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Rheological and optical study of starch gelatinization in cassava flour suspensions

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1 Introduction

Cassava, *Manihot esculenta* Crantz (Euphorbiaceae), is a root from South America, traditionally cultivated and consumed in Brazil as an indigenous heritage. Nowadays family farmers are the mainly responsible for fresh cassava and cassava flour production, while starch is produced by industry, which has a higher added value.

For instance, by studying the aspects of producing cassava flour can be of great value for helping family farmers who are mainly responsible for maintaining this traditional crop in Brazil. Therefore, creating alternative uses of this crop may result in income increase. Also, cassava crop in Brazil is crucially important as a staple food for poor people and also plays a major role as an industrial input for varied uses not only for food, but also for textile, petroleum and steel (iron separation) companies.

The ability of starch swelling, in presence of excess of water, heat and shearing, known as gelatinization, plays an important role as a food ingredient (thickener) and other uses as a biopolymer for bioplastic manufacturing. Starch is the major component in cassava flour and water is the main plasticizer. In order to follow what happens during the gelatinization under controlled shear stress can be observed using optical microscopy associated to an oscillatory rheometer, which was then investigated by the present work

The use of cassava flour instead of isolated starch might be interesting because there is a very low production of residue when cassava starch is produced. As a bulk material, cassava flour contains not only starch, but also other hydrocolloids, and according to Phillips and Williams (2000) synergism among hydrocolloids can promote interesting results with varied applications, especially in obtaining gels with new rheological characteristics.

Therefore, the aim of this work is at studying the effect of glycerol content on the gelatinization of starch present in solutions of cassava flour under controlled stress condition.

2 Materials

Cassava flour was produced in Embrapa Agroindústria de Alimentos from fresh cassava produced locally in Rio de Janeiro. Glycerol, analytical degree, (Proquimios, RJ) was used as secondary plasticizer.

3 Methods

Cassava flour at 4% (w/w, d.b.) was dispersed in 10 mL of an aqueous solution of mixture of water and glycerol (0, 30, 50 and 100 g/100 g of flour) that was placed in a pre-heated (50 °C) Rheoscope (Thermo Haake, Karlsruhe, Germany) plate fitted with a 20 x lens, attached to a oscillatory rheometer MARS (Thermo Haake Mars, Karlsruhe, Germany) following the methodology described by Tan *et al* (2008), with some modifications. The suspensions were kept for 2 min at 50°C, then heated to 90 °C over a period of 14 min, held at 90 °C for 8 min, cooled back over 14 min and finally held for 2 min, giving a total of 40 min. The heat was controlled by a computer using a Phoenix (Thermo Haake, Karlsruhe, Germany) water bath.

During heating, the starch suspension was sheared at a constant rate of 100 s⁻¹ using a 60 mm reflective stainless steel probe and a gap of 0.2 mm. Gelatinization of the flour suspensions were then visualized using a digital video camera.

4 Results and Discussion

Figure 1 presents curves of viscosity as a function of time, for each content of glycerol used herein. It can be observed that under excess of plasticizer, heating and shearing, gelatinization occurs, characterized by the increase in viscosity. Because of a destruction of crystalline region of starch granules, gelatinization is quite important as it is the basis of the conversion of starch into a new rearranged structure composed by dispersed continuous amylose molecules and non-continuous amylopectin molecules. Other phenomena including water diffusion and granule expansion are also involved in this process (Liu *et al*, 2009). As a result of gelatinization, a suspension of starch molecules into low molecular weight fluids become a gel-like fluid, whose characteristics are dominated by starch molecules (Taghizadeh and Favis, 2013).

Table 1 shows the temperature and time values when the viscosity starts to increase, indicating the gelatinization of starch has started. We can conclude that higher contents of glycerol promoted an elevation of temperature necessary to increase the apparent viscosity of solution and retarding the gelatinization process.

Table 1 – Gelatinization onset temperatures and times.

Glycerol Content (g/100 g flour)	Temperature (°C)	Time (s)
0	61.4	406.0
30	66.0	558.5
50	68.0	556.6
100	73.0	723.0

These findings are related to antiplasticizing effect of glycerol that can decrease the levels of available water content, which would be able to enter into starch granule. According to Taghizadeh and Favis (2013), shear has no influence on the initiation temperature of gelatinization. It seems that the beginning of gelatinization is correlated to the capacity of the plasticizer to diffuse into the amorphous phase of the starch granule.

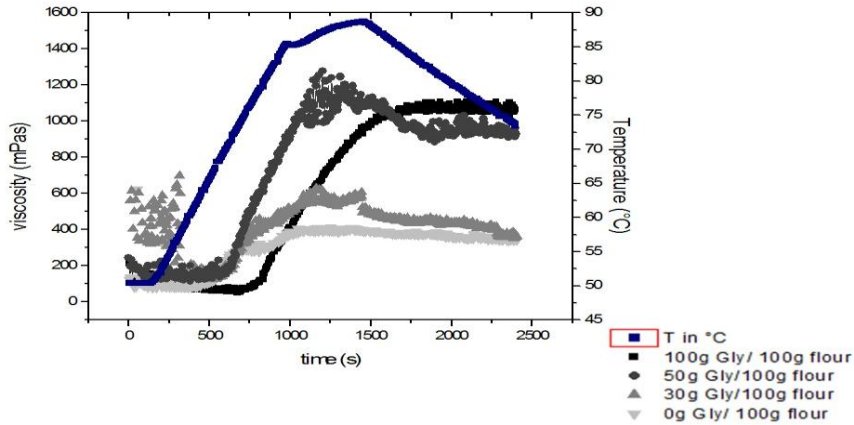


Figure 1 – Temperature *versus* time curve for cassava flour solutions with different glycerol concentrations

