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Effects of controlled storage on thermal, mechanical and barrier properties of plasticized films from different starch sources

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Abstract

Thermal, mechanical and barrier properties of corn, cassava and yam starch films were determined and the behavior of these three starches films under a controlled storage (64% RH and 20 °C) was compared. Glass transition (T_g) in all unplasticized films was higher than in plasticized, and during storage, T_g decreased, except for samples with 40 g glycerol/100 g starch. Crystallinity was affected by plasticizer concentration and storage time; in unplasticized samples the increase in crystallinity was higher than in plasticized ones during storage, thus, unplasticized source samples become more brittle and less permeable during storage. Unplasticized films showed water vapor permeability (WVP) values ranged from 6.75 to 8.33×10^{-10} g m⁻¹ s⁻¹ Pa⁻¹. These values decrease when glycerol content reached at 20 g/100 g starch because a more compact structure was formed and, then, at 40 g glycerol/100 g starch, WVP increased because film matrixes became less dense.

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1. Introduction

Over the last few years, there has been a renewed interest in 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 (Lourdin, Valle, & Colonna, 1995; Arvanitoyannis, Billiaderis, Ogawa, & Kawasaki, 1998; García, Martino, & Zaritzky, 1999, 2000; Mali, Grossmann, García, Martino, & Zaritzky, 2002; Mali & Grossmann, 2003). Edible and/or biodegradable films are not meant to totally

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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 (Mali & Grossmann, 2003).

Starch consists primarily of branched and linear chains of glucose molecules, named as amylopectin and amylose, respectively. Amylose is essentially a linear molecule with a few branches, whereas amylopectin is a highly branched molecule. Preponderance of amylose in starches gives stronger films. Branched structure of amylopectin generally leads to films with different mechanical properties, such as decreased tensile stress (Tharanathan, 2003).

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Starch is present in semicrystalline granules that varies in composition, size, shape and functionality when obtained from different botanical sources (Tharanathan, 1995; Tharanathan & Saroja, 2001). Several different starches are available on the market, including corn, cassava, wheat, rice, among others, and each type has specific properties and, hence, special application (Riaz, 1999). Others, as yam starch, although not commercially available, have some interesting functional properties (Alves et al., 2002). Worldwide corn represents the major commercial source of starch, while cassava is an important starch source in some parts of the word, like Brazil, which is the largest cassava-producing country (Leonel & Cereda, 2002). Cassava starch is appreciated for its paste clarity, low gelatinization temperature and good gel stability (Sedas & Kubiak, 1994). Native yam starch (Dioscorea alata) contains about 30% of amylose, and this is important for film production because amylose is responsible for the film-forming capacity of starches (Mali et al., 2002).

Recently, many works dealt with the addition of plasticizers to pure starch-based materials to overcome film brittleness caused by high intermolecular forces. Plasticizers increase film flexibility due to their ability to reduce internal hydrogen bonding between polymer chains while increasing molecular volume. The most commonly plasticizers used in starch-based films are polyols, such as sorbitol and glycerol, they avoid cracking of the film during handling and storage (Gontard, Guilbert, & Cuq, 1993), affect gas, water vapor and solute permeabilities (Banker, 1966) and sorption characteristics.

Depending upon the plasticizer concentration, the botanical origin of starch and storage conditions, materials with different mechanical properties can be produced. Glass transition temperature (T_g) is the most parameter in determining the mechanical properties of amorphous and semicrystalline materials and in controlling the recrystallization process of them. Thus, the objectives of this work were to characterize the thermal (glass transition temperature), mechanical and barrier properties of corn, cassava and yam starch films and to compare the behavior of these three starches films under a controlled storage.

2. Materials and methods

2.1. Materials

Corn starch was provided by Corn Products (Curitiba—PR, Brazil) and cassava starch by Hiraki Industry (São Paulo—SP, Brazil). Yam starch was extracted from fresh tubers of yam (*Dioscorea alata*) according to Alves, Grossmann, and Silva (1999). Amylose and amylopectin were determined simultaneously by the Landers, Gbur, and Sharp (1991) method; ash, proteins and fat were determined according to the standard AOAC (1995) methods.

