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Rheological and thermal characterization of *Okenia hypogaea* (Schlech. & Cham.) starch

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Abstract

The objective of this work was to characterize the thermal and rheological properties of okenia (*Okenia hypogaea)* starch compared with those of a commercial one (corn). Chemical analysis, differential scanning calorimetry, viscoamylography, swelling and solubility, viscometry and oscillatory dynamic tests were applied to starch samples with 5 and 10% (w/v) of total solids. The chemical analysis indicated that okenia starch could be classified as 'normal'. The thermal analysis showed that okenia starch had a gelatinization temperature (71.3 °C) significantly smaller ($\alpha = 0.05$), than that of corn starch (73 °C). The melting temperature of okenia starch presented a significant increase starting from the 7th day of storage, but from the 14th day onwards, this was constant, while for corn starch it increased until the end of the storage period. Overall, okenia starch presented higher values of swelling capacity than corn starch while for the solubility, the opposite effect was observed. The amylograms of the starch pastes showed higher maximum viscosity for okenia starch, as well as a smaller tendency to the molecular dissociation and re-association than for corn starch. The flow curves showed for both starches a non-Newtonian behavior, the samples with 5% (w/v) of solids exhibiting thixotropy. The dynamic tests showed that both Okenia and corn starch dispersions presented changes in their rheological properties when the temperature increased, going from a highly viscous system (loss modulus, G'' predominating), to a mainly elastic one (storage modulus, G' predominating), both starches forming weak viscoelastic gels.

Keywords: Okenia; Starch dispersions; Thermal properties; Rheological behavior

1. Introduction

Okenia hypogaea (Schlech. & Cham.) belongs to the family of the Nyctaginacea, with a probable origin in Mexico. It is a perennial herbaceous plant distributed practically throughout the Mexican Republic, as well as in great part of the Pacific and the Atlantic coast of the United States and in Central America (Fay, 1980). It can be found in inundable sandy soils, and of volcanic origin with poor content of organic matter and nitrogen, located from sea level up to 1100 m in altitude. This plant is able to grow wild in humid, warm, semi-warm and subhumid tropical climates. *Okenia* grows during the whole year as an abundant grass, close to the ground, with long branches and perfect flowers of bright color (Huitchinson, 1969). It produces a seed that is composed mainly of starch which is the major storage polysaccharide of higher plants, it 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 (French, 1984). A previous work have reported a yield of starch from okenia seeds of 36% on a dry basis with a purity of 95% (Sánchez-Hernández, Solorza-Feria, Méndez-Montealvo, Paredes-López, & Bello-Pérez, 2002).

This biopolymer is used in various industries, e.g. the pharmaceutical, textile, chemical, the industry of fermentations and especially in the food industry. In this last case, it is used as a thickener to give consistency, or as a binding agent; among other functions, it retains water and it provides clarity or opacity. During processing foods undergo

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different shear rates, cooking–cooling cycles and pH changes causing variations in texture, forms, size, color and odor. In spite of its extensive use, processing of starch has not been completely understood since many parameters are known to be involved in its behavior. The characteristics of starch dispersions are determined in order to understand fluid flow and processing parameters. The physicochemical response of these materials depends on its molecular interactions, e.g. the ability of starches to thicken fluids depends on their molecular structure and their solubility (Thebaudin, Lefebvre, & Doublier, 1998).

The objective of this work was to characterize the starch of a non-conventional source as it is the *Okenia hypogaea* in relation to their thermal and rheological properties and to compare them with commercial corn starch.

2. Materials and methods

2.1. Starch isolation

Mature seeds of *O. hypogaea* were harvested at a local experimental farm, the seeds were washed with distilled water to eliminate dust and other contaminants and then cleaned and stored at 4 °C in sealed containers until use. Okenia starch was isolated using the method suggested by Adkins and Greenwood (1966). The seeds were soaked in a buffer solution of 0.02 M (pH 6.5) sodium acetate, containing 0.01 M of mercury chloride. The ratio of soaking solution to seeds was 2:1 (v/w). The mixture was held at 5 °C, with agitation (50 rpm) in an orbital shaker for 24 h, changing the solution each 12 h. The solution was drained off and the softened seeds were washed thoroughly with distilled water. Later on, the seeds were ground mildly with a mortar and pestle and then sifted through meshes 20, 40, 100, 200 and 320 successively. In each mesh the residual was washed with distilled water until obtaining a mass of golden color without any leak out of residuals of starch. The starch dispersion obtained was centrifuged (6573 × *g* 5 °C, 30 min) and the supernatant was discarded. The precipitate was formed by two layers: the superior of slimy aspect and brown color, and the inferior of white color (starch). The white residual of starch was re-suspended in a solution of NaCl 0.1 M: toluene (7:1 v/v) and then, it was homogenized and let in agitation (5 °C, 50 rpm) overnight. The dispersion was centrifuged (6573 × *g* for 30 min) where two phases were formed; in the toluene phase there were the proteins, fat and small granules that were not separated by centrifugation, and in the watery phase there was the fraction rich in starch. Repeated washings of this fraction was done with the NaCl–toluene solution. The isolated starch was dried off at 40–45 °C for 24 h. and stored at room temperature in a sealed container. Commercial corn starch supplied by Industrializadora de maíz S.A. de C.V. (Guadalajara, Jalisco), (Industrializadora de Maíz, 1998) was used to compare with okenia starch results.

2.2. Chemical analysis

Moisture content, ash, protein and fat were obtained according to the AOAC (1990), methods 925.10, 923.03, 979.09 and 939.05, respectively. The amylose content was determined using the colorimetric method suggested by Gilbert and Spragg (1964). The amylopectin content was determined by difference with the total carbohydrates.

2.3. X-ray diffraction

The X-ray diffraction patterns were obtained in a diffractometer Rigaku D-MAX-2200 (Tokio, Japan) with the following operating conditions: Cu K radiation; voltage of 40 kV, chart speed of 10 $\mathrm{mm}2\theta^{-1}$ and a running rate of $2\theta\,\mathrm{min}^{-1}$.

2.4. Thermal analysis

The thermal properties of okenia and corn starches, were studied using a differential scanning calorimeter (DSC, TA Instruments, model 2010, New Castle, USA) previously calibrated with indium. The gelatinization of the starches was evaluated by the method proposed by Paredes-López, Bello-Perez and Lopez (1994), 2 mg sample (dry basis) was weighed on an aluminum pan, 7 μl of deionised water was added. The pan was sealed tightly and then it was allowed to stand for 1 h before carrying out the analysis. An empty aluminum pan was used as reference. The sample was subjected to a heating program over a range of temperature from 30 to 140 °C and a heating rate of 10 °C/min. The gelatinization or peak temperature (T_p) and the transition enthalpy (ΔH), were obtained directly from the analysis of the software TA Instruments OS/2 version 2.1. To determine the melting temperature and melting enthalpy, gelatinized samples as mentioned above were stored for 1, 2, 3, 7, 14 and 21 days at 4 °C. After completion of the storage time, the pans were allowed to stand for 1 h at room temperature and then analyzed in the DSC, using the same conditions described previously.

