10.345	10.3
11.100	10	12.430	10.7
14.400	50	14.240	30.4
17.200	100	17.040	100
19.501	30	19.805	78.6
22.201	50	22.420	53.2
24.001	40	23.795	42.0
26.301	20	–	–
34.401	20	34.555	23.0

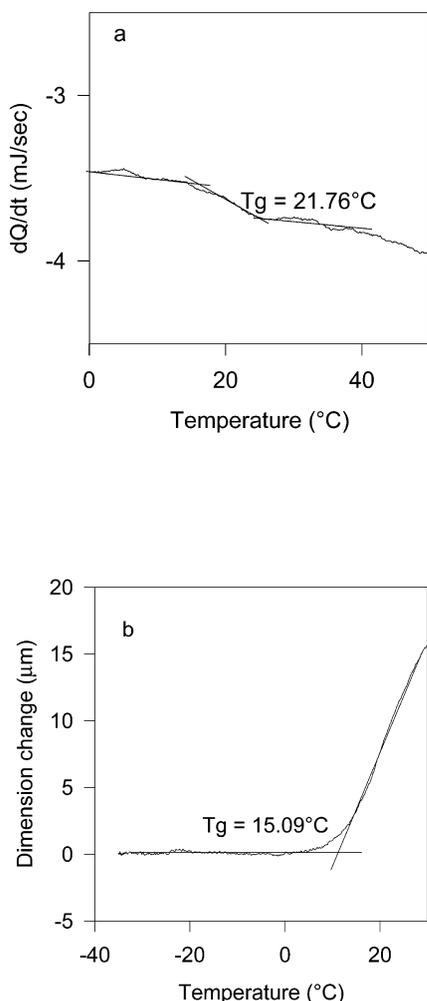[a] Typical data of potato starch (B-type) from Zobel (1964).

Fig. 5. Glass transition determination of 3.3% yam starch and 1.3% glycerol film. (a) DSC thermogram and (b) TMA thermomechanical diagram.

showing a tendency towards an increase in crystallite size what could correspond to a slow recrystallization process.

The water content of the tested yam starch films stored at RH = 65% ranged from 16 to 25 g water/100 g dry film as seen in the sorption isotherms (Fig. 2), and these values should be below critical equilibrium water content for which molecule mobility may take place. As reported by Garcia et al. (2000), at the same storage temperature a matrix of starch film with low water content is stable during storage, while a matrix with higher water content becomes unstable.

Fig. 4 shows the effect of glycerol on the X-ray patterns of the films, and the different levels of starch and glycerol in film formulation did not markedly influence the X-ray pattern of the yam starch films, glycerol addition did not significantly modify the position of the diffraction peaks.

3.5. Thermal analysis

Yam starch films did not show any peak in DSC thermograms at the beginning of the storage time, indicating that starch gelatinization during the film production was complete; this result was in agreement with polarized light microscopy observations. With storage time, the films did not show any peak in DSC thermograms at the tested range of temperatures (−40 to 120 °C). In this temperature range only amylopectin retrogradation could be detected but was not observed during the storage of the films; amylose recrystallization requires temperatures higher than 140 °C to be detected by DSC (Miles, Morris, Orford, & Ring, 1985), and our DSC equipment are not recommended to obtain accurate results at higher temperatures.

Fig. 5a,b shows typical curves of T_g determination by DSC and TMA, respectively. Films formulated with high yam starch concentrations showed higher T_g values and T_g of films without plasticizer were higher than those of films with glycerol (Table 2); the plasticizer decreased T_g because it facilitates chain mobility. According to Guilbert and

Table 2
Glass transition temperature (T_g) and WVP of yam starch films

Film formulation		Glass transition temperature, T_g (°C)		Water vapor permeability $\times 10^{10}$ (g/Pa/m/s)[a]	
Yam starch[b]	Glycerol[b]	By DSC[c]	By TMA[c]	Initial permeability	Stored samples[d]
3.30	0.00	–	–	0.960 cA	0.945 cA
3.30	1.30	21.76	15.09	1.298 aA	1.290 aA
3.30	2.00	12.13	8.81	1.550 abA	1.510 bA
3.65	0.00	48.03	44.21	1.020 cA	0.980 cA
3.65	1.65	12.20	10.86	1.320 aA	1.165 aA
4.00	0.00	–	–	1.150 cA	1.125 cA
4.00	1.30	29.23	24.86	1.685 bA	1.540 bA
4.00	2.00	27.02	20.17	1.810 bA	1.800 bA

[a] Means at same line with different capital letters are significantly different ($p \leq 0.05$); means at same column with different small letters are significantly different ($p \leq 0.05$).
[b] Percentage w/w on dry basis.
[c] DSC: differential scanning calorimetry. TMA: thermomechanical analysis.
[d] Films stored 90 days at 20°C and 65% RH.

