

Antiplasticizing effect of glycerol and sorbitol on the properties of cassava starch films

Efeito antiplastificante de glicerol e sorbitol nas propriedades de filmes de amido de mandioca

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■ Summary

The effects of glycerol and sorbitol on the mechanical and thermal properties and water adsorption capacity of cassava starch films were studied. Films with different water activities (0.11 to 0.90) were tested and when these films were plasticized with any glycerol or sorbitol content at a water activity (a_w) \leq 0.58, the plasticized films adsorbed less water than the unplasticized ones. Glycerol films, under all a_w values, presented higher equilibrium moisture contents than sorbitol ones. Only with plasticizer contents above 15 g.100 g⁻¹ starch could a decrease in the glass transition temperature (T_g) be observed in relation to the unplasticized samples, which presented a T_g of 52.77 °C. In contrast to glycerol, sorbitol exerted an antiplasticizing effect that could be detected by tensile stress tests, and both plasticizers had an antiplasticizing effect on film strain. The results indicated that the presence of small amounts of the plasticizers employed (<15 g.100 g⁻¹ starch) was able to exert an antiplasticizing effect in systems with low water contents.

Key words: Mechanical properties; Glass transition and water sorption capacity.

■ Resumo

Os efeitos do glicerol e sorbitol nas propriedades mecânicas e térmicas e na capacidade de adsorção de água de filmes de amido foram estudados. Filmes com diferentes atividades de água (0,11 a 0,90) foram estudados e quando estes filmes foram plastificados com qualquer teor de glicerol ou sorbitol, sob atividade de água (a_w) \leq 0,58, adsorveram menos água que os não plastificados. Filmes com glicerol, em todos os valores de a_w , apresentaram maior umidade de equilíbrio que os com sorbitol. Somente em conteúdos de plastificante acima de 15 g.100 g⁻¹ amido pôde ser observado um decréscimo da temperatura de transição vítrea em relação às amostras não plastificadas, que apresentaram T_g de 52,77 °C. Ao contrário do glicerol, o sorbitol exerceu um efeito antiplastificante detectável por testes de tensão e ambos os plastificantes apresentaram efeito antiplastificante sobre a elongação dos filmes. Os resultados indicaram que a presença de pequenas quantidades dos plastificantes empregados (<15 g.100 g⁻¹ amido) foi capaz de exercer efeito antiplastificante em sistemas com baixos conteúdos de água.

Palavras-chave: Propriedades mecânicas; Transição vítrea e capacidade de sorção de água.

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1 Introduction

Since the 1970s, there has been a renewed interest in biodegradable plastics made from renewable and natural polymers. Among the natural polymers, starch has been considered as one of the most promising candidates for future materials because of an attractive combination of price, abundance and thermoplastic behaviour.

Starch-based films are rigid and present poor mechanical properties, particularly poor elongation (around 6%) under ambient conditions (LOURDIN *et al.*, 1997b) and the incorporation of a plasticizer is required to overcome the brittleness inherent in these materials. Plasticizers must be compatible with the film-forming polymers; hydrophilic compounds, such as polyols (glycerol and sorbitol) are commonly used in starch films (MALI *et al.*, 2004; 2005).

Low-molecular mass compounds or diluents, acting as plasticizers, increase film flexibility due to their ability to reduce internal hydrogen bonding between polymer chains, while increasing molecular space. They avoid cracking of the film during handling and storage, and affect the gas, water vapour and solute permeabilities and sorption characteristics (GARCÍA *et al.*, 1999; 2000). However, they may serve as mechanical antiplasticizers when present in low concentrations, resulting in stiffer polymer–diluent blends instead of more flexible ones as compared to the pure polymer (CHANG *et al.*, 2006).

The phenomena of plasticization and antiplasticization have received increasing attention from food scientists and technologists in recent years. Studies on the addition of plasticizers to starch films were initially undertaken to decrease the T_g to below ambient temperature, and obtain a deformable rubbery material. However, these additives can produce an antiplasticizer effect when present in low concentrations, by inducing rigidity in the glassy material due to a decrease in flexibility and an increase in the elastic modulus (LOURDIN *et al.*, 1997a; LOURDIN *et al.*, 1997b; GAUDIN *et al.*, 1999; CHANG *et al.*, 2000; GAUDIN *et al.*, 2000; MYLLARINEN *et al.*, 2002; MALI *et al.*, 2005; CHANG *et al.*, 2006).