2.2. Films preparation

Starch films were prepared by casting, employing corn, cassava and yam starches (3 g of starch/100 g of filmogenic solution), with different glycerol concentrations (0, 20 and 40/100 g of starch). 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 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). Gelatinized suspensions were immediately poured on rectangular acrylic plates $(10 \times 20 \text{ cm})$. For each experiment, the quantity of starch suspension poured onto the plate was calculated to obtain a constant weight of dried matter of approximately 9.00 mg/cm², resulting films with 0.08 \pm 0.01 mm of thickness, measured with a Mitutoyo micrometer (Japan) with an accuracy of $\pm 1 \,\mu m$. The starch suspensions were dried (40 °C) in a ventilated oven model TE-394-3 (Tecnal, Piracicaba, SP, Brazil) to constant weight (about 20 h). The result was translucent films, which can be easily removed from the plate. The films were equilibrated at 20 °C and a relative humidity (RH) of 64%, for 48 h, before being tested at initial storage time and after 90 days at these conditions.

2.3. Films characterization

2.3.1. Glass transition (T_g) of starch films

Samples of the formulated films 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 1-2.5 mg were weighed in aluminum pans and were hermetically sealed; an empty pan was used as reference. Samples were run between -40 and 120 °C with 10 °C/ min heating rate. Once analyzed, pans were punctured and dried until constant weight at 105 °C to get sample dried weight. Samples were analyzed at initial time and after storage time at 20 °C and 64% RH to evaluate thermal transitions (enthalpic changes and glass transition temperature, T_g), (Lund, 1983). The glass transition temperature was defined as the midpoint of the transition inflection observed in thermograms. All measurements were performed in triplicates and reported values are the mean of measurements.

2.3.2. Crystallinity of starch films

Samples were analyzed between $2\theta = 3^{\circ}$ and $2\theta = 40^{\circ}$ in a diffractometer Phillips PW 1390 (The Netherlands)

using K α Cu radiation ($\lambda = 1.5418$ Å), 50 kV and 30 mA. The diffractometer was equipped with 1° divergence slit and a 0.1 mm receiving slit. Modifications of the crystalline structure of films stored at 20 °C and 64% RH were evaluated.

X-ray diffraction patterns of starch films are characterized by sharp peaks associated with the crystalline diffraction and an amorphous zone. The amorphous fraction of the sample can be estimated by the area between the smooth curve drawn following the scattering hump and the baseline joining the background within the low and high-angle points. The crystalline fraction (CF) can be estimated by the upper region above the smooth curve (Snyder & Bish, 1989; Köksel, Şahbaz, & Özboy, 1993). The degree of crystallinity variation of stored films was calculated as follows: Crystallinity variation (%) = (CF stored film—CF film at initial time) * 100/CF film at initial time.

2.3.3. Mechanical properties

The tensile properties were studied using a TA.TX2i Stable Micro Systems texture analyzer (Surrey—England) in accordance with ASTM D-882-91 (1996). Five sample strips (25.4×100 mm) of each formulation were cut and clamped between tensile grips. Force (*N*) and deformation (mm) were recorded during extension at 50 mm min⁻¹ and with an initial distance between the grips of 50 mm. The parameters determined were: tensile stress (MPa), strain at break (%) and Young's Modulus (MPa).

2.3.4. Water vapor permeability (WVP)

WVP tests were conducted using ASTM method E96 (1996) 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 desiccator. To maintain 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 desiccator. The RH inside the cell was always lower than the outside, and water vapor trans-

Table 1			
Chemical composition of corn,	cassava and	yam starches	(dry basis) ^a

port was determined from the weight gain of the permeation cell. After steady state conditions were reached (about 2 h), the weight measurements were made at each 2 h, 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 transfer 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 $(R_1 - R_2) \cdot D$]; where S is the saturation vapor pressure of water (Pa) at the test temperature (25 °C), R_1 , the RH in the desiccator, 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. All tests were conducted in duplicate.

3. Results and discussion

All plasticized formulations gave easy handling, homogeneous and transparent films without any insoluble particles, except cassava starch film formulated with 40 g glycerol/100 g starch, that presented a higher adhesiveness and a more difficulty to handling. Films formulated without plasticizer became brittle and difficult to manipulate.

