Isothermal Rheological Profiles of Filmogenic Solutions from Native and Oxidized Starch with Plasticizers Addition

Cynthia Gama Abundez[1], Rodolfo Rendón Villalobos[1], Emmanuel Flores Huicochea[1], Francisco Rodríguez González[1] and Javier Solorza Feria[1*]

[1] Ceprobi, Instituto Politécnico Nacional, Km. 6 Carr. Yautepec-Jojutla. Calle Ceprobi 8, Col San Isidro. Apdo Postal 24. C. P. 62731, Yautepec, Morelos, México.

[1]Abstract. Filmogenic solutions (FS) with 4 % w/w total solids, with either native (NS), or oxidized (OX2 and OX3) banana starch, were prepared using two plasticizers: starch-glicerol (1:1), starch-sorbitol (1:1). Amplitude and frequency sweeps were carried out using a stress controlled Rheometer TA Instruments (strain mode), model AR1000, with a cone and plate system, 60 mm of diameter and angle of 2 °. Isothermal tests were run at 25°C. The storage (G') and viscous (G") modulus as well as the complex viscosity ($\eta*$) were measured. All FS from NS behaved as weak gel-like viscoelastic materials, with G' > G", while the oxidized specimens behaved as viscous solutions. The moduli values (G' and G") of NS predominated over those of the oxidized specimens (NS>OX2>OX3). Overall, sorbitol enhanced the samples structure to a higher degree than glycerol. Shear-thinning, shear-thickening and Newtonian behavior were seen in the FS viscosity profiles.

Keywords: filmogenic solutions, rheology, glycerol, sorbitol, banana starch.

1. Introduction

An edible film is a continuous layer of edible material, it has the function of providing a barrier to mass transfer (e.g. water, gas), An edible film is a continuous layer of edible material, it has the function of providing a barrier to mass transfer (e.g. water, gas), to serve as a carrier of food ingredients and additives, or to provide mechanical protection (Peressini et al., 2003). The use of edible films barriers for shelf life extension of foods has been recognized because of several factors, such as consumer expectation for fresh foods and shelf life extension of foods (Kroshta et al., 1994). Among the materials used to manufacture edible films are polysaccharides and proteins or its combinations. The two usual mechanisms for making edible materials are the dry process, such as thermoplastic extrusion, based on the thermoplastic properties of polymers and the wet process; based on a film-forming solution or dispersion, where polymers in combination with a low molecular weight component (plasticizer) are solubilized into a liquid phase and dried (Cuq et al., 1998). Casting belongs to this latter group, it involves drying a colloidal dispersion previously applied on a support. Starch is a renewable biopolymer that has gained interest because is readily available from various sources (e.g. tubers, legumes and fruits). Starch which is the major storage polysaccharide of higher plants, is a granule built up by two kinds of macromolecular glucans, one essentially linear α-(1- 4) glycosidically linked amylose and the other one branched with α -(1-6) glycosidic bonds forming the branching points or amylopectin (Zhang et al., 2005).

Oxidized starch has become important in the food industry, for its improved functional properties such as low viscosity, high stability and film forming properties (Kuakpetoon and Wang 2001). This modified starch has proved effective to replace native starch in various practical applications, because of its better functional properties as a result of its granules modification (Wang and Wang, 2003). The aim of this work was to

---

determine the effect of the plasticizers glycerol and sorbitol, on the viscoelastic and viscosity profile of filmogenic solutions of banana starch.

2. Materials and Methods

2.1. Sample preparation

Sodium hypochlorite (NaOCl) with 2 and 3 % w/w active chlorine was used for native starch oxidation (Wang and Wang 2003). Nine different types of filmogenic solutions (FS) with 4 % w/w total solids, composed of either native (NS), or modified banana starch by oxidation (Kuakpetoon and Wang, 2001); named OX2 and OX3 respectively, were prepared with solely starch or adding a plasticizer, conforming the treatments starch-glycerol (1:1) and starch-sorbitol (1:1). All filmogenic solutions were heated for 15 min at 85 ℃ to achieve starch gelatinization.