2.5. Microviscoamilography

To determine the viscosity (Brabender Units, BU) profile of okenia and corn starch pastes, the technique proposed by the AACC (2000), was used. Starch dispersions with 5 and 10% (w/v) of total solids were prepared, 100 ml of dispersion (sample) were transferred to the bowl of the microviscoamilograph (Brabender OHG, Duisburg, Germany). The machine was programmed to run a heating–cooking–cooling cycle that began at 30 °C and then increased to 95 °C, staying at this temperature for 20 min, then cooled to 50 °C and also maintained at this temperature for 20 min. A heating rate of 1.5 °C/min was used along the whole cycle with a speed of agitation of 125 rpm.

2.6. Swelling and solubility

The technique proposed by Tecante and Doublier (1999), was used. Okenia and corn starch dispersions with 5 and 10% (w/v) of total solids on dry basis were prepared, a kinetics of heating was followed using the microviscoamylograph bowl as heating devise, starting at room temperature with a heating rate of 1.5 °C/min until 95 °C and maintaining the sample isothermal for 20 min, and then cooling to 50 °C at the same rate (1.5 °C/min). The temperature profile followed is shown in Fig. 1. In the course of cooking of the starches, samples were taken at different temperatures, using tubes with deionised water, in such a way that the final concentration was of 0.5% (w/v) solids. The slurries were centrifuged at 2200 rpm for 15 min. The supernatant was decanted, and the volume was measured; aliquots were used to estimate the total carbohydrates (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956). The precipitate was used to determine the moisture content (24 h at 100 °C). The swelling of the granules was calculated from the mass of the centrifuged residual and the mass of the dry residual.

2.7. Flow curves

To determine the flow curves of the starch pastes of okenia and corn with 5 and 10% (w/v) solids, the same temperature profile used in the determination of swelling and solubility was followed (Fig. 1). The bowl of the microviscoamilograph was used as heating devise. The rheological measurements were carried out at 50 °C in a rotational viscometer (Haake rotovisco, model RV20, Karlsruhe, Germany), using a cone and plate geometry (cone pK 100, needle pK5 1.0°) of 50 mm diameter. Two serial sweepings of shear rate over the range from 30 to 3000 s^{-1} were carried out, continued by a descending sweep from 3000 to 30 s^{-1} to complete a test, each test lasting 12 min (Tecante & Doublier, 1999). The Power Law model:

$$\eta = k\gamma^{n-1}$$

where η is the apparent viscosity, k, the consistency coefficient and n, the flow behavior index) and the Cross equation.

$$\eta = \frac{\eta_0}{1 + (k\gamma^n)}$$

(η_0 : zero shear rate viscosity) were applied to the data (Macosko, 1994).

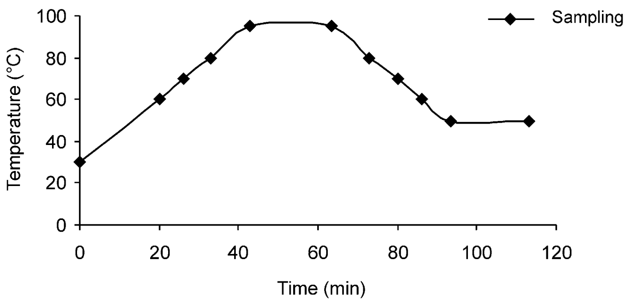

Fig. 1. Profile of temperature used for the determination of swelling and solubility of okenia and corn starches with 5% (w/v) and 10% (w/v) total solids.

2.8. Dynamic tests

Starch dispersions with 5 and 10% (w/v) total solids were prepared using distilled water. Their viscoelastic properties were measured running oscillatory tests in a Paar Physica Rheolab Rheometer, model US200 (GmbH, Stuttgart, Germany), using a parallel plate system, with 50 mm of diameter and a gap of 0.5 mm. Strain sweeps were run over the range from 0.01 to 100%, at a constant frequency of 10 s^{-1} and either a heating or cooling rate of 10 °C/min, in a heating (25–95 °C)–cooking (95 °C, isothermal, 20 min)–cooling (95–25 °C) cycle, to determine the linear viscoelastic region. Once this region was found, the machine was programmed for measuring the gelatinization and retrogradation kinetics of the resulting gels, following the same heating–cooking–cooling cycle mentioned above, over the strain ranges from 0.15 to 51.1% and 0.29 to 49.6%, for samples with 5 and 10% (w/v) solids, respectively.

2.9. Statistical analysis

One and two way analysis of variance (ANOVA) at the significance level of 5% ($\alpha = 0.05$) was applied to the obtained results using the statistical program Sigma-stat, version 2.1 (Fox, Shotton, & Urlich, 1995), and when statistical differences were found, the test of multiple comparison of Tukey was applied (Montgomery, 1976).

3. Results and discussion

The chemical composition of okenia and corn starch are reported in Table 1. The isolated starches presented similar percentages of moisture; the obtained values are comparable with those reported by Abdel-Aal, Hucl and Sosulski (1997), for corn starch. The protein content was slightly smaller for okenia starch. This parameter is important when starch is used as a raw material to produce glucose syrups, low protein contents avoid Maillard reaction. It is also an indication of the starch purity, (Carcea & Acquistucci, 1992); according to what is reported in the literature, it is not uncommon to find a smaller percentage than 0.5% of protein (Vasudeva, Hiroshi, Hidechika, Seiichiro, & Ke'nichi, 2000). Usually, the lipids content in starches is on the order of 1% or less, higher values may influence the starch gelatinization temperature, due to formation of amylose–lipids complexes (Lund, 1984); as it is observed in Table 1, the obtained values of lipids, for okenia and corn starch, are

Table 1
Chemical composition of okenia and corn starch (average of three determinations ± standard error)

Botanical source	Moisture (%)	Protein[a,b] (%)	Lipids[a] (%)	Ash[a] (%)	Amylose (%)
Okenia	10.08 ± 0.05	0.18 ± 0.001	0.17 ± 0.02	0.14 ± 0.001	26.1
Corn	10.30 ± 0.03	0.55 ± 0.001	0.10 ± 0.05	0.52 ± 0.01	28

[a] Dry basis.
[b] N X 6.25.

smaller than 1%. Ash content of okenia starch also was smaller than that of corn starch.