Water is the most active plasticizer in the gelatinization process, because of its low molecular weight, high affinity with starch and capacity of lowering the melting point. When water is used alone as plasticizer, after some time it tends to evaporate, depending on the environmental conditions, what reduces thermoplastic starch qualities. On the other hand, affinity between a second plasticizer with water will influence the gelatinization phenomenon (Pittia and Sacchetti, 2008; Liu *et al*, 2009).

Rheological measurements presented some discontinuities, especially under low glycerol concentration. Probably some water evaporation during the process and the macromolecular changes under thermomechanical treatment during rheological measurement can cause changes in rheological properties, which are difficult to follow (Xie *et al*, 2012). Besides of that the rapid sedimentation of starch molecules during the measurements difficult the analysis, and can create some irregular points in the apparent viscosity plot (Tan *et al*, 2008). The presence of glycerol content probably helped holding starch granules in solution decreasing sedimentation by suspending the granules which was more evident with 100% (w/w flour) glycerol.

The images at different time capture of cassava flour showing the starch granules dispersed in water/glycerol are displayed in Figure 2. It is possible to see the birefringence, which is represented by the presence of Maltese cross inside the granule at the beginning of the analysis for all glycerol content. The presence of glycerol clearly retarded the gelatinization process (Figure 2d). After the starch granules absorb plasticizers, the crystallinity region is disrupted and starch swells, characterizing the gelatinization process, what is an irreversible state (Figure 2). It is observed that larger granules started to absorb plasticizer before the smaller granules, which was also seen by Tan *et al* (2008) in maize, barley and wheat starches. Continuous stress, during the heating cycle, leads to continuous starch damage, starting from small to larger granules. As a consequence, the birefringence of the light passing through the crystalline region of the starch granules was lost and plasticizer diffused into the granules leading to swelling causing a substantial increase of viscosity, which is better represented in Figures 2a and 2c.

The cassava flour dispersed in water rapidly formed a homogeneous matrix (Figure 2a) at 603 s, whereas similar image was only seen at 804 s for 30% glycerol and twice (1233 s) for 50% glycerol. However, it is still possible to see remnants of starch granule, also called ghost.

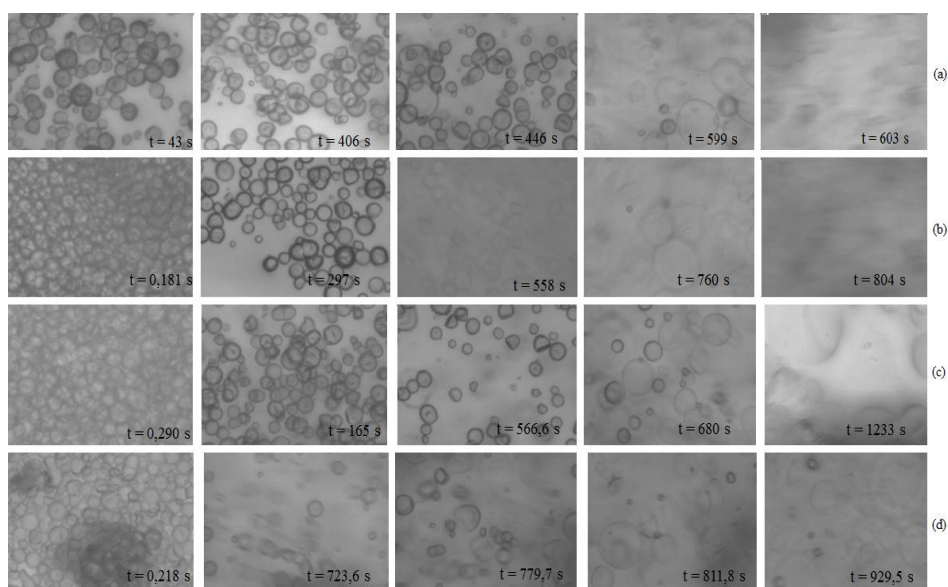


Figure 2 – Images of starch gelatinization of cassava flour in a) 0 g glycerol /100 g flour, b) 30 g glycerol /100 g flour, c) 50 g glycerol /100 g flour and d) 100 g glycerol /100 g flour captured during gelatinization in the Rheoscope

5 Conclusion

A reliable characterization of the rheological responses of cassava flour during the gelatinization could be obtained with the Rheoscope, which allowed the simultaneous optical and rheological measurements with temperature. Starch swelling was responsible for changes in viscosity, which clearly increased by at least two times as starch gelatinized. By using Rheoscope, we could show that addition of glycerol clearly retarded the gelatinization process of cassava flour.

6 Acknowledgements

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7 References

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