GRANULES MORPHOLOGY AND RHEOLOGICAL BEHAVIOR OF GREEN BANANA (*Musa cavendishii*) AND CORN (*Zea mays*) STARCH GELS

Morfologia dos grânulos e comportamento reológico dos géis de amido de banana verde (*Musa cavendishii*) e milho (*Zea mays*)

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ABSTRACT

In this work, it was used starch obtained from green banana (*Musa cavendishii*) and commercial corn (*Zea mays*) starch in order to compare the granule morphology and the rheological behavior of these gel-starches. Images of starch granules morphology were obtained from scanning electron microscope (SEM). The banana starch granules presented an oval and ellipsoidal shape with irregular diameters. Neverthless, the granules of corn starch showed a poliedric shape, with different sizes. The rheological behavior of gel starch solutions showed a non-newtonian character with a pseudoplastic behavior. Herschel-Bulkley model gave a good description on the rheological behavior of the gel starch. Banana gel-starch solutions showed higher values of shear stress and apparent viscosity when compared with corn gel-starch solutions. A progressive decrease in shear stress and viscosity occurred with the addition of sodium chloride and sucrose.

Index terms: Starch, green banana, corn, microscopy, rheology.

RESUMO

No presente trabalho foi utilizado amido obtido de banana verde *(Musa cavendishii*) e amido de milho (*Zea mays*) comercial, com o objetivo de comparar a morfologia dos grânulos e o comportamento reológico dos géis. As imagens da morfologia dos grânulos foram obtidas por microscopia eletrônica de varredura. Os grânulos de amido da banana apresentaram forma oval e elipsoidal com diâmetros irregulares, todavia, os grânulos do amido de milho mostraram forma poliédrica e diferentes tamanhos. As análises reológicas dos géis das soluções de amido mostraram caráter não-newtoniano, pseudoplástico. O modelo de Herschel-Bulkley foi o que melhor representou comportamento reológico dos géis. O gel de amido de banana verde obteve maiores valores de tensão de cisalhamento e viscosidade aparente quando comparada ao gel de amido de milho. Ocorreu um decréscimo progressivo na tensão de cisalhamento e na viscosidade com a adição de cloreto de sódio e sacarose aos géis.

Termos para indexação: Amido, banana verde, milho, microscopia, reologia.

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INTRODUCTION

Originated from Asia, banana (*Musa paradisiaca L.*) is produced in large quantities in tropical and subtropical areas (FAO, 2003).

About one-fifth of all bananas harvested become culls. When banana bunches arrive at central collection stations, bananas to small for shipping are removed, along with those that have damaged or spoiled areas that could cause microbial contamination of the bunch. Rejected bananas are normally disposed of improperly. Attempts are made to use these culled bananas in animal feed and products such as chips, flakes and powders, but they are used only to a limited extend for these purposes due to the low value of such products (PINGYI- PINGYI-ZHANG et al., 2005).

The composition of bananas changes dramatically during ripening. Starch is the principal component of green bananas, which undergoes important changes during ripening. The average starch content drops from 70 to 80% in the pre-climateric (prior to starch breakdown) period to less than 1% at the end of the climacteric period, while sugars, mainly sucrose, accumulate to more than 10% of the fresh weight of the fruit (CORDENUNSI et al., 1998).

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Starch is occurs as insoluble granules in many plant tissues, and is widely distributed in nature. Like all starches, the size and shape of commercial starch granule is characteristic of the plant source and this enables them to be identified microscopically. When heated in water to a sufficiently high temperature starch form a viscous paste which sets to a gel on cooling. It involves a process called starch gelatinization which occurs to a greater or lesser extent whenever starch is cooked in the presence of water (FLINT, 1994).

According to Branco (1995), the knowledge of rheological parameters is important in industrial applications not only to determine the energy consumption to pump a fluid with greater viscosity, but also to solve problems with air incorporation, which causes difficulties in pump operation, and with undesired reactions such as oxidation and contamination.

Examination of the rheological properties of starches is an important step in the characterization and understanding of their functional properties. When starch is cooked in a large excess of water, the granules swell and at the same time part of the components solubilize giving rise to a suspension of swollen particles dispersed in a macromolecular continuous phase (THEBAUDIN et al., 1998).