Thus, the objectives of this work were to study the plasticizing - antiplasticizing effects of glycerol and sorbitol on the water sorption capacity, glass transition and mechanical properties of cassava starch films, and although some research has already been done in this area, studies of this kind are important to provide more information and to compare the roles of different plasticizers in biopolymeric systems.

2 Material and methods

2.1 Materials

Cassava starch (19% amylose) was provided by the Hiraki Company (São Paulo – SP – Brazil). Glycerol

and sorbitol were purchased from Synth (Diadema – São Paulo).

2.2 Film preparation

Cassava starch films were prepared by casting, employing 3 g of starch / 100 g of filmogenic solution. Two types of plasticizer (glycerol or sorbitol) were added at six levels (0, 5, 10, 15, 30 and 40 g.100 g⁻¹ of starch). Filmogenic solutions (3.0 g starch.100 g⁻¹ solution and plasticizers at different levels) were prepared in a Brabender Viscograph (OHG, Duisburg, Germany) and each solution heated from 30 to 95 °C and maintained at 95 °C for 10 min, with regular shaking (75 rpm) and a constant (3 °C/min) heating rate. For each experiment, 100 g of filmogenic solution was poured onto the acrylic plates (100 x 200 mm), which were dried to constant weight (about 20 h) at 40 °C in a ventilated model TE-394-3 oven (Tecnal - Brazil).

2.3 Thickness measurements

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

2.4 Moisture sorption isotherms

Cassava starch film specimens (30 x 30 mm) were pre-dried for 7 days over phosphorous pentoxide (P₂O₅) and then placed at 25 ± 2 °C over saturated salt solutions with the desired water activities (0.11, 0.33, 0.58, 0.75 and 0.90) in separate desiccators (ROCKLAND, 1960). Each film specimen was weighed at regular intervals (minimum 1 hour and maximum 6 h), and when two consecutive weights were the same, it was assumed that an equilibrium condition had been reached. Under the above conditions, an equilibration period of 3 days was sufficient to establish moisture equilibrium. The equilibrium moisture content was calculated from the increase in mass of the dried sample after equilibration at a given RH. All tests were carried out in triplicate.

2.5 Differential scanning calorimetry (DSC) – determination of glass transition temperature (T_g)

The glass transition temperatures of the films were determined by DSC. The samples were maintained in a room at 20 °C and 64% RH and tested using a Polymer Laboratories DSC (Rheometric Scientific, Surrey, UK) working with PL-V5.41 software. Indium was used to calibrate the temperature and heat flux. The samples (1-2.5 mg) were weighed in aluminium pans and hermetically sealed and an empty pan was used as the reference. The runs were between –40 and 120 °C with

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a heating rate of 5 °C/min (SOBRAL et al., 2001, 2002; MENDIETA-TABOADA, 2008). Once analyzed, the pans were punctured and dried to constant weight at 105 °C to get the dry weight of the sample. The glass transition temperatures (onset and peak) were obtained from the thermograms (LUND, 1983). The values reported are the means of three measurements.

2.6 Mechanical properties of starch films

Five film specimens (100 x 25 mm) of each formulation were pre-dried for 7 days over phosphorous pentoxide (P_2O_5) and then placed at 25 ± 2 °C over saturated salt solutions with the desired water activities (0.11, 0.33, 0.58, 0.75 and 0.90) in separate desiccators (ROCKLAND, 1960). The tensile properties were determined using a TA.TX2i Stable Micro Systems texture analyzer (Surrey – England) according to the ASTM D-882-91 method (1996). The samples were clamped between pneumatic grips and the force (N) and deformation (mm) recorded during extension at 50 mm.min⁻¹ with an initial distance between the grips of 50 mm. The parameters determined were: tensile stress (MPa) and strain at break (%).

