

# Physical Properties of Cassava Starch Films Containing Glycerol

by

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## Abstract

The aim of this work was to investigate some physical properties of cassava starch films containing glycerol. Films were prepared from film-forming solutions with 2 g cassava starch per 100 g water plus 0, 15, 30 and 45 g glycerol per 100 g starch, and analyzed to determine its mechanical properties by tensile tests, the glass transition temperature ( $T_g$ ) by differential scanning calorimetry, the crystallinity by X-ray diffraction, and moisture content by a new, fast and non-destructive microwave methods. The infrared spectra of the films were also recorded. The resistance values of the films decreased while those of the elasticity increased with the increase of the glycerol concentration, due to plasticizer effect of glycerol, which was also observed in DSC curves. The  $T_g$  of the films prepared decreased with the glycerol content. However, for samples with 30 and 45 g glycerol per 100 g starch, two  $T_g$  curves were observed, probably due to a phase separation phenomenon. According to the XRD diffractograms, films with 0 and 15 g glycerol per 100 g starch presented an amorphous character, but some tendency to show crystalline peaks was observed for films with 30 and 45 g glycerol per 100 g starch. The results obtained with FTIR corroborated these observations. Microwave measurements were sensitive to the moisture on films.

## Introduction

Edible films are thin materials based on biopolymers, such as polysaccharides. Starch is a polysaccharide composed by the amylose, a linear or sparsely branched polymer, and the amylopectin, a highly branched polymer (Mali et al. 2005, Famá et al. 2005). This biopolymer could be interesting in the edible film technology because it is produced abundantly around the world, and it could be considered as inexpensive.

An important starch source is cassava, which is a tropical root crop. Cassava starch is able to form transparent coatings (Vicentini and Cereda 1999) and flexible films (Vicentini et al. 2005) without any previous chemical treatment, neither plasticizer addition. However, for the production of edible films with good workability, a plasticizer such as the glycerol is usually used. The plasticizer modifies the interactions

between the macromolecules, resulting in an increase in the chains mobility and consequently, causing a reduction in the glass transition temperature of the system (Sobral et al. 2001). Thus, plasticizers may affect all physical properties of films. The aim of this work was to investigate some selected physical properties of cassava starch films containing different glycerol content, by means of mechanical analysis, X-ray diffraction, differential scanning calorimetry, microwave methods and Fourier-transform infrared.

## Materials and Methods

Cassava starch, supplied by a local industry (Flor de Lotus Co., Brazil), had the following characteristics (Vicentini et al. 2005): 14.9% moisture; 16% amylose, 0.21% soluble total sugars, 0.23% ash, 0.39% fiber, 0.24% total nitrogen, and 0.15% lipids. For edible film production, film-forming solutions (FFS) were previously prepared with 2g of starch per 100g of water and 0, 15, 30 and 45g of glycerol per 100g of starch. The starch gelatinization was undertaken by thermal treatment at 70°C for 1 min. in a water bath (Tecnal, TE 184). The FFS was poured in an acrylic plate and dehydrated in an oven with air circulation and renewal (Marconi, MA037), at 30°C for 18 to 24 h. Thus, transparent and flexible films with 0.07 ± 0.002 mm thickness were obtained. Mechanical properties were determined by tensile tests, using a Texturometer (TA.XT2i, SMS), following the method suggested by Paschoalik et al. (2003). Each test was done in quadruplicate. These tests were performed at room temperature (22-25°C) with samples previously conditioned at 25°C and 58% of relative humidity (NaBr saturated solution), for one week. However, for the subsequent analysis, samples were conditioned over silica gel. The glass transition temperature of the films were measured using a differential scanning calorimeter (DSC-2010, TA Instruments), in duplicate. The samples were weighted (± 0.01 mg, Analytical Plus, Ohaus) in aluminum pans, hermetically sealed and heated at a rate of 5°C per min (Sobral et al. 2001). The reference was a void pan. The crystallinity of films was studied with an X-ray diffractometer (Rigaku), with Cu source, operating at room temperature, 40kV and 30mA. Rectangular samples were analyzed between  $2\theta = 10^\circ$  and  $2\theta = 30^\circ$  with a step size  $2\theta = 4^\circ$ . Also, infrared spectra (FTIR) of films were recorded between 4000 and 600  $\text{cm}^{-1}$  at 4  $\text{cm}^{-1}$  of resolution, with a Spectrum One (Perkin Elmer) spectrometer, supplied with a universal attenuated total reflectance (UATR) accessory, as suggested by Vicentini et al. (2005). For each spectrum, 25 scans were co-added. These analyzes were run in duplicate. Finally, microwave insertion loss was performed by varying the microwave frequency and at the same time, measuring the attenuation of the energy, after passing through the film. The method is well described in Bergo et al. (2006).