3.1. Chemical composition of starches

Corn, cassava and yam starches presented a carbohydrate content up to 99% (Table 1). Amylose and amylopectin contents are showed in Table 1; corn starch showed 25% of amylose and cassava 19%; these data agreed with other authors (Hoover, 2001; Li & Yeh, 2001), that observed values of 25% for corn and values ranging from 16% to 20% in cassava starches. Yam starch showed the highest amylose level (29%), higher than the values obtained by some authors (Ciacco, 1978; Emiola & Delarosa, 1981; Hoover & Vasanthan,

*			
Component	Corn starch	Cassava starch	Yam starch
Ash (%)	0.06 (0.005)	0.22 (0.01)	0.17 (0.01)
Fat (%)	0.29 (0.01)	0.28 (0.01)	0.27 (0.01)
Protein (%)	0.27 (0.01)	0.11 (0.01)	0.20 (0.01)
Carbohydrates (%) ^b	99.38 (5)	99.39 (5)	99.56 (5)
Amylose (%)	25 (2)	19 (2)	29 (2)
Amylopectin (%)	75 (5)	81 (5)	69 (5)
Gelatinization temperature (°C) ^c	65–79	62–79	72-83
Granule diameter (µm) ^c	5–20	7–14	12–37

^a Numbers in parenthesis are the standard deviation of the analysis.

^b Calculated by difference.

^c Adapted from Mali, Karam, Ramos, and Grossmann (2004).

1994) and similar to those reported by others (Alves et al., 1999; Mali & Grossmann, 2003). The differences could be explained by the different plantation conditions of yam tubers and by the methods used in this analysis. The amylose content is relevant for film forming capacity of the starch although in plasticized films the final characteristics are strongly influenced by amylopectin and plasticizer interaction.

As reported by Mali et al. (2004) and cited in Table 1, corn, cassava and yam starches differ in size and shape. In corn starch, the granules presented a polyhedral irregular shape with an average granule diameter of 5–20 μ m. Cassava starch granules were elliptical and truncated in shape with diameters ranging from 7 to 14 μ m. Yam starch had granules with diameters ranging from 12 to 37 μ m. The gelatinization temperature of yam starch was higher than corn and cassava starches (Table 1), these data was according to other authors (Freitas, Paula, Feitosa, Rocha, & Sierakowski, 2003), that stressed that this behavior is dependent on the amylose content of each starch.

3.2. Glass transition (T_g) of starch films

Glass transition temperatures of corn, cassava and yam starch films were affected by plasticizer concentration and storage time, while in general starch source did not affect T_g values (Table 2). Increasing glycerol content, T_g decreased (Table 2) and this behavior could be related to the structural modifications of starch network when glycerol was incorporated; the film matrix become less dense and under stress movements of polymer chains were facilitated. Plasticizers are expected to decrease intermolecular forces between polymers chains and reduce T_g , imparting increased film flexibility while decreasing barrier properties (McHugh & Krochta, 1994). This effect of glycerol was extensively related by other authors (Forssell, Mikkilä, Moates, & Parker, 1997; Forssell, Hulleman, Millärinen, Moates, & Parker,

Table 2

Glass transition (T_g) of starch films at initial time and after 90 days storage at 64% relative humidity and 20 °C

Starch base	Glycerol (g/100 starch)	Glass transition— T_{g} (°C) ^a		
		Initial time	Stored samples	
Corn	0	54.23 ± 3.20	44.64 ± 4.93	
	20	35.12 ± 6.85	29.57 ± 2.93	
	40	20.97 ± 2.47	25.98 ± 2.60	
Cassava	0	55.61 ± 0.55	39.6 ± 1.61	
	20	42.42 ± 1.75	38.17 ± 0.35	
	40	26.96 ± 4.36	27.34 ± 3.83	
Yam	0	52.7 ± 3.22	47.69 ± 2.11	
	20	39.26 ± 3.47	26.52 ± 4.16	
	40	18.7 ± 3.02	21.34 ± 2.38	

^a Mean \pm standard deviation of each analysis.

1999; García, Martino, & Zaritzky, 2000; Mali et al., 2002).