2.7 Statistical analysis

The analysis of Variance (ANOVA) and the Tukey means comparison test ($p \leq 0.05$) were applied employing the Statistica software (Statsoft, Oklahoma – USA).

3 Results and discussion

All formulations gave homogeneous, transparent films with no insoluble particles. All the films were easy to handle except the films with 40 g glycerol.100 g⁻¹ starch, which were highly adhesive, indicating that such films could be in the rubbery state at the temperature tested (25 °C). Phase separation was not observed in any of the films, and the film thicknesses ranged from 70 to 100 µm.

3.1 Moisture sorption isotherms

Figures 1 and 2 show the moisture sorption isotherms and the sorption profiles, respectively, of the starch films as a function of the glycerol content. The water activity (a_w) and glycerol content influenced the moisture sorption of the samples. At low a_w , the water content decreased when the plasticizer content increased. For example, at an a_w of 0.11, the unplasticized samples adsorbed more water than the plasticized ones at any glycerol level; at a_w of 0.33 and 0.58, only samples with 30 and 40 g glycerol.100 g⁻¹ starch adsorbed more water than the unplasticized samples. At a_w 0.75 and 0.90, the water content increased when the plasticizer content increased, and all the plasticized samples were more hydrophilic than the samples without plasticizer (Figures 1 and 2). It could also be observed

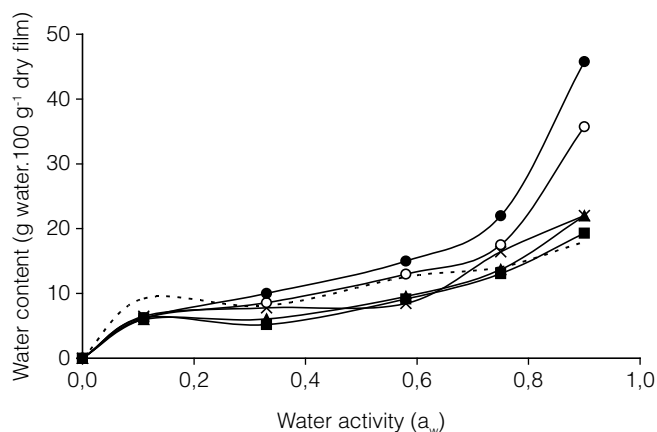


Figure 1. Adsorption isotherms of cassava starch films with different glycerol contents: (—) 0 g.100 g⁻¹ starch; (■) 5 g.100 g⁻¹ starch; (▲) 10 g.100 g⁻¹ starch; (x) 15 g.100 g⁻¹ starch; (O) 30 g.100 g⁻¹ starch; and (●) 40 g.100 g⁻¹ starch.

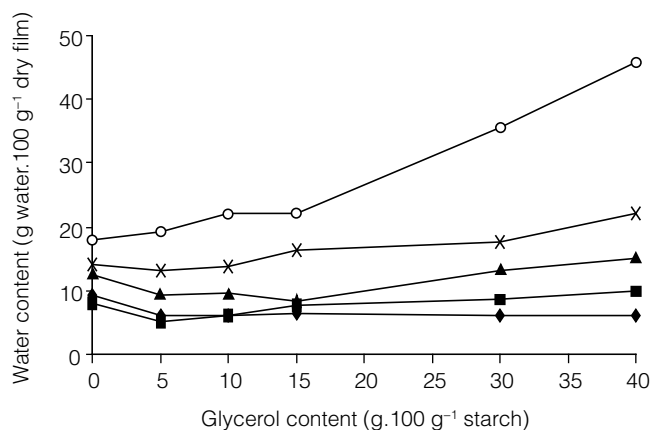


Figure 2. Moisture sorption of starch films as a function of glycerol content at different water activities: (◆) 0.11; (■) 0.33; (▲) 0.58; (x) 0.75; and (O) 0.90.

that in films with glycerol concentrations ≤ 15 g.100 g⁻¹ starch and stored at any $a_w \leq 0.58$, glycerol exerted an antiplasticizing effect, decreasing the hydration capacity. This was similarly observed by other authors who reported a minimum hydration capacity at a glycerol content of 10-15% (LOURDIN et al., 1997b; CHANG et al., 2006).