The amylose content however, was slightly higher for corn starch (28 ± 0.7%) than for okenia starch (26 ± 0.5%). According to Thomas and Atwell (1999), ordinary starches are those with an amylose content between 17 and 30%, on the basis of the results found for okenia starch, it could be classified as of the 'normal' type. The amylopectin content was also similar (71.2% for corn starch and 73.1% for okenia starch).

The thermal properties of okenia and corn starches are shown in Fig. 2. In both cases, a single endothermic transition is observed. Maximum flow of heat for okenia starch ($\Delta H = 11.94$ J/g) and corn starch ($\Delta H = 13.1$ J/g) was observed at the gelatinization or peak temperature ($T_p = 71.3$ and 73 °C for okenia and corn starch, respectively). This transition corresponds to the dissociation of the amylose and amylopectin molecules within the starch granules and leaching out of amylose to the continuos phase (Fujita, Lida, & Fujiyama, 1992; Liu, Leliévre, & Ayoung, 1991; Russel & Juliano, 1983). This is corroborated by the gelatinization temperature that Paredes-López et al. (1994), reported when using this technique with various starches.

The involved starches presented significant differences in the gelatinization temperature ($\alpha = 0.05$). Since as mentioned previously, there was only a 2% difference in the content of amylose for okenia starch respect to corn starch, further investigation involving factors such as polydispersity, total molecular dimension, hydrodynamic behavior, and internal mobility, among others, is needed to be able to explain these differences, as suggested by Noda et al. (1998).

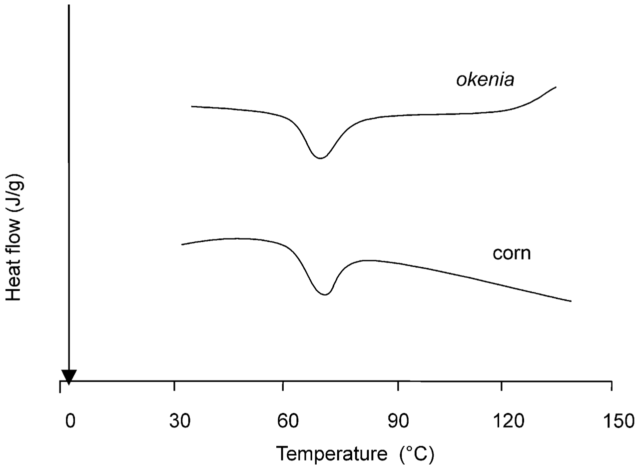

Fig. 2. Gelatinization thermograms of okenia and corn starches.

The values obtained for the gelatinization temperature (T_p) and the transition enthalpy (ΔH) of corn starch are similar to those reported by Lewandowicz, Jankowski, and Fornal (2000), for commercial corn starch, with a T_p of 69.5 °C and ΔH of 13.8 J/g, as well as with those obtained by Wang and White (1994); T_p of 71.5 °C and ΔH of 12.8 J/g.

The exact relationship between the amylose content and the gelatinization temperature of starches, has not been completely elucidated, since some researchers as Cheetam and Tao (1997), have proposed that certain correlation exists between them, however, others as Sasaki et al. (2001) and Paredes-López et al. (1994), have proposed just the opposite. On the other hand, T_p is considered a characteristic parameter to identify the type of starch (e.g. waxy, normal or high amylose), ranges reported for normal starches comprise from 50 to 80 °C (Thomas & Atwell, 1999), being T_p for okenia starch within such ranges. Respect to ΔH, it is generally accepted that this parameter is not actually correlated with the amylose content.

Okenia and corn starch presented endothermic transitions (retrogradation) at different storage times and lower temperatures (Table 2) than the one showed in its native state. This transition has been identified by numerous investigators, as the dissociation of the amylopectin crystallites (Levine & Slade, 1991; Zhang & Jackson, 1992). The retrogradation phenomenon is a process of re-crystallization of the starch polymers, the reorganization of the crystallites in this process is not presented in a homogeneous way, being reflected in the widest and somehow undefined form of the peak compared to the one obtained when it gelatinized (not shown). Okenia starch showed the tendency to have a significant increase ($\alpha = 0.05$) on the T_m starting from the seventh day of storage; for corn starch this parameter was constant throughout the storage period. Similar results were found by Paredes-López et al. (1994), concluding that during retrogradation non-perfect crystallites are formed which collapse at low temperature.

Both starches showed a significant increment ($\alpha = 0.05$) on ΔH_m values, starting from the 7th day, but at the 14th day, this was constant for okenia starch, while for corn starch it continued increasing until the end of the storage period. From the statistical analysis (not shown), it was concluded that T_m varied significantly solely with respect to

Table 2
Temperature and enthalpies of melting of okenia and corn starches, obtained by differential scanning calorimetry (average of 10 determinations ± standard error)

	Days of storage					
	1	2	3	7	14	21
Okenia						
T_{m} (°C)	49.83 ± 1.64a	5080 ± 0.78a	50.27 ± 0.43a	51.67 ± 0.87b	52.34 ± 0.73b	52.03 ± 0.58b
ΔH_{m} (J/g)	0.47 ± 0.08a	0.760 ± 0.20a	0.79 ± 0.14a	1.57 ± 0.33b	4.10 ± 0.54c	4.33 ± 0.29c
Corn						
T_{m} (°C)	54.76 ± 1.34a	52.59 ± 0.98a	52.84 ± 0.97a	53.73 ± 1.10a	53.81 ± 0.54a	53.95 ± 0.31a
ΔH_{m} (J/g)	2.86 ± 0.38a	3.07 ± 0.20a	3.32 ± 0.68a	5.03 ± .38b	6.47 ± 0.52c	8.47 ± 0.64d

Same letters inside each column indicate that there are not significant differences ($\alpha = 0.05$). T_{m} and ΔH_{m} stand for temperature of melting, and melting enthalpy.

the days of storage. The melting enthalpy (ΔH_{m}) presented significant differences ($\alpha = 0.05$) when varying either the botanical source or the days of storage as well as for the interaction of these factors. To the T_{m} and ΔH_{m} values that presented significant differences, the test of multiple comparison of Tukey was applied. Based on this test it was found that the values of ΔH_{m} presented significant differences starting from the 7th day of storage, independently of the botanical source (data not shown). T_{m} of okenia starch presented significant differences starting from the 7th day of storage as well.

To explain the differences presented in the parameters obtained by DSC, various investigators have studied the molecular structure of starch. Some authors have reported that the distribution and length of the amylopectin chains might influence the retrogradation of corn starch due to the formation of mixtures of crystallites of different sizes (Yuan, Thompson, & Boyer, 1993). This suggests that further research involving analysis of the molecular structure of okenia is needed to determine the exact causes of these differences.