Moreover, the decrease of T_g with increase of glycerol concentration was related to hydrophilicity of this plasticizer. The addition of glycerol in starch films provides more active sites by exposing its hydrophilic hydroxyl groups in which the water molecules could be adsorbed. Water exerted a plasticizing effect acting as a mobility enhancer; its low molecular weight leads a large increase in molecular mobility of amorphous and partially crystalline polymers due an increased free volume (Van der Berg, 1991), thus, decreasing glass transition of films. This could be observed in Table 3, in which films with higher plasticizer content (40/100 g starch) exhibit higher water contents and subsequently, the lower T_g values (Table 2). In general, starch type and storage time did not affect water content of the films.

As shown in Table 2, in general, the studied films were stored below their glass transition temperature, in a glassy state, except those formulated with 40 g glycerol/100 g starch that showed $T_{\rm g}$ values around to storage temperature. With 90 days of storage (64% RH and 20 °C), the T_g of starch films decreased (Table 2) and this was according to data reported by Chung and Lim (2003a, 2003b), who stressed that when starchy samples are stored below its T_{g} and have time to reach its thermodynamic equilibrium, T_{g} values become lower; the chain mobility becomes more uniform as the glassy starch reaches an thermodynamic equilibrium. In films with higher level of plasticizer (40/100 g starch) $T_{\rm g}$ values became constant during storage (Table 2) probably because higher glycerol concentration provided more possibilities of interactions: plasticizer-plasticizer, plasticizer-water or plasticizer-starch types, and thus, a more mobile film matrix were produced, with fewer chances to reach the thermodynamic equilibrium.

Other authors reported the effect of plasticizer decreasing T_g ; according to Lourdin, Coignard, Bizot,

Table 3

Water content of starch films at initial time and after 90 days storage at 64% relative humidity and 20 $^{\circ}\mathrm{C}$

Starch base	Glycerol (g/100 starch)	Water content (%—dry basis) ^a		
		Initial time	Stored samples	
Corn	0	11.79 ± 1.37	11.98 ± 7.79	
	20	10.94 ± 0.59	11.59 ± 1.04	
	40	23.13 ± 2.46	25.09 ± 1.27	
Cassava	0	9.83 ± 1.04	12.19 ± 2.64	
	20	9.43 ± 0.31	10.88 ± 1.75	
	40	29.79 ± 3.23	28.06 ± 0.21	
Yam	0	11.51 ± 2.81	13.80 ± 0.54	
	20	8.71 ± 0.61	14.32 ± 0.06	
	40	21.39 ± 0.26	28.35 ± 0.92	

^a Mean ± standard deviation of each analysis.

and Colonna (1997) who worked with potato starch films, T_g values ranged from 90 to 30 °C when plasticizer content increased from 0% to 27% (starch basis). Arvanitoyannis, Psomiadou, and Nakayama (1996), observed that corn starch films T_g ranged from 55.4 to -4.2 °C when glycerol content increased from 10% to 19%. Our data showed the same tendency, with values slight different; the differences could be explained by the different starch sources and by the methods and equipments used in this analysis.

3.3. Crystallinity of starch films

The crystalline area of several films did not differ at the initial time, and corresponded to 12–15% of total area of the X-ray diffraction curves. As shown in Table 4, the relative crystallinity of starch films increased slightly with storage time and films without glycerol were more affected. Plasticizer seemed to limit crystal growth and recrystallization due to the interaction with the polymeric chains, interfering with polymer chain alignment due to steric hindrances. This was according to results reported by Van Soest, Hulleman, De Wit, and Vliegenthart (1996) and García et al. (2000). The slightly increase in crystallization can be explained because, if our films were stored below or around, not above its glass transition temperature, they were in a sta-

Table 4

Relative crystallinity variation after	90 days s	storage ^a	of starch	films a	at
64% relative humidity and 20 °C					

Starch base	Glycerol (g/100 starch)	Crystalline fraction increase (%)
Corn	0	15.01
	40	6.59
Cassava	0	8.51
	40	6.43
Yam	0	18.39
	40	5.10

ble glassy state, and according to Slade and Levine (1991), crystallization does not occur or is extremely slow at temperatures below T_g , but it can occur at temperatures above T_g , at a rate depending on difference between T_g and temperature of storage.