For sorbitol films, the equilibrium moisture increased with increase in a_w and for all the formulations these films presented a lower hydration capacity than the glycerol films (Figures 3 and 4). According to Sothornvit and Krochta (2001), molecular differences between glycerol and sorbitol are probably responsible for the different sorption capacities of films plasticized with them. Glycerol and sorbitol are polyols with similar straight-chain molecules; however, the glycerol molecule is smaller (molecular weight of 92) and has three hydroxyl groups while the sorbitol molecule (molecular weight of 182) has six hydroxyl

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groups. Although sorbitol presents more hydroxyl groups to interact with the water via hydrogen bonds, the glycerol presented greater water affinity as demonstrated by the adsorption and desorption isotherms (LEUNG, 1986). As reported by García et al. (2000), since sorbitol is more similar to the molecular structure of glucose units than glycerol, the chances of sorbitol interacting with polymeric starch chains are higher, thus, sorbitol-containing films presented higher intermolecular forces and showed a lower capacity to interact with water.

Films plasticized at any sorbitol level and at $a_w \leq 0.58$ were less hydrophilic than the unplasticized films, and this was indicative of its antiplasticizing effect (Figures 3 and 4). According to Gaudin et al. (1999), low contents (below 27) of plasticizers may be strongly bound with starch, exerting an antiplasticization effect, which results in lower water binding capacity by these materials.

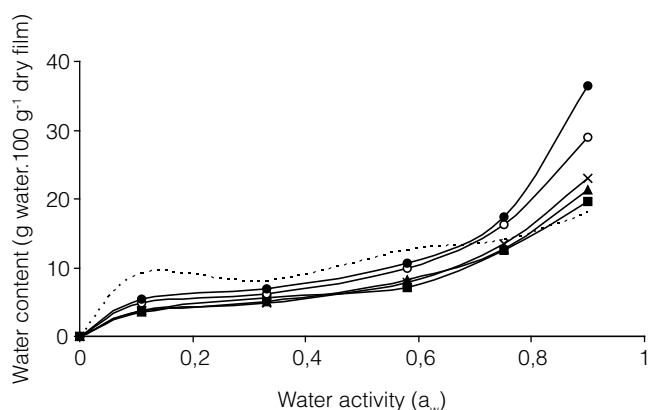


Figure 3. Adsorption isotherms of cassava starch films with different sorbitol contents: (—) 0 g.100 g⁻¹ starch; (■) 5 g.100 g⁻¹ starch; (▲) 10 g.100 g⁻¹ starch; (x) 15 g.100 g⁻¹ starch; (○) 30 g.100 g⁻¹ starch; and (●) 40 g.100 g⁻¹ starch.

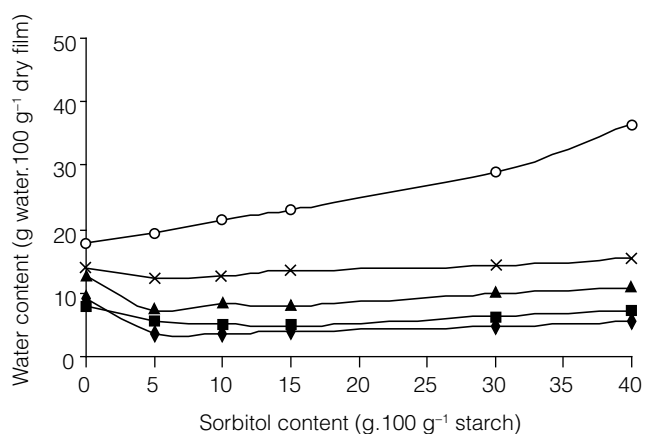


Figure 4. Moisture sorption of starch films as a function of sorbitol content with different water activities: (◆) 0.11, (■) 0.33, (▲) 0.58, (x) 0.75 and (○) 0.90.