In Fig. 3a, it is observed the effect of temperature on the swelling of the dispersions of okenia and corn starches with 5% (w/v) total solids. Okenia starch presented a slight increment in the swelling values over the range from 30 to 60 °C, but corn starch maintained a constant value in this range. When increasing the temperature a gradual increment in the swelling of both starches up to 95 °C (isothermal for 20 min) was observed; according to Whistler and Daniel (1985), this is due to breaking of the molecular interactions when increasing the temperature of the starch granules, having as a consequence the incorporation of molecules of water within their structure. These results are consistent with those reported in the literature (Fasihuddin & Peter, 1998; Thebaudin et al., 1998; Walter, Truong, Wiesenborn, & Carvajal, 2000).

When carrying out a progressive cooling of the resulting paste (from 95 to 50 °C), it was observed that the swelling values of corn starch paste tended to remain constant, while those of okenia starch continued increasing. In previous studies, some investigators (Doublier, Paton, & Llamas, 1987; Tester, Debon, & Sommerville, 2000; Vasudeva et al., 2000), observed that the ratio amylose/amylopectin plays an important role in the process of swelling of starch granules, concluding that the higher the percentage of amylopectin, the more the granules tend to swell and in combination with amylose, the granules are more resistant to this phenomenon. In this particular case, because of their similar content, this ratio was similar for both starches, however, okenia starch presented higher swelling values than corn starch at the different temperatures involved. This difference is due to crystallinity of starches, because okenia starch presented higher crystallinity level than corn starch when measured as areas under the X-ray diffraction peaks (Fig. 4).

In Fig. 3b, the effect of temperature on the swelling of the dispersions of okenia and corn starch with 10% solids is shown. A progressive increase is presented in the swelling values, being higher for okenia starch up to 80 °C. When reaching 95 °C, both starches showed the same value, and its maximum value was obtained when maintaining constant this temperature. In the cooling stage, the dispersion of both starches showed a gradual decrease in the swelling values. The results indicate that at both level of solids, the values of swelling of the dispersion of okenia starch are higher than those of corn starch. When the level of solids increased, the dispersion of okenia starch showed a decrease in the swelling; this phenomenon is possibly a consequence of the amount of water available, i.e. the water available in the granules is higher for dispersions with 5% than with 10% solids, where a higher competition for water of the granules is presented, as suggested by Doublier et al. (1987). From the results obtained on application of ANOVA to the swelling values (statistical data not shown), it was concluded that at 30 °C, the botanical source of the starch, the level of solids and the interaction botany source-level of solids, did not produce a significant effect. Over the range from 60 to 70 °C, the results denoted that the botanical source and the level of solids had a significant effect, although the interaction of both factors did not produce such an effect. Starting from 80 °C until the end of the cooling period (50 °C, isothermal for 20 min), the values were affected by the botanical source, the level of solids and

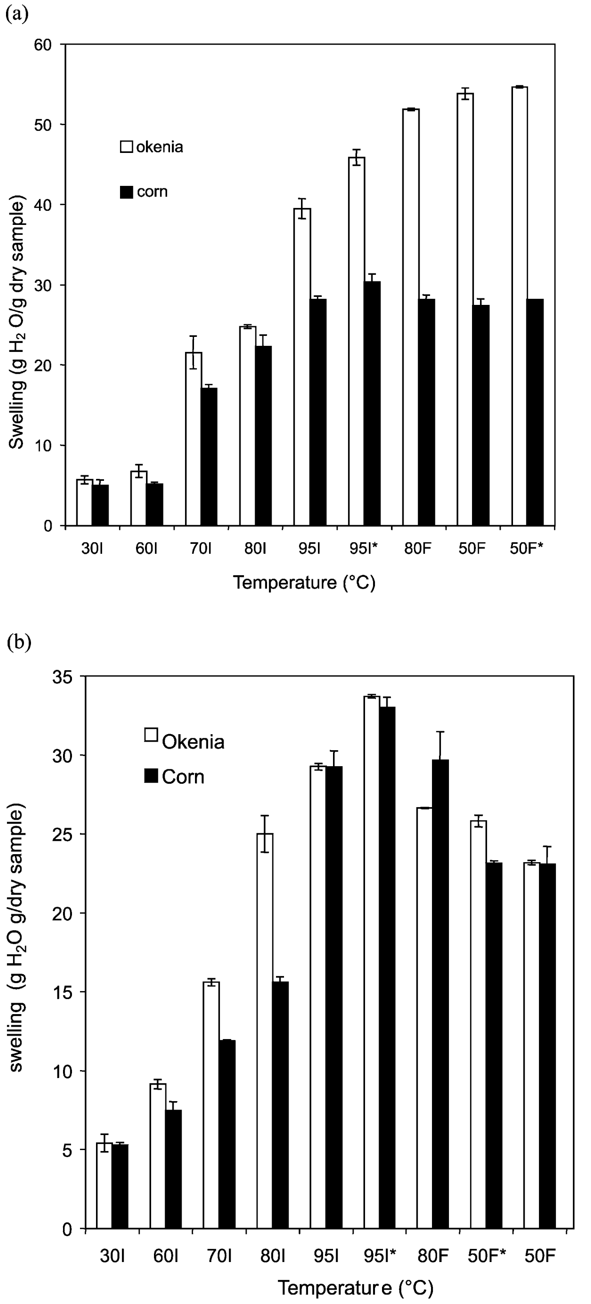

Fig. 3. Effect of temperature in the swelling of the dispersions of okenia and corn starch with (a) 5% (w/v), (b) 10% (w/v) total solids. I: heating stage; F: cooling stage, *isothermal for 20 min.

the interaction of both. The Tukey test of multiple comparison showed that at 60 °C, the swelling values of the dispersions of okenia and corn starch with 10% solids, were statistically different, in comparison with the dispersions with 5% (data not shown). At 70 and 80 °C, the dispersions of both starches with 5% solids and okenia starch with 10% solids, presented swelling values statistically different to the starch of corn with 10% solids. At 95 °C okenia starch dispersions with 5% solids presented swelling values statistically different to the other dispersions, and during the cooling stage the same trend was observed.