The rheological model of power law (eq. 1) is used do characterize the behavior of fluids because it fits well the experimental data, being a simple model and having a wide technological application (BRANCO & GASPARETTO, 2003):

$$\tau = K\gamma^n \qquad (1)$$

where τ is the shear stress (Pa), γ is the shear rate (s^{-1}), K is the consistency coefficient (Pa s^n) and n is the flow behavior index (dimensionless).

Herschel-Bulkley model (eq. 2) is used in fluids that start flowing process when shear stress applied is higher yield-stress rate (CRANDALL et al., 1982):

$$\tau - \tau_{OH} = K_H \gamma^{nH} \qquad (2)$$

where τ is the shear stress (Pa), τ_{OH} is the initial shear stress (Pa), K_H is the consistency coefficient (Pa s^n), γ is the shear rate (s^{-1}), and n_H is the flow behavior index (dimensionless).

The aim of this work was to determinate the morphology of green banana and commercial corn starch, as well as, characterize the rheological behavior of its gels. Sucrose and sodium chloride were used as solvents in order to verify the influence of these substances on the rheological behavior.

MATERIALS AND METHODS

Starch extraction

The banana starch was obtained from the *Musa cavendishii*, with maturation stadium around 11.23 °Brix (soluble solids). According to Bobbio & Bobbio (2003), the green bananas were weighted, manually peeled, sliced and immersed in a solution of sodium metabissulphite of 0.3%. The pieces were disintegrated in a blender at low speed for 2 minutes. The paste obtained was disposed in plastic container and stirred for 2 minutes, being this paste filtered in a cloth and the crude starch was manually squeezed. The extraction process was repeated with the crude starch until the filtered liquid present a whiter appearance. The filtered liquid rested for 12 hours for the starch to settle. The liquid on the top of the decanted starch was removed. The starch on the bottom of the container was mixed with water and again filtered in a cloth. The filtered liquid was stood for the starch to settle, for about one hour.

The starch with water was filtered in a Buchner and washed with water and ethanol (95%). After the drying process under vacuum for 10 minutes the starch was distributed in trays and dried in a laboratory oven at 40°C for 12 hours. The dried starch was weighted, disintegrated using a porcelain capsule until the starch acquires a uniform grainy aspect and stored in a plastic bag. The commercial corn (*Zea mays*) starch was acquired in the local market.

Scanning Electron Microscopy (SEM)

The starch granules morphology was characterized by an electronic microscope. Granules were sprinkled over a duplex adhesive tape and placed on a metallic bracket. In order to provide conductivity, the samples were recovered with gold. The images were obtained from a JEOL JSM-6360 LV Scanning Electron Microscope under 10 kV.

Gel sample preparation

Banana and corn starch solutions were prepared in a concentration of 5%. It was used, as solvent, distilled water (standard gel), sucrose solution (30%) and sodium chloride (10%) to dissolve the granules (BOBBIO & BOBBIO, 2003). Each solution was heated until it reaches the gelatinization temperature. Three different gels were obtained.

Measurements of rheological properties

The rheological measurements of the samples were carried out with a concentric cylinder Brookfield, DV-III+, using a small sample and spindle SC4-34. The rheometer was interfaced to a microcomputer for control and data acquisition. The sample compartment was monitored at a constant temperature using a water bath/circulator (Brookfield TC-500). Each experimental run to the upward curve had duration of 4 min with shear rate range from 0 to 70 s^{-1} and 4 min to the downward curve with shear rate range from 70 to 0 s^{-1}. Both at decreasing and increasing shear rate, 25 points of shear stress were obtained resulting in a total of 50 points, whose average value of shear stress was taken for each shear rate. Two experimental runs were done for each material, and the resulting shear stress was the average of the three experimental values. The experimental data were evaluated and fitted according to the rheological models of Herschel-Bulkley and Power Law, using the software Origin 7.0 to obtain the rheological (τ_o, n and K) and statistical parameters (R^2 and χ^2). For each fitted model, the determination coefficient (R^2), sum of the squared residual (SSR) and the chi-square (χ^2) were analyzed.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

The granule sizes distributions are shown in Fig. 01 and Fig. 02.