Gontard (1995), plasticization decreases the intermolecular forces between polymer chains, consequently the overall cohesion, and reduces T_g.

Both analytical techniques showed similar trends for T_g variations, although T_g values obtained by DSC were slightly higher than those of TMA (Table 2). Chang and Randall (1992) stressed that the sensitivity of TMA with the penetration probe is superior to that of DSC for defining glass transitions. T_g values of yam starch films are in agreement with those reported by Chang et al. (2000), who worked on tapioca films.

3.6. Water vapor permeability

Table 2 shows WVP of plasticized and unplasticized starch films. WVP values of plasticized films were significantly higher ($p < 0.05$) than those of unplasticized ones. Storage time (90 days) did not modify WVP values ($p > 0.05$). Increasing glycerol concentration did not produce significant ($p > 0.05$) differences, although a slightly tendency to increase WVP of the plasticized starch films has been observed as glycerol concentration increased. These results could be related to the structural modifications of the starch network produced by the plasticizer and to the hydrophilic character of glycerol, which favors the absorption and desorption of water molecules. Gontard, et al. (1993) working on other hydrophilic films such as wheat gluten films found similar results. The use of a plasticizer like glycerol avoids cracking of films during handling and storage, but, on the other hand, increases gas, water vapor and solute permeability of the films (Banker, 1966).

With regard to synthetic polymers, yam starch films have WVP values slightly higher than those of cellophane ($0.84 \times 10^{-10}\,\mathrm{g^{-1}\,m^{-1}\,s^{-1}\,Pa^{-1}}$) and higher than low density polyethylene (LPDE) ($0.0036 \times 10^{-10}\,\mathrm{g^{-1}\,m^{-1}\,s^{-1}\,Pa^{-1}}$), (Shellhammer & Krochta, 1997). However, yam starch film permeabilities were lower than those of other edible and biodegradable films such as wheat gluten plasticized with glycerol ($7.00 \times 10^{-10}\,\mathrm{g^{-1}\,m^{-1}\,s^{-1}\,Pa^{-1}}$), amylose ($3.80 \times 10^{-10}\,\mathrm{g^{-1}\,m^{-1}\,s^{-1}\,Pa^{-1}}$) and hydroxy-propyl-methylcellulose with plasticizer and oil ($1.90 \times 10^{-10}\,\mathrm{g^{-1}\,m^{-1}\,s^{-1}\,Pa^{-1}}$), (Gennadios, Weller, & Gooding, 1994).

4. Conclusions

Data obtained by polarized light microscopy and DSC showed that thermal processing of native yam starch for film production led to a complete gelatinization of the granules.

SEM observations showed that plasticized films had smooth surfaces without pores or cracks, and a compact structure. At $a_w > 0.43$, the plasticized films showed higher equilibrium moisture contents than the unplasticized films, due to the hydrophilic character of glycerol. X-ray pattern of the starch films could be assigned to a B-type starch. During

90 days storage this pattern remained almost the same, however a slight recrystallization process occurred. Amylopectin retrogradation was not observed by DSC during the storage.

Glycerol behaved as a typical plasticizer. (i) Glass transition temperatures of films without glycerol were higher than those of films with plasticizer as measured by DSC and TMA. (ii) WVP values of plasticized films were significantly higher than those without glycerol. Storage time (90 days) did not modify significantly WVP values of films in agreement with the slight modifications of the film structure observed by X-ray diffraction.

Yam starch films can be described as biofilms with an homogeneous matrix with stable structure at ambient conditions and interesting water barrier properties with great possibilities of application, and with the advantage of biodegradability.

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