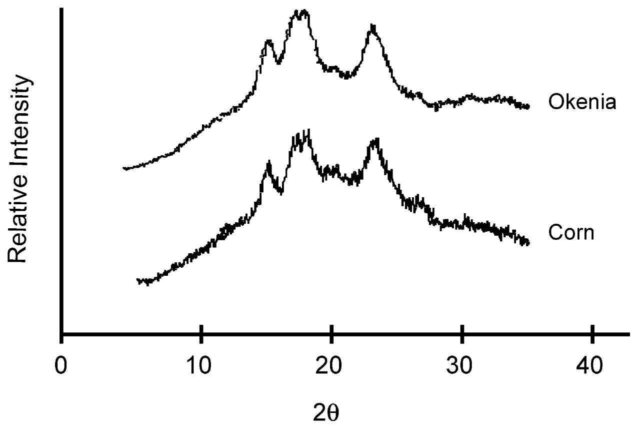

Fig. 4. X-ray diffraction patterns of okenia and corn starches.

In the case of the solubility for starch samples with 5% solids (Fig. 5a), it is observed that over the range from 30 to 60 °C, the values increased slightly; but starting from 70 °C, they increased significantly ($\alpha = 0.05$); this increase could again be explained by the values of gelatinization temperature ($T_p = 71.3$ °C for okenia and 73 °C for corn); it has been established that, when reaching this temperature, the granular structure is lost and solubilisation of the constituent polymers is promoted (Thomas & Atwell, 1999). During the cooling stage (from 95 to 50 °C), the values of solubility of okenia starch increased, while those of corn starch decreased. Okenia starch showed lower solubility values than those of corn starch, at the different temperatures. For starch samples with 10% solids, solubility is presented in two stages (Fig. 5b); the first one is carried out from 30 to 60 °C, where the starches show a limited increment in the solubility values; when reaching 70 °C, the second stage is accomplished, here it is observed that the solubility increases notably as an effect of heating of the dispersions; this change is remarkable in this point when the gelatinization temperatures mentioned previously are reached and it is evident that the molecular association that maintains the integrity of the granules of starch modifies when heated in aqueous dispersion, suggesting that rupture of hydrogen bonds is taking place, allowing the liberation of the amylose during the solubilisation stage (Jiangsu, Kweon, Hanover, Sosulski, & Saskatoon, 1997). The tendency shown by these starches is characteristic of cereals (Delpeuch & Favier, 1980; Madamba, Bustillos, & San Pedro, 1989). When subjected to isothermal heating for 20 min at 95 °C, okenia dispersions presented a decrease in the solubility values, when cooling, it was observed a tendency to stay constant. In the corn starch the opposite effect was presented, i.e. there was an increment in solubility, reaching its maximum point at 95 °C. When cooling the dispersions to 80 °C, this starch showed a progressive decrease, up to 50 °C, staying constant in this point. The decrease in solubility is possibly due to the available water in the system, where it is absorbed within the granular structure, affecting the mobility or

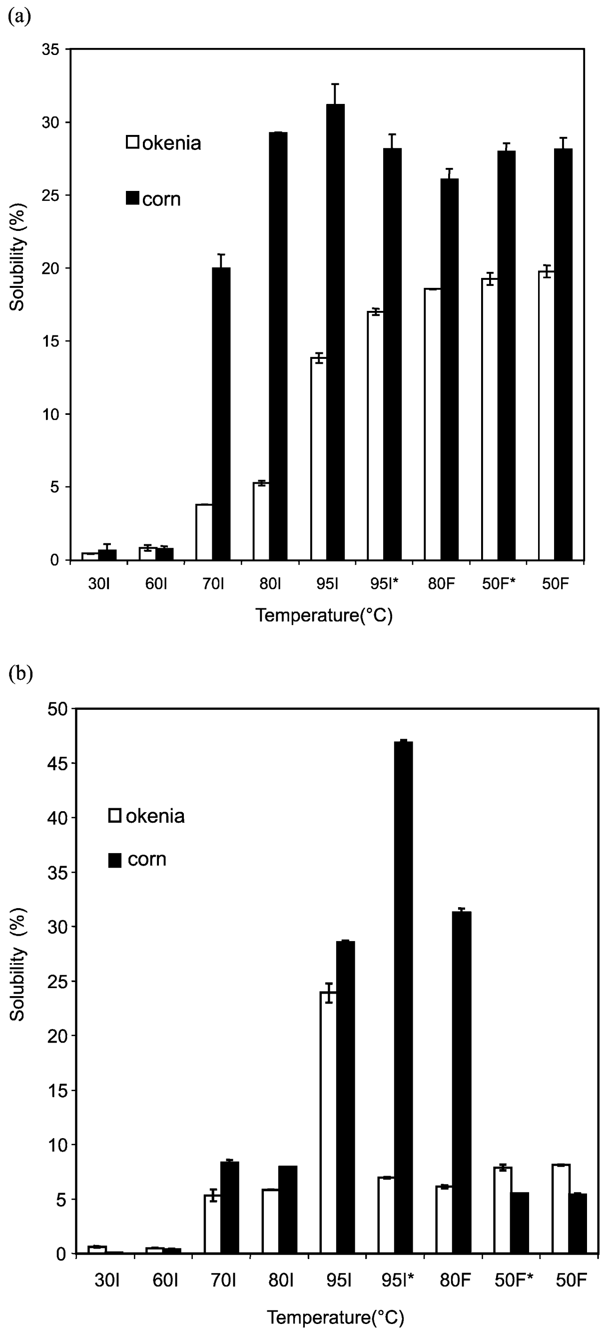

Fig. 5. Effect of temperature in the solubility okenia and corn starch with (a) 5% (w/v), (b) 10% (w/v) total solids. I: heating stage; F: cooling stage, *isothermal for 20 min.

displacement of the amylose towards the dispersed phase (Doublier, 1981; Thebaudin et al., 1998).

When ANOVA was applied to the solubility data, it was found that at 30 °C there were not significant differences presented in the values for effect of the botanical source, nor for the level of solids and neither for the interaction of both. At 60 °C, these values were only affected significantly by effect of the variation of the level of solids. Starting from 70 °C and until the end of the period of cooling, the variation of the botanical source and the level of solids, as well as the interaction of both presented a significant effect on the solubility ($\alpha = 0.05$).