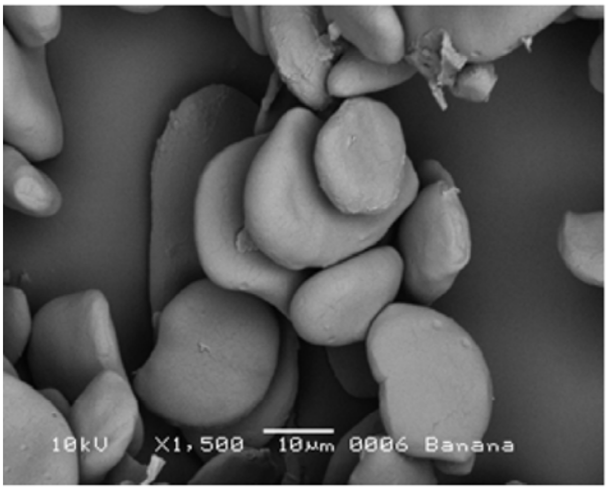

FIGURE 1 – Scanning electron micrographs of starch granules from green banana (1500 x).

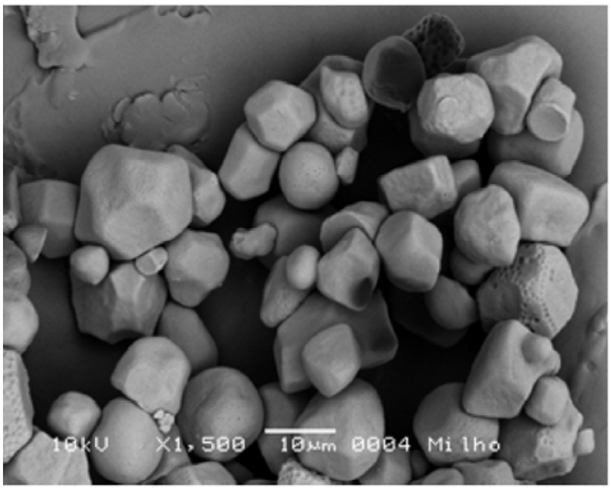

FIGURE 2 – Scanning electron micrographs of starch granules from corn (1500 x).

There was a difference between the sizes and shapes of green banana starch and corn starch, which shows the variability of morphology due to starch sources. The green banana starch granules showed an oval-ellipsoidal shape, with irregular sizes (10mm). This observations are in agreement with Lii et al. (1982) and Ling (1982). The corn starch granules showed poliedric shape and irregular sizes, with a variability of diameters. Teixeira et al. (1998), studying corn starch morphology found similar results.

Rheological behavior

The rheological behaviors of gel-starch (banana and corn) are shown in Figures 03 and 04.

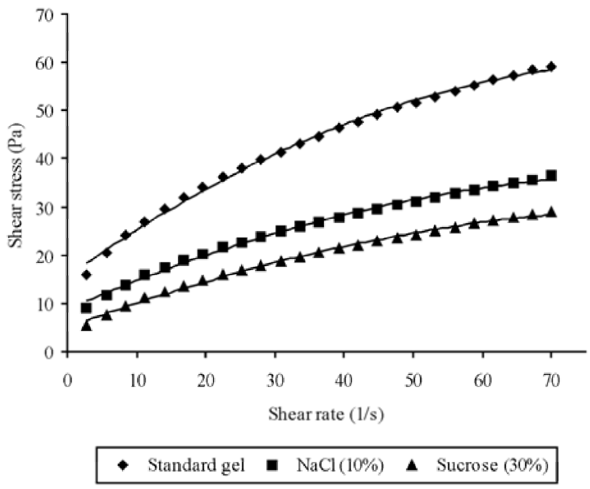

FIGURE 3 – Flow curves of the banana's gel fitted to the Herschel-Bulkley model at 25ºC.