Cassava starch films showed the lower increase in crystallinity, continued by corn and yam starch (Table 4), agreeing with the different tendency of each of these amylopectin starches to crystallize during storage (Karam, 2003).

3.4. Mechanical properties

The tensile stress, strain at break and Young's Modulus in starch films were affected by glycerol content (Table 5). Tensile stress and Young's Modulus decreased and strain increased with increase of glycerol in all starch films; when a plasticizer, as glycerol, was incorporated in a starch network, direct interactions and the proximity between starch chains were reduced, thus under tensile forces, movements of starch chains were facilitated, decreasing the glass transition temperature of these materials and improving their flexibility (García et al., 1999, 2000; Mali et al., 2002).

Among films, those from cassava starch were less strong and more flexible in all glycerol contents, and with increase of the glycerol content, showed the higher decrease in tensile stress and Young's Modulus and the higher increase in strain at break (Table 5); this probably occurred because cassava starch presented the lower amylose content. Lourdin et al. (1995) showed that mechanical properties of starch plasticized films were dependent from amylose/amylopectin ratio. The linear amylose and the branched amylopectin exhibit different behavior with regard to gelation, development of crystallinity and film forming capacity. When the starch granules are heated in water, they start to swell, rupture and collapse releasing amylose and amylopectin; branched amylopectin chains in solution present a little tendency to interact and, consequently, amylopectin gels

Table 5

Mechanical properties of starch films at initial time and after stored for 90 days at 64% relative humidity and 20 °C

Starch base	Glycerol (g/100 starch)	Tensile stress (MPa) ^a		Strain at break (%) ^a		Young's modulus (MPa) ^a	
		Initial time	Stored samples	Initial time	Stored samples	Initial time	Stored samples
Corn	0	37 ± 5	48 ± 4	3 ± 0.7	2 ± 0.6	1188 ± 146	1229 ± 390
	20	17 ± 6	13 ± 2	9 ± 5	11 ± 5	550 ± 50	551 ± 150
	40	9 ± 1	9 ± 1	28 ± 6	27 ± 7	162 ± 15	139 ± 35
Cassava	0	26 ± 5	39 ± 2	6 ± 0.6	3 ± 1	737 ± 108	868 ± 200
	20	10 ± 3	11 ± 3	33 ± 1	21 ± 2	409 ± 30	482 ± 86
	40	4 ± 0.2	3 ± 0.3	46 ± 2	49 ± 9	9 ± 1	14 ± 3
Yam	0	49 ± 2	60 ± 5	3 ± 0.7	2 ± 0.1	1003 ± 50	1280 ± 50
	20	30 ± 5	29 ± 5	13 ± 5	9 ± 3	546 ± 80	605 ± 161
	40	10 ± 1	9 ± 1	25 ± 8	20 ± 5	159 ± 64	137 ± 25

^a Mean ± standard deviation of each analysis.

and films are weak, cohesive and flexible. Linear chains of amylose in solution present high trend to interact by hydrogen bonds, and consequently, amylose gels and films are stiffer and stronger than amylopectin gels and films (Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998; Wurzburg, 1986).

Unplasticized stored films showed a tendency to become stiffer, with slightly increase in tensile stress and Young's Modulus and decrease in strain at break (Table 5). These changes in mechanical properties could be related with the formation of chain-chain associations in starch film matrix seen by increase in films crystallinity (Table 4). Mechanical properties of plasticized samples, which presented a low increase in crystallinity during storage, were not affected by storage time (Table 5). Although Van Soest and Knooren (1997) point out that even when crystallinity is low, entangled starch network and chain-chain association can be formed during storage and change mechanical properties, this was not observed. The plasticizer action (which difficult the starch chain interactions), together with the amylopectin characteristics of starches and storage conditions (below T_g), could explain this stability.

3.5. Water vapor permeability (WVP)

Since a main function of a food packaging is often to avoid or at least to decrease moisture transfer between the food and the surrounding atmosphere, or between two components of a heterogeneous food product, water vapor permeability should be as low as possible (Gontard, Guilbert, & Cuq, 1992).