The amylographic profiles of the dispersions of okenia and corn starch with 5% of solids is presented in Fig. 6a. As it is shown, during the heating stage (30–95 °C), the viscosity increases gradually until obtaining a maximum value, this is due to the fact that when the granules of starch are heated in excess of water, the phenomenon of heat and moisture transfer is presented, causing swelling of the granules; when reaching the stage of cooking of the paste (95 °C for 20 min), okenia starch had a slight increase in viscosity that was higher in the cooling step, and corn starch showed a slight decrease in the viscosity values that increased in the cooling step, but they were lower than those of okenia starch. The increment observed in the viscosity values during the cooling step is due to a molecular re-association, i.e. the liberated amylose forms three-dimensional networks (entanglements) since it interacts with the molecules of water by means of hydrogen bonds (Lii, Shao, & Tseng, 1995; Thomas & Atwell, 1999). The higher viscosity values found in okenia starch agree with their higher swelling values (Fig. 3). Previous works have reported that these maximum values depend mainly on starch granules swelling (García & Walter, 1998; Ming, Morris, Batey, & Wrigley, 1997) and that amylopectin is especially involved (Bahnassey & Breene, 1994; Hoseney, 1994; Tester & Morrison, 1990); consequently, if okenia starch presented a peak of higher viscosity and its swelling values were higher than those of corn starch, crystallinity degree in okenia starch might play an important role in this pattern. During the stage of molecular dissociation (95 °C, isothermal for 20 min), okenia starch presented significantly smaller values than corn starch, and since okenia solubilised less amylose (Fig. 5), the swollen granules are probably maintaining its structure for the presence of this fraction (Hermansson & Svegmark, 1996; Sasaki, Yasui, & Matsuki, 2001). According to García and Walter (1998), the viscosity of starch pastes after heating at 95 °C for 20 min, provides an estimate of its stability or resistance to the disintegration as a result of heating and agitation. In the cooling stage, the values of viscosity suggest that okenia starch presented a smaller tendency to molecular re-association (lower differences between the initial and final viscosity). This was as expected, supporting the tendency observed in the cooking stage, where the amylose which is involved in the formation of three-dimensional networks (Lineback & Rasper, 1988), is probably being retained in the swollen granules. Amylographic profiles also were obtained with 10% of solids (Fig. 6b). The maximum viscosity in okenia and corn starches was obtained in the heating stage and decreasing of viscosity began before the ‘holdup’ stage. This effect is due to starch concentration that could be explained by the volumetric fraction occupied by the granules, i.e. at higher concentration, a more compact system is formed, increasing the resistance to shear rates in the heating stage; but the combined effect of the agitation and the friction causes

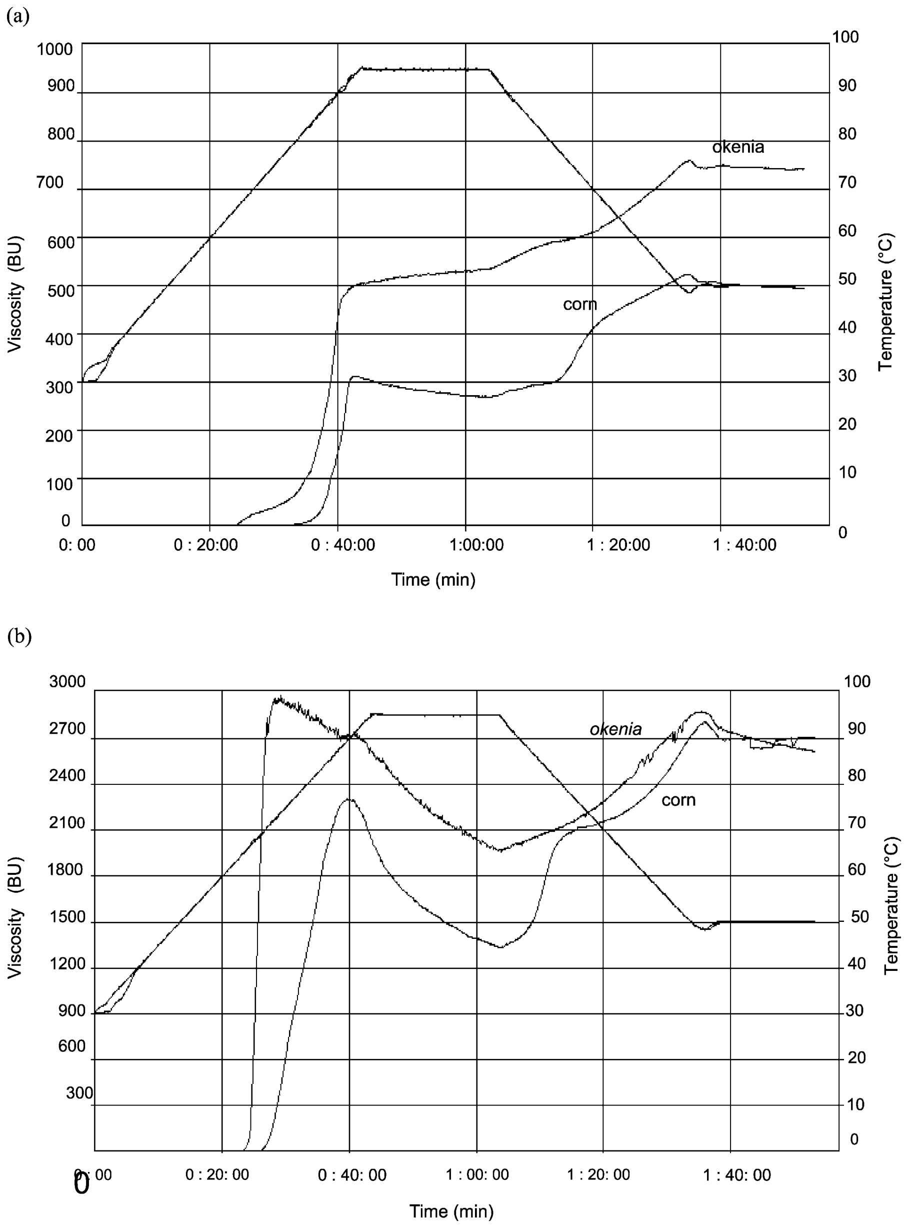

Fig. 6. Amilograms of okenia and corn starch with (a) 5% (w/v) and (b) 10% (w/v) total solids.

the fragmentation of the granules and in consequence, an increase in the BU values in the molecular dissociation and re-association stages (Kayisu, Hood, & Vansoest, 1981).

Fig. 7 shows the variation of the shear stress in function of the shear rate for the dispersions of okenia and corn starches with 5 and 10% solids. The plots denote a non-Newtonian behavior because although they exhibit a uniform flow, the relationship between shear stress and shear rate is not constant (Steffe, 1992). This type of behavior has been reported for dispersions of starch from other botanical sources (Kapoor & Bhattacharya, 2001; Rao & Tattiyakul, 1999; Tecante & Doublier, 1999; Thebaudin et al., 1998).