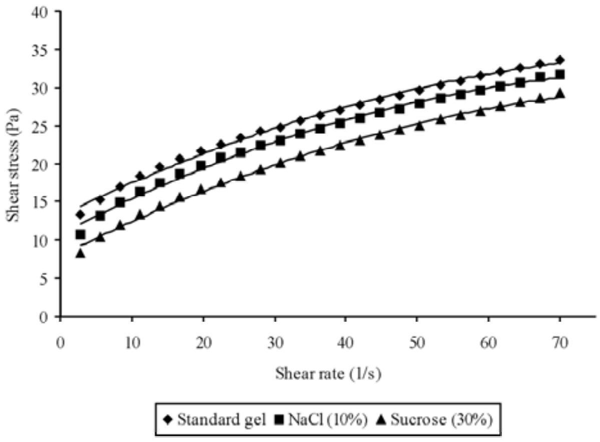

FIGURE 4 – Flow curves of the corn gel fitted to the Herschel-Bulkley model at 25°C.

Shear stress versus shear rate curves had showed the non-newtonian character of the gels. The marked points represent the average values of the experimental data of the rheograms and the continuous lines are the fit results calculated from the Herschel-Bulkley model (HAMINIUK, 2005). From Table 01, it can be noted that the Herschel-Bulkley model presents higher values of coefficient determination (R^2) and the chi-square (χ^2) values were less than 0.01.

From Table 2, it can be perceived that the Power Law model also presented higher values of coefficient determination (R^2) and the chi-square (χ^2) values were less than 0.24. Those results confirms the good fit for both models, however, in this work, the discussion about the rheological parameters of the gel-starch will be limited to the Herschel-Bulkley model, since this equation has consider the yield stress, which is an important parameter.

Working with fruit purées, Guerrero (1993) also selected the H-B model from others (Power Law, Casson and Bingham) because of its inherent compatibility as far as yield stress was concerned.

As can be seen in Table 1, the gel-starch of green banana and corn showed a shear-thinning behavior due to the values of flow behavior index (n) were less than 1. According to Fig.03 and 04, it can be noted that green banana gel presented higher values of shear stress than corn gel. The differences between the flow curves are due to the competition among starch, and sucrose and NaCl for the available water. Besides, the addition of sucrose and sodium chloride delayed the gelatinization temperature, influencing the rheological behavior of the gels. Regarding to yield stress, the corn gels showed higher values when compared to green banana gels. This could be explained by the tendency of the flow curves, since the green banana gels presented higher inclination (flow curves) than corn gels, which during the fit, it resulted in lower values of yield stress (Figure 03 and 04).

Guerrero and Alzamora (1997) found that glucose addition, pH value and temperature significantly affected the flow characteristics of banana purées, the reduction of a_w, (by the glucose addition) generally decreased shear stress values under a given shear rate. As pH decreases, the dependence of flow curves on temperature and a_w was more pronounced.

Bhattacharya & Bhattachalya (1994) studied cooked debranned maize flour suspensions (2-10% concentration) and verified that all formulations were pseudoplastic in nature and exhibited yield stress and the shear-rate and shear-stress data were best fitted into the Mizrahi-Berk and Herschel-Bulkley models. An increase in the concentration of the flour increased the consistency index and the experimental yield stress of the suspensions, but decreased the flow behavior index of the Herschel-Bulkley model, and the power index of the Mizrahi-Berk model.

A typical viscosity curves are shown in Fig. 05 and 06. The difference in apparent viscosity between the standard gels and those with sucrose and sodium chloride is related to the same reason which affect the shear stress values, since that the apparent viscosity is a ratio between shear stress and shear rate. With an increase in shear rate occurs a decrease in apparent viscosity of the gel-starches.

When shear force are applied, the particles may rearrange themselves into parallel direction with shear force and big particles may break into small particles. The particles can flow easily as a result of resistance arising from particle–particle interaction which results in decreasing of viscosity (CHARM, 1962).

After a sharp reduction, the apparent viscosity changed slightly and became steady at higher shear rates. This can be related to the reduction in the size of colloidal aggregates as the shear rate increases (IBANOGLU, 2002). According to the apparent viscosity data, the banana gel-starch solution showed higher apparent viscosity values than corn gel-starch solution. The difference in apparent viscosity between both solutions can be related to the size of the starch granules.

TABLE 1 – Parameters of Herschel-Bulkley model of green banana and corn gels.