2.2 Rheological tests

Amplitude (range from 0.1–15% strain, at 0.628 rad/s, to define the linear viscoelastic region) and frequency (0.628 to 62.8 rad/s, at 10% strain) sweeps (Ferry, 1980), were carried out using a stress controlled Rheometer TA Instruments (strain mode), model AR1000, using a cone and plate system with 60 mm of diameter and angle of 2 °. All tests were run isothermally at 25°C. The storage (G') and loss (G") modulus as well as the complex viscosity (η^*), were measured for each sample.

3. Results and Discussion

The typical amplitude strain plots from the FS corresponding to the storage and loss modulus (G', G") were usually flat (not shown), indicating that the values of both above mentioned moduli, were not a function of the applied strain range and so, this did not cause any sample disruption, being thus within the linear viscoelastic region (LVR).

Fig. 1a shows both moduli (G´, G") with essentially linear profiles (Pa) for the Frequency Sweep from Native Starch control and with plasticizers addition, it is notorious that the profiles of the native specimen (NS) predominate over those of starch with plasticizers, usually, values of G´ were higher than those of G" especially for native starch with sorbitol (NS-S), a typical behavior of weak gels (Makosco, 1994), but for NS control and that with glycerol addition (NS-G), this trend was seen only at frequencies lower than 10 rad/s, reversing this behavior at higher frequencies.

Within this range, the glycerol addition decreased the profile values more than that with sorbitol treatment. The FS with sorbitol (NS-S), showed a plateau between 6 and 10 rad/s, followed by a decrease on its moduli values. This suggests that although the starch was previously gelatinized during the FS heating, this might be incomplete since a weak gel had still been formed at the measuring temperature. It also suggests that on the one hand, as indicated in previous reports (Kuakpetoon and Wang, 2006), the starch oxidation process affected the oxidized starch FS consistency, since hypochlorite is mainly consumed for lipid oxidation, depolymerization of amylose and amylopectin and carboxyl and carbonyl groups formation. On the other hand, it may well be that the interaction degree between the plasticizers and starch is different, being overall the predominating profiles, those with sorbitol addition. The native specimen (NS) and that with sorbitol (NS-S), showed shear-thinning behavior, while NS-G displayed a trend towards shear-thickening behavior.

Fig.2a, shows the profiles for oxidized starch (OX2) samples, all FS showed the behavior of viscous solutions (G" > G´) over the applied frequency range, with the trend of the descendent order being OX2>OX2-G>OX2-S for the loss modulus, while the descendent order for the storage modulus was OX2-G>OX2>OX2-S.

The trend observed for the η^* (Fig. 2b) was as expected, consistent with that presented by the viscous modulus, but while OX2 control presented shear-thinning behavior, that with glycerol (OX2-G) and sorbitol (OX2-S) showed a trend to present shear-thickening profile.

Fig. 3a shows the moduli (G', G") profiles from oxidized starch with 3% w/w hypochlorite (OX3) at 25°C. In all cases, predomination of G" persisted (open signals). Overall, the G ́profiles of the sorbitol