For the dispersions with 5% solids, certain thixotropic behavior is observed, since shear stress is not only related to shear rate, but also to time; this is confirmed by the formation of a curl when descending on the shear rate values, phenomenon named as hysteresis (process of deformation in which the load phase and its discharge phase do not coincide), which is particular for each starch source (Steffe, 1992; Tecante & Doublier, 1999). Likewise, it was observed that okenia starch was less sensitive to the shear stress, since bigger values were required to make it flow. Amylose outside the granules forms a three-dimensional network whose structure is determined by the starch concentration, the structure of the swollen granules, the ratio amylose/amylopectin, the proportion of solubilised amylose, as well as by the method of pastes preparation (Cheng, Tsai, & Tseng, 1996); taking into account these factors and considering the swelling and solubility patterns of both

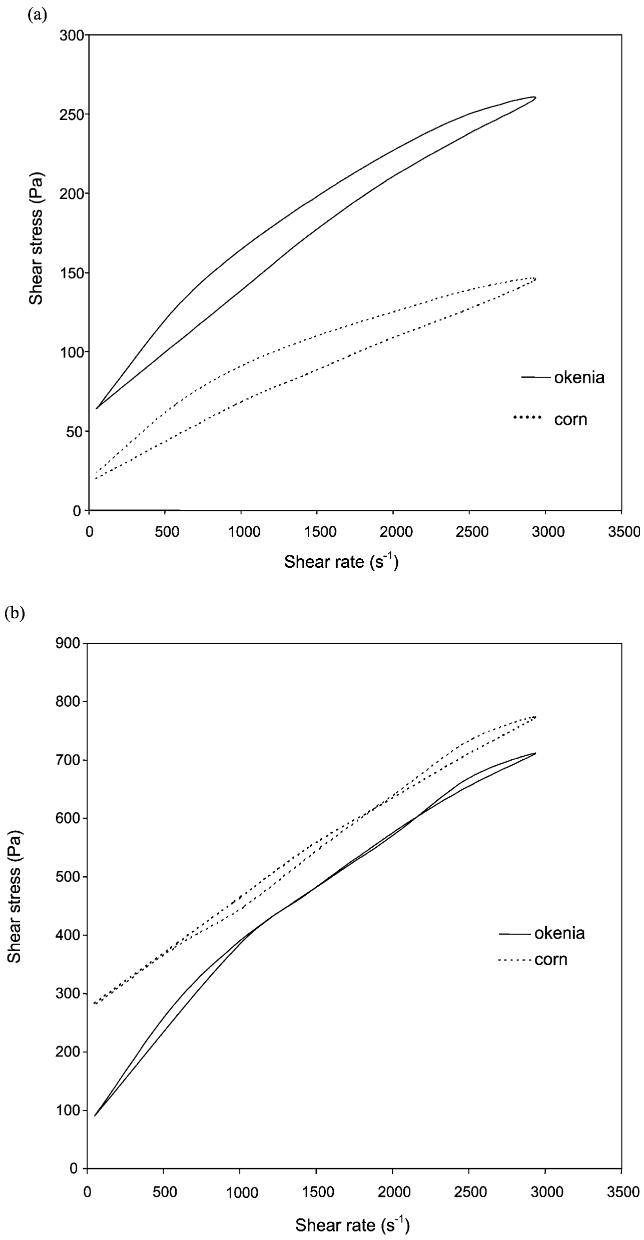

Fig. 7. Flow curves of okenia and corn starch pastes with (a) 5% (w/v), (b) 10% (w/v) total solids, evaluated at 50 °C.

starches, it was noticed that okenia presented higher granules swelling but lower solubility; suggesting that the amylose within these granules in combination with the amylopectin could be strengthening such a structure. When the concentration of solids increased to 10% (Fig. 7), the hysteresis was much smaller (slight thixotropic behavior). There was also a significant increase in the shear stress values when varying the concentration from 5 to 10% solids; this change in the flow behavior agrees with the idea that the viscosity is dependent on the concentration (Crockford & Knight, 1997; Fasihuddin & Peter, 1998).

To describe the flow behavior of okenia and corn starch dispersions at 10% concentration, the apparent viscosity (η) as a function of the shear rate (γ) was plotted (Fig. 8). The results show characteristic shear-thinning behavior (Steffe, 1992). Doublier et al. (1987) described that the pastes of starch are mixtures of three fractions: (a) soluble macromolecules (amylose), (b) finely dispersed particles (amylopectin) obtained after the breakage of the swollen granules during the liberation of amylose when shaking is enough, and (c) solid particles corresponding to fragments of swollen granules. Taking into account their investigation and observing the profiles of swelling of okenia and corn starches, which showed that the dispersions with 5% solids presented higher values than those of 10% solids, it could be inferred that the flow behavior of the pastes formed at the highest concentration, is being governed by the volumetric

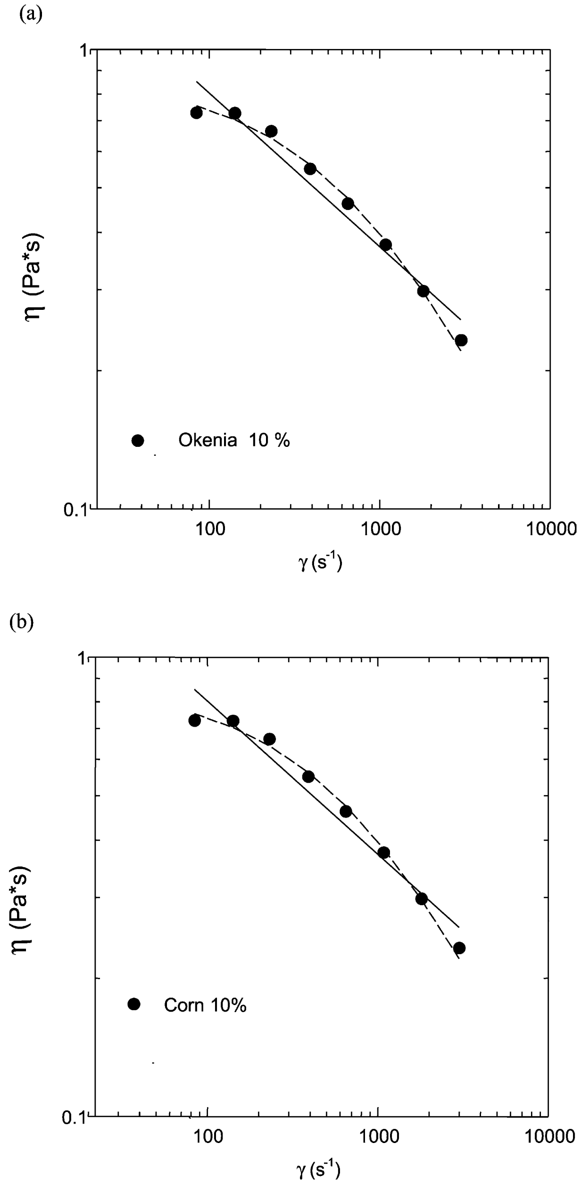

Fig. 8. Variation of the viscosity from (a) okenia starch, (Power Law model, —, $\eta = 3.74\gamma^{0.666-1}$; Cross equation, - - - $\eta = 0.8701/1 + (1.23 \times 10^{-3}\gamma)$ 0.823), (b) corn starch (Power Law model, — $\eta = 3.46\gamma^{0.69-1}$; Cross equation, - - - $\eta = 0.886/1 + (1.04 \times 10^{-3}\gamma)0.816$) with 10% (w/v) total solids, in function of shear rate, evaluated at 50 °C.

fraction occupied by the granules, i.e. partially swollen granules are caught inside the viscous matrix formed by the solubilised amylose, achieving a more rigid structure and being as a consequence less sensitive to deformation.