Gel	Yield Stress (Pa)	Consistence Coefficient K (Pa.s^n)	Flow behavior index (n)	χ^2	SSR	R^2
Banana starch						
Standard	3.36	7.40	0.47	0.010	0.34	0.999
NaCl (10%)	2.17	4.11	0.50	0.002	0.19	0.999
Sucrose (30%)	0.03	3.05	0.53	0.003	0.22	0.999
Corn starch						
Standard	8.62	2.76	0.52	0.005	0.11	0.999
NaCl (10%)	4.97	3.62	0.47	0.003	0.26	0.999
Sucrose (30%)	3.79	2.57	0.54	0.002	0.18	0.999

χ^2 – Chi-square R^2 – Determination coefficient SSR – Sum of the squared residual.

TABLE 2 – Parameters of Power Law model of green banana and corn gels.

Gel	Consistence coefficient K (Pa.s^n)	Flow behavior index (n)	χ^2	SSR	R^2
Banana starch					
Standard	9.42	0.420	0.060	1.52	0.980
NaCl (10%)	5.36	0.449	0.028	0.05	0.999
Sucrose (30%)	3.07	0.528	0.003	0.01	0.999
Corn starch					
Standard	8.46	0.32	0.240	5.55	0.980
NaCl (10%)	6.87	0.36	0.084	0.11	0.991
Sucrose (30%)	4.73	0.42	0.084	0.09	0.997

χ^2 – Chi-square R^2 – Determination coefficient SSR – Sum of the squared residual.

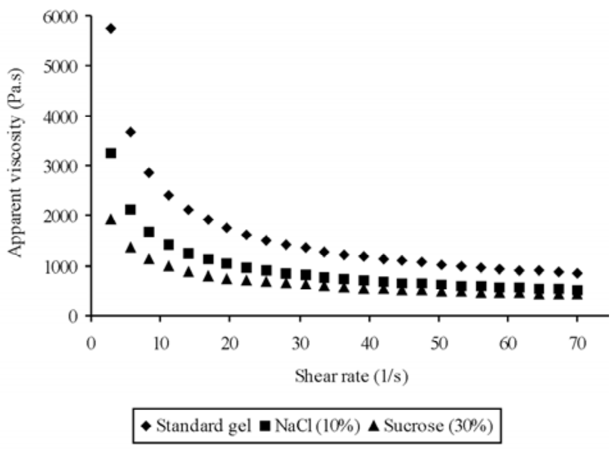

FIGURE 5 – Apparent viscosity of green banana gels at 25ºC.

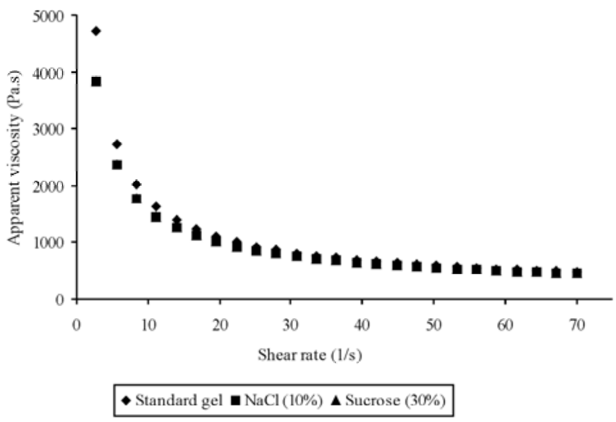

FIGURE 6 – Apparent viscosity of corn gels at 25ºC.

CONCLUSIONS

According to the results obtained in this work, the granules of green banana starch presented and oval-ellipsoidal shape and irregular sizes. Concerning to corn starch, the granules presented a poliedric shape, as well as irregular sizes. Regarding to the rheological behavior, it can be stated that both gels (green banana and corn) had a shear-thinning characteristics due to the flow behavior index were less than 1. Power Law and Herschel-Bulkley models had a good representation for the rheological parameters for both starches and it was verified a progressive decrease in shear stress occurred with the addition of sodium chloride and sucrose. The green banana gels showed higher values to the apparent viscosity when compared with corn gels, which allows the calculation of the pumping requirements and the heat transfer parameters in industrial applications of these starches gels.

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