added sample presented the highest values, while the glycerol treated FS showed the lowest profile. The loss modulus (G"), also showed an effect due to starch oxidation and plasticizer addition (Fig.3a), the profile of the FS from OX3 predominated over those of sorbitol and glycerol treated samples respectively. The same trend (OX3>OX3-S>OX3-G) was observed on the η^* results (Fig. 3b), but with different profiles; while Ox3 was shear-thinning, OX3-S tended to be Newtonian and OX3-G displayed shear-thickening behavior (Makosco, 1994).
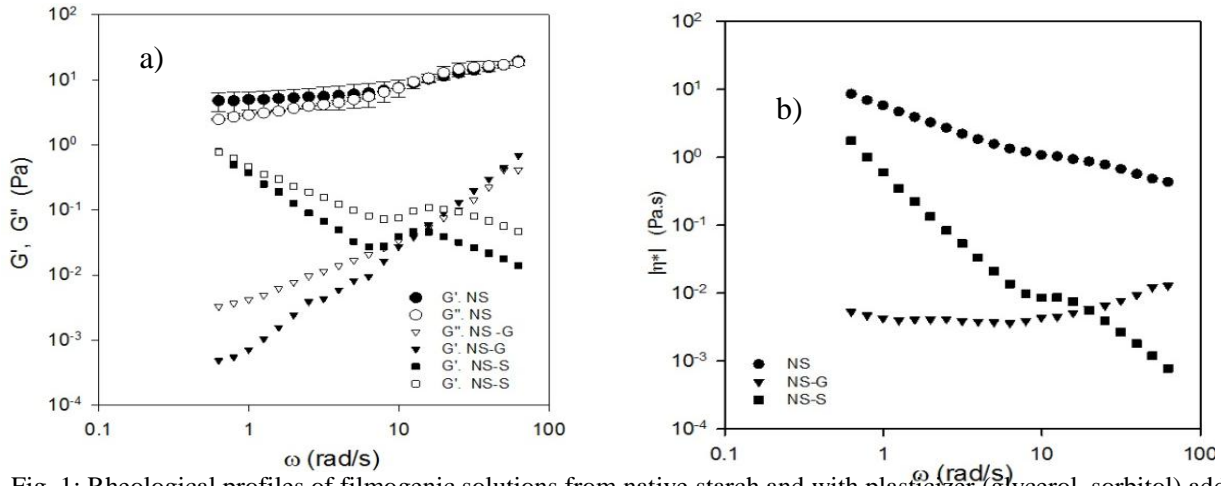

Fig. 1: Rheological profiles of filmogenic solutions from native starch and with plasticizer (glycerol, sorbitol) addition at 25 ℃. a)viscoelastic profiles, b)complex viscosity profiles.
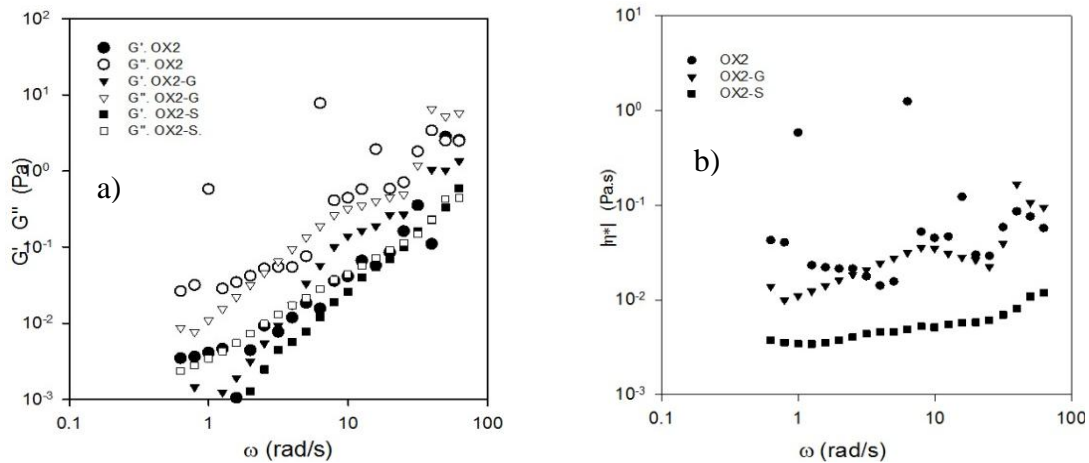