3.2 Glass transition temperature

Figure 5 shows a typical DSC curve for the determination of T_g, and in all the thermograms only one transition could be observed for the samples analysed.

In general, an increase in plasticizer content decreases the intermolecular forces between polymer chains, and consequently the overall cohesion and T_g of these materials decrease (MCHUGH and KROCHTA, 1994; LOURDIN et al., 1997b; GAUDIN et al., 2000; MALI et al., 2002; 2005), but in the present work it was observed that at low plasticizer contents, the T_g showed a different type of variation: films with 5 g plasticizer.100 g⁻¹ starch presented significantly higher T_g values than unplasticized ones and films with 10 g plasticizer.100 g⁻¹ starch had T_g values similar to the unplasticized ones (Tukey test, $p \leq 0.05$). Only at plasticizer levels ≥ 15 g.100 g⁻¹ and ≥ 30 g.100 g⁻¹ starch could a decrease in T_g and an increase in moisture content, respectively, of the samples be observed (Table 1). This phenomenon, occurring at low plasticizer contents was indicative of the antiplasticization effect exerted by glycerol and sorbitol. According to Lourdin et al. (1997), the first plasticizer molecules added form relatively strong interactions (hydrogen type bonds) with monomeric units of the starch. As a result, some sites initially occupied by water molecules become occupied by the plasticizer, resulting in more rigid polymers, which are in the glassy state at room temperature.

The films were stored at 64% RH for the glass transition analyses and the system with the largest amounts of diluents (40 g glycerol.100 g⁻¹ starch and 32.05 g water.100 g⁻¹ dry starch) presented the lowest T_g values (Table 1). Films with higher glycerol contents

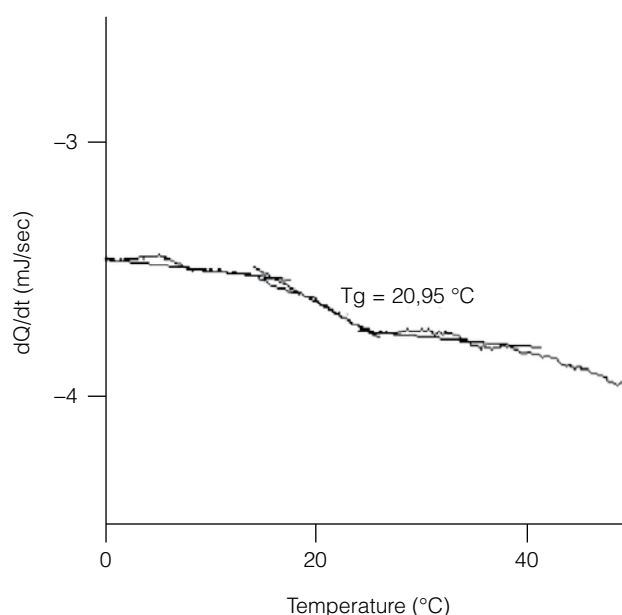


Figure 5. Example of a DSC thermogram for a starch film formulated with 40 g glycerol. 100 g⁻¹ starch.

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Table 1. Glass transition temperatures of films stored at 64% RH and 25 °C.

Plasticizer	Concentration (g.100 g ⁻¹ starch)	Glass transition temperature ^a		Moisture content ^a
		T _g (°C)		(g water.100 g ⁻¹ dry starch)
Glycerol	0	52.77 ± 0.45 ^b		8.16 ± 3.17 ^d
	5	76.36 ± 4.95 ^a		8.83 ± 2.07 ^d
	10	54.64 ± 1.80 ^b		8.98 ± 1.04 ^d
	15	45.04 ± 3.71 ^c		7.53 ± 0.66 ^d
	30	32.59 ± 1.34 ^e		16.99 ± 3.70 ^c
	40	20.95 ± 2.50 ^g		32.05 ± 7.97 ^a
Sorbitol	0	52.77 ± 0.45 ^b		8.16 ± 3.17 ^d
	5	73.36 ± 3.32 ^a		7.70 ± 3.20 ^d
	10	51.66 ± 0.90 ^b		14.54 ± 4.85 ^c
	15	46.02 ± 2.64 ^c		9.38 ± 2.56 ^d
	30	38.29 ± 0.18 ^d		13.66 ± 6.40 ^c
	40	29.66 ± 0.08 ^f		21.39 ± 0.26 ^b

^aMeans in the same column with different letters are significantly different ($p \leq 0.05$).