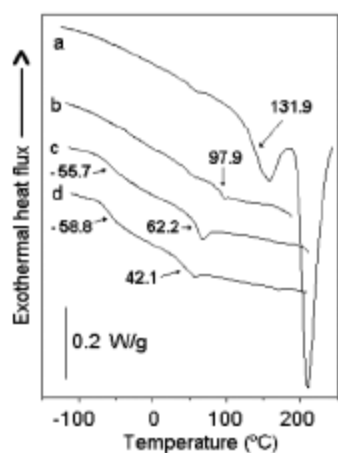
## Results and Discussion

As expected, the increase in the glycerol concentration on the FFS produced films less stiff and rigid, and more extendible; i.e., it caused a reduction on the tensile strength and increase of the elongation at break of films, respectively (Fig. 1). These trends were probably due to the reduction in interactions between the biopolymers chains. This effect of the plasticizer concentration on the mechanical properties is well known and broadly discussed in the literature (Arvanitoyannis and Biliaderis 1998, Sobral et al. 2001, Mali et al. 2005).



**Fig. 1.** Effect of the glycerol concentration on tensile strength and elongation at break of cassava starch films

The resulting trends of the mechanical properties of the films could be explained in a general manner, by the effect of the glycerol on the state properties of the films. It can be observed in the DSC curves of the films (Fig. 2), that the glass transition temperature ( $T_g$ ) decreased from 131.9 to 42.1°C, when the glycerol content increased from 0 to 45%, respectively; i.e., the films became less glassy with the addition of glycerol. This behavior was also observed by Mali et al. (2002) working with yam starch based films, and by Forssell et al. (1997), dealing with films based on barley starch, in both cases with glycerol. These latter authors also observed an endothermic peak as the one observed in this work (Fig. 2) with samples without glycerol. In this case, this phenomenon, observed at a temperature of about 197°C in films without glycerol, was due to thermal degradation of starch, which shifted to higher temperatures by the increase of the glycerol content, attaining 218°C in films with 45% of glycerol.



**Fig. 2.** DSC curves of cassava starch films containing (a) 0%; (b) 15%; (c) 30%; and (d) 45% of glycerol. Numbers indicated in the plots are values of temperature (°C)

It can be also observed in DSC curves (Fig. 2) of cassava starch films, that another glass transition was visible at very low temperature when glycerol concentration was 30% ( $T_g = -55.7^\circ\text{C}$ ) and 45% ( $T_g = -58.8^\circ\text{C}$ ). This behavior was also observed by Forssell et al. (1997), who suggested that a phase separation has occurred between a starch rich phase and glycerol rich phase. This phenomenon may explain the high standard deviation on data of elongation at break of films with 30 and 45% of glycerol. In fact, these films presented less workability than those with 0 or 15% of glycerol due to a “sticky” character.

Figure 3 shows the X-ray diffractograms (XRD) obtained with the films studied in this work. They can be related to complex structures like B-V type crystal structure, typical of tuber starches (Mali et al. 2002, Famá et al. 2005). According to these XRDs, films with 0 and 15g glycerol per 100 g starch presented an amorphous characteristic, but some tendency to crystalline peaks, at  $2\theta \approx 20^\circ$ , were observed for films with 30 and 45 g glycerol per 100 g starch. Starch films could have amorphous character because the thermal

treatment of FFS provoked starch gelatinization, causing disruption of the double helix conformations of the yam starch. However, the increase in glycerol content in the films may have increased the macromolecular mobility, allowing the formation of microcrystalline junctions, i.e. some re-crystallization occurred. Mali et al. (2002) observed that glycerol in FFS did not noticeably influence the X-ray pattern of yam starch films.

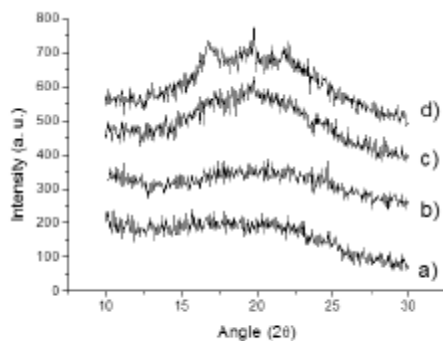


Fig. 3. X-ray diffraction pattern of cassava starch films containing (a) 0%; (b) 15%; (c) 30%; (d) 45% glycerol

Some small differences in terms of band shape and intensity can be observed in the fingerprint of yam starch in the FTIR spectra (Fig. 4), as a result of the glycerol content variation. The peak observed at 1011.8 cm<sup>-1</sup>, that appeared as a shoulder in films without glycerol, became more prominent and presented a displacement to 1013.4, 1014 and 1014.8 cm<sup>-1</sup>, for glycerol concentrations of 15, 30 and 45%, respectively. These peaks could be associated with COH bond vibrations or solvation, and could also be associated to changes from an amorphous to a semi-crystalline state (van Soest et al. 1995, Vicentini et al. 2005). The displacement of the peak observed from 995 to 997.9 cm<sup>-1</sup> when the glycerol content increased from 0 to 45%, could also be associated to the amorphous-crystalline transition in these films.