Fig. 2: Rheological profiles of filmogenic solutions from oxidized starch (2% hypochlorite) and with plasticizer (glycerol, sorbitol) addition at 25 ℃. a)viscoelastic profiles, b)complex viscosity profiles.
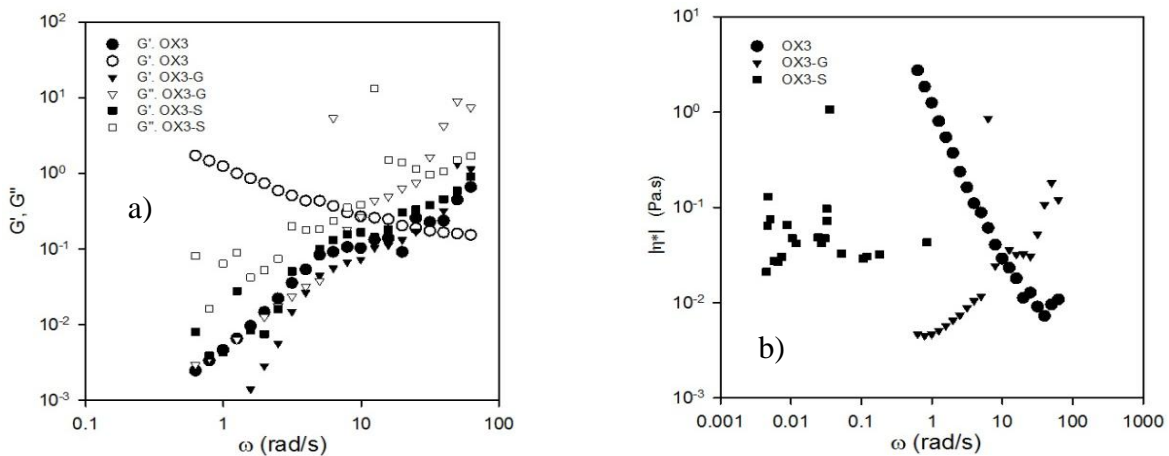

Fig. 3: Rheological profiles of filmogenic solutions from oxidized starch (3% hypochlorite) and with plasticizer (glycerol, sorbitol) addition at 25 ℃. a)viscoelastic profiles, b)complex viscosity profiles.

3.1. Conclusions

All filmogenic native starch solutions either control or with any plasticizer addition, behaved as weak gel-like viscoelastic materials at 25°C, with G' > G" over the frequency ranges, possibly because of the effect of starch oxidation and incomplete starch gelatinization. The FS from native and oxidized starch with glycerol, showed an increase in its viscosity with the applied shear, while the control and sorbitol treated sample showed the opposite trend. Both glycerol and sorbitol caused an increase in viscosity in FS from the 2% oxidized starch. The starch oxidation process irrespective of the oxidant level, seemed to interfere with any real gel formation, rendering the FS as mainly viscous solutions. The highest level of oxidation (3%), affected mainly the viscosity profiles of control and glycerol added filmogenic solutions.

4. Acknowledgements

5. References

[1] D. Peressini, B. Bravin, R. Lapasin, C. Rizzoti, and A. Sensidoni Starch-methylcellulose based edible films: rheological properties of film forming dispersions. *Journal of Food Engineering.* 2003, *59*, 25–32.

[2] J. M. Krochta, E. A. Baldwin, and M. Nisperon-Carriedo. *Edible coatings and films to improve food quality*. Technomic Publishing, Co. Basilea, Suitzerland. 1994.

[3] B. Cuq, N. Gontard, and S. Guilbert. Proteins as agricultural polymers for packaging production. *Cereal Chemistry*. 1998, **75** (1): 1-9.

[4] P. Zhang, R. L. Whistler, J.N. BeMiller, and B. R. Hamaker Banana starch: production, physicochemical properties, and digestibility. *Carbohydr Polym*. 2005, **59**, 443–458

[5] D. Kuakpetoon, and Y. Wang. Characterization of different starches oxidized by hypoclorite. *Starch/Stärke*. 2001, **53**, 211-218.

[6] Y. J. Wang and L. Wang. Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite. *Carbohydr Polym*. 2003, **53**, 207-217.

[7] J. D. Ferry. *Viscoelastic properties of polymers*, John Wiley & Sons, New York. 1980.

[8] W.C. Makosco. *Rheology. Principles, Measurements and Applications*. Wiley-VCH.New York. 1994.

[9] D. Kuakpetoon, and Y. Wang. Structural characteristics and physicochemical properties of oxidized corn starches varying in amylose content. *Carbohydr Res*. 2006. **341**, 1896-1915.