(30 and 40 g.100 g⁻¹ starch) presented significantly lower T_g values than sorbitol films (Tukey test, $p \leq 0.05$) under the same conditions, and these data agree with the data from the isotherms, which demonstrated that glycerol films presented greater water affinity.

Only films with 30 and 40 g plasticizer.100 g⁻¹ starch showed T_g values closer to room temperature at 64% RH, and in the other formulations, the films were in the glassy state.

3.3 Mechanical properties

In general, the starch films presented a decrease in tensile stress (TS) with increase in a_w and with higher plasticizer levels (30 and 40 g.100 g⁻¹ starch) (Figure 6a,b), but it could be observed that in the case of the glycerol films with a_w of 0.11 and 0.33, an increase in plasticizer level was less effective in decreasing the TS, and in the case of the sorbitol films this occurred for films with a_w of 0.11, 0.33 and 0.58. The lower water content in the samples with lower a_w values explained this behaviour.

The effects of glycerol and sorbitol on tensile stress appear to be more complicated than that of water. The plasticizer type and concentration affected the mechanical properties of the cassava starch films. Glycerol-containing films showed the lowest values for TS, which decreased progressively with increasing glycerol concentration (Figure 6a,b), symptomatic of plasticization. Cuq *et al.* (1997) stressed that plasticizers with lower molecular weights produced more film plasticization than those with higher molecular weights, for the same mass basis, and suggested that the plasticizer effect should be examined on a molar basis, i.e., when used on the same mass basis, the number of moles of glycerol incorporated in the films were higher than the number of sorbitol ones, and this is certainly more important to the plasticizing effect.

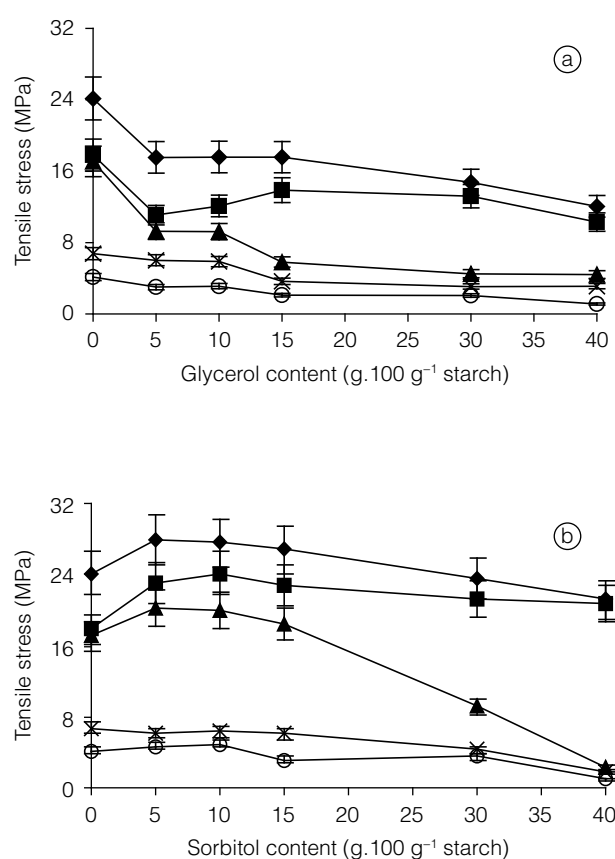


Figure 6. Tensile stress of cassava starch films with different glycerol (a) and sorbitol (b) contents, at different water activities: (\blacklozenge) 0.11; (\blacksquare) 0.33; (\blacktriangle) 0.58; (\times) 0.75; and (\circ) 0.90.