The glycerol also affected the peak normally associated to COC anti-symmetric bridge stretching (van Soest et al. 1995). This peak, initially observed at 1148.6 cm<sup>-1</sup> in films without glycerol, was displaced to 1149.6, 1150.2 and 1150.5 cm<sup>-1</sup> when the glycerol concentration was 15, 30 and 45%, respectively. It can be therefore suggested that the thin difference between these last two data may be explained by a phase separation, such as that observed in DSC curves (Fig. 2).

Figure 5 shows two examples of microwave insertion loss response as a function of frequency (frequency domain), obtained from that films conditioned in a) silica-gel and b) NaBr. The results show that the main changes are prominent in the region between 11 and 13 GHz. These changes were attributed to the moisture that tends to accumulate in the films, due to the glycerol hygroscopic character.

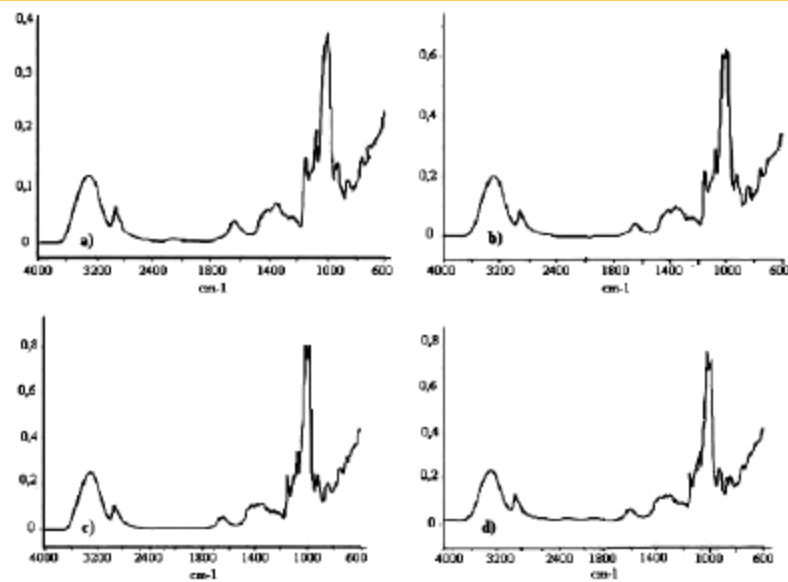


Fig. 4. FTIR spectra of cassava starch films containing (a) 0%; (b) 15%; (c) 30%; (d) 45% glycerol

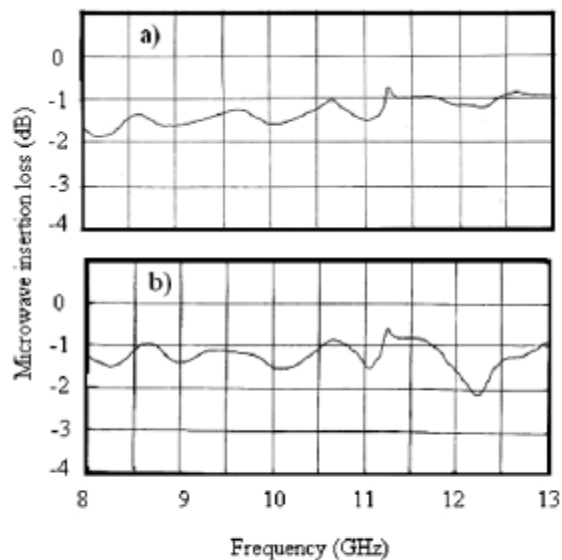


Fig. 5. Example of microwave insertion loss in cassava starch films containing 15% glycerol, conditioned in: a) silica-gel and b) NaBr; for a week

## Conclusions

The increase of glycerol content in cassava starch films, increase the macromolecular mobility, probably by solvation of COH bonds of the starch, which allowed some polymer re-crystallization. However, at the macroscopic scale, cassava starch films became less stiff and more flexible. In fact, the glycerol addition had two effects: it caused an increase in the mobility of amylose and amylopectin chains which overcame the opposite effect of the re-crystallization. Also, the increase of the flexibility of the films with plasticizer could be attributed to a lubrication effect of glycerol, associated to a phase separation observed at the highest concentrations. Microwave insertion loss response as a function of frequency shows that this technique is sensitive to the moisture, due to different conditioning of the films. The moisture affects the region between 11 and 13 GHz.

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