Water vapor permeability in all films showed the same trend with increase of glycerol content (Table 6); the films analysed at initial time, formulated without glycerol, showed WVP values ranged from 6.75 to 8.33×10^{-10} g m⁻¹ s⁻¹ Pa⁻¹, these values decreased when glycerol content reached at 20 g/100 g of starch

Table 6 Water vapor transmission of starch films at initial time and stored for 90 days at 64% relative humidity and 20 °C

Starch base	Glycerol (g/100 starch)	WVP $(\times 10^{-10} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1})^{a}$		
	(8)	Initial time	Stored samples	
Corn	0	8.33 ± 0.21	5.13 ± 0.51	
	20	5.37 ± 0.21	5.00 ± 0.75	
	40	6.70 ± 0.21	5.95 ± 0.75	
Cassava	0	7.59 ± 1.26	5.59 ± 0.89	
	20	4.02 ± 1.26	4.02 ± 1.01	
	40	6.25 ± 1.26	5.65 ± 0.99	
Yam	0	6.75 ± 1.05	5.25 ± 0.58	
	20	4.46 ± 1.05	4.00 ± 0.55	
	40	7.59 ± 1.05	6.66 ± 0.99	

^a Mean ± standard deviation of each analysis.

and then, at a glycerol content of 40/100 g of starch, the WVP increased (Table 6). This behavior could be related to structural modifications of starch network that occurs when glycerol is added; initially, unplasticized starches form brittle films with pore or cracks, which facilities the water vapor permeation (García et al., 2000), then, when glycerol is added (20 g glycerol/100 g starch) the formation of pores or cracks was avoided, a more compact structure was formed, and this probably resulted in lower WVP values. According to Gaudin, Lourdin, Le Botlan, Ilari, and Colonna (1999), plasticizer may be strongly bound with starch under low contents (below 27%), exerting an antiplasticization effect.

Increasing glycerol content from 20 to 40/100 g of starch increased WVP values; the films matrix became less dense, and this, added to the hydrophilic character of glycerol, is favorable to adsorption and desorption of water molecules (Sobral, 2000; Sobral, Menegalli, Hubinger, & Roques, 2001). This effect was more pronounced in yam starch films that presented higher WVP increase with increase of glycerol content (Table 6).

During storage time (90 days), WVP values of plasticized films showed a tendency to remain constant (Table 6), and this was related to the stability of starch films at this storage conditions, agreeing with crystallinity and mechanical properties values. Table 6 shows that unplasticized samples presented a higher decrease in WVP values compared to plasticized ones. As for synthetic materials, water vapor permeability depend on factors such as the ratio between crystalline and amorphous zones and according to Donhowe and Fennema (1993), water vapor permeability decreases with increasing crystalline zones because permeation occur through the amorphous zones of the film.

4. Conclusions

Glass transition temperatures of corn, cassava and yam starch films were affected by plasticizer concentration and storage time; in general starch source did not affect T_g values. Glycerol behaved as a typical plasticizer, glass transition temperatures of films without glycerol were higher than those of films with plasticizer as measured by DSC.

With 90 days of storage, the T_g of starch films decreased and this occurred because samples were storage below its T_g (in a glassy state) and have time to reach its thermodynamic equilibrium, when the chain mobility becomes more uniform. In films with higher level of plasticizer (40/100 g starch) this did not occur; higher glycerol concentration provided more possibilities of interactions, and thus, a more mobile film matrix were produced, with fewer chances to reach its thermodynamic equilibrium.

Crystallinity of starch films increased with storage time and films without glycerol were more affected; plasticizer seemed to limit crystal growth and recrystallization due to the interaction with the polymeric chains. The increases in crystallinity were reflected by the changes in mechanical properties with time, mainly in unplasticized films, with increases in Young's modulus and tensile stresses, decreases in strains at break and water vapor permeabilities.

Corn, cassava and yam starch films did not differ among them in its water vapor permeability after storage and the differences in mechanical properties were small. This occurred because, in general, all samples were stored in a glassy state, with higher stability, thus, could be concluded that the storage condition was more important than the starch source in these properties of studied films.

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