In contrast, sorbitol films with 5, 10 and 15 g plasticizer.100 g⁻¹ starch, over the range of a_w from 0.11 to 0.58, were more resistant than the non plasticized films. Thus it appears that sorbitol can exert an antiplasticizing effect that can be detected by observing the tensile stress.

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Strain at break in glycerol and sorbitol films was dependent on a_w and the plasticizer content (Figure 7a,b). Strain increased to a maximum (at $a_w = 0.75$) and then decreased with further humidification; these data are according to Chang et al. (2006). Glycerol and sorbitol did not affect the extensibility of starch films when employed at low levels (≤ 15 g.100 g⁻¹ starch), and this effect was evident at low a_w values (0.11 and 0.33) (Figure 7a,b), suggesting that glycerol and sorbitol could have an antiplasticizing effect on film strain. Other authors also reported that glycerol (LOURDIN et al., 1997; CHANG et al., 2006) and sorbitol (GAUDIN et al., 1999) had an antiplasticizing effect on the strain of starch films.

In general, glycerol films were more flexible than sorbitol ones at all a_w values and contents (Figure 7a,b), confirming that glycerol exerts a more effective plasticization, and agreeing with other researchers (SOTHORNVIT and KROCHTA, 2001; CHO and RHEE, 2002 and MALI et al., 2005).

The physical state of films strongly affects their mechanical properties. The T_g is a good indicator of the physical state of partially crystalline materials, such as starch films. The lowest T_g values obtained in the present work (Table 1), 20.95 and 29.66 °C, corresponded to films with higher glycerol and sorbitol levels

(40 g.100 g⁻¹ starch), respectively. In general, these films showed the higher strain at break values (Figure 7a,b), evidencing the structural modifications of the starch network when glycerol or sorbitol was incorporated. The matrix of the films becomes less dense and, under stress, the movements of polymer chains were facilitated, improving deformation (MALI et al., 2004).

4 Conclusions

The presence of small amounts of glycerol and sorbitol (<15 g.100 g⁻¹ starch) was able to exert antiplasticizing effects in systems with low water contents, and this effect was detectable from the water sorption capacity of the films, and the tensile and thermal properties. Glycerol and sorbitol films showed different behaviours, indicating that glycerol was a more effective plasticizer, and this variation may be due to differences in molecular characteristics and their dissimilar interaction with the starch matrix.

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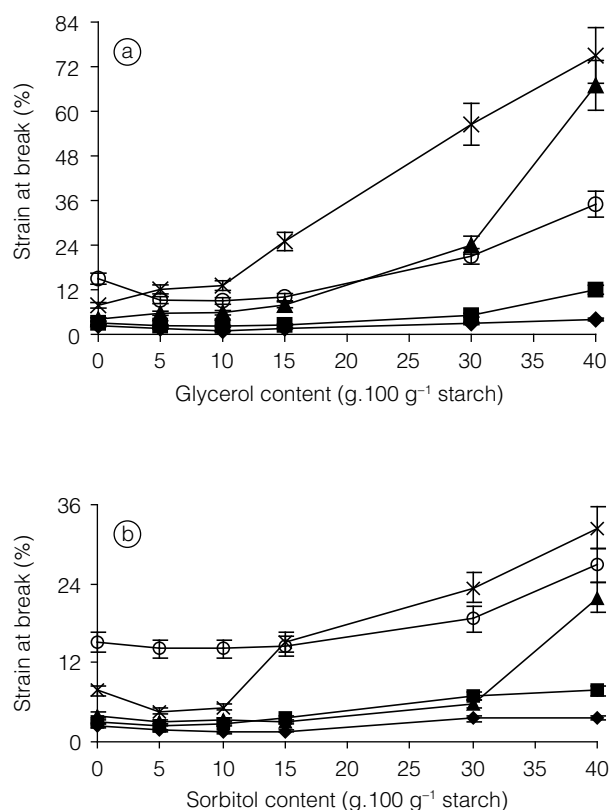


Figure 7. Strain at break of cassava starch films with different glycerol (a) and sorbitol (b) contents, at different water activities: (◆) 0.11; (■) 0.33; (▲) 0.58; (x) 0.75 and (○) 0.90.

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