To describe the relationship of the experimental data with the flow behavior of okenia and corn starch dispersions, the mathematical Power Law model was applied One of the restrictions of this method is that the behavior of the analyzed material should not depend on time, for this reason it was solely applied to the dispersions with 10% solids. The coefficient of determination obtained with this model, for both starches was of about 0.95, which in this case is not considered a good fitting; however, both starches (Fig. 8) presented the initial part of a Newtonian plateau (region where the viscosity remains approximately constant), that is why it was decided to apply the Cross equation; which can be determined through a non-linear regression. The coefficients of determination (R^2) obtained with this model were higher (0.99) than those obtained with the Power Law model, i.e. the Cross model fitted better the experimental data. Although the parameters n (index of flow behavior, okenia > corn) and k (coefficient of consistency, okenia > corn) do not have any physical meaning on their own, they are used as reference to a regression model in a given range of shear rates and, traditionally they are used to express the flow behavior (Steffe, 1992).

Figs. 9 and 10, show the rheological profiles of okenia and corn starch dispersions at the two levels of solids analyzed (5 and 10%); these show the structural transitions associated to a process of phase change in the system that are detected by modifications in the profile and are described by the parameters G' (the storage modulus, which shows the solid or elastic character), G'' (the loss modulus, it shows the liquid or viscous character), and tan δ (ratio G''/G'); these parameters characterize the viscoelastic behavior of a sample.

In Fig. 9, it is observed that during the heating previous to the gelatinization of starch (range from 25 to 60 °C), the values of G'' are higher than those of G', in this range the system is predominantly viscous, and it is evident that the dispersion starch-water begins with a mainly liquid behavior, during which the initial swelling of the granule

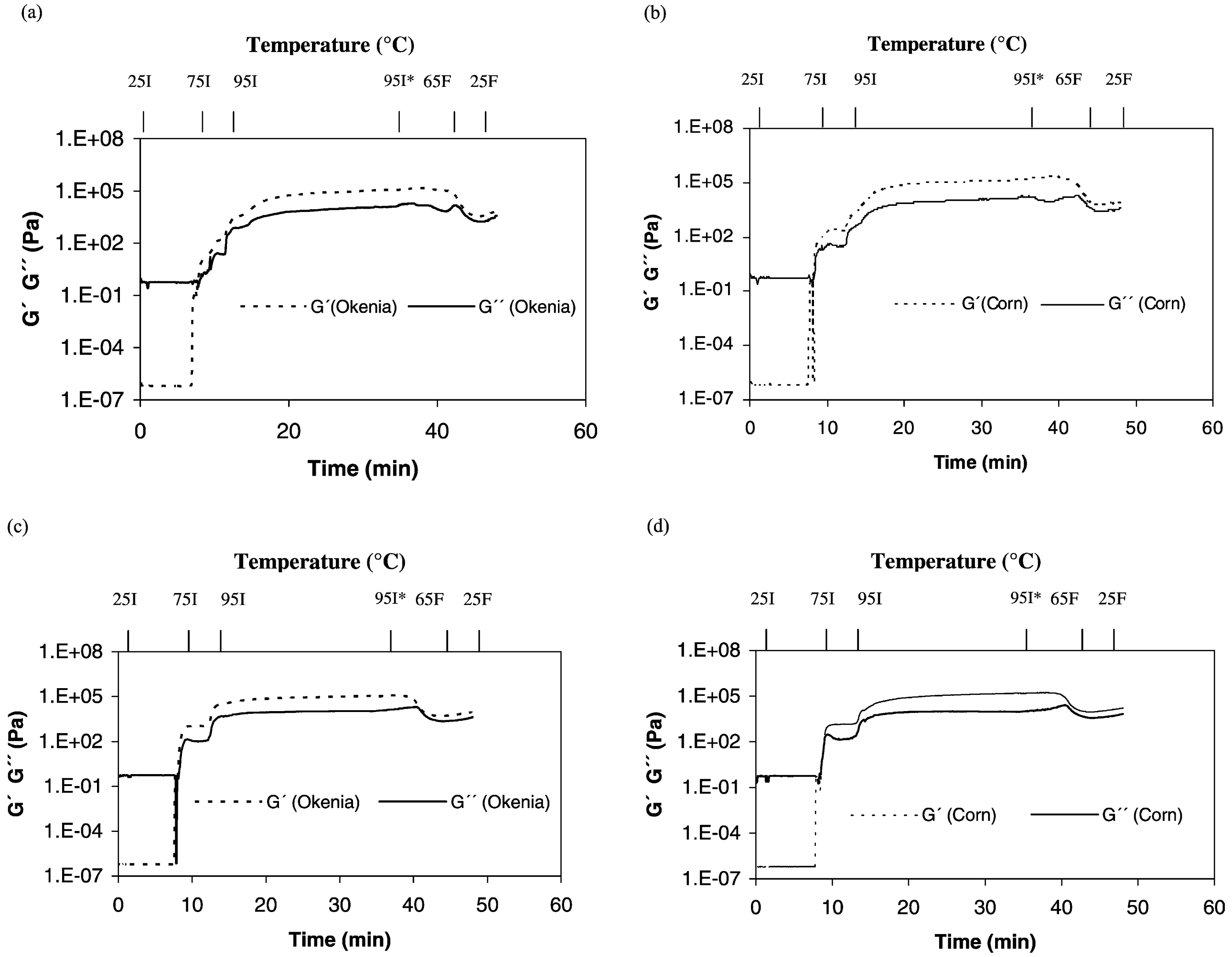

Fig. 9. Kinetics of the storage (G') and loss (G'') moduli of okenia and corn starch dispersions with (a), (b) 5% (w/v) and (c), (d) 10% (w/v) total solids in function of time and temperature. I: heating stage, F: cooling stage, *isothermal for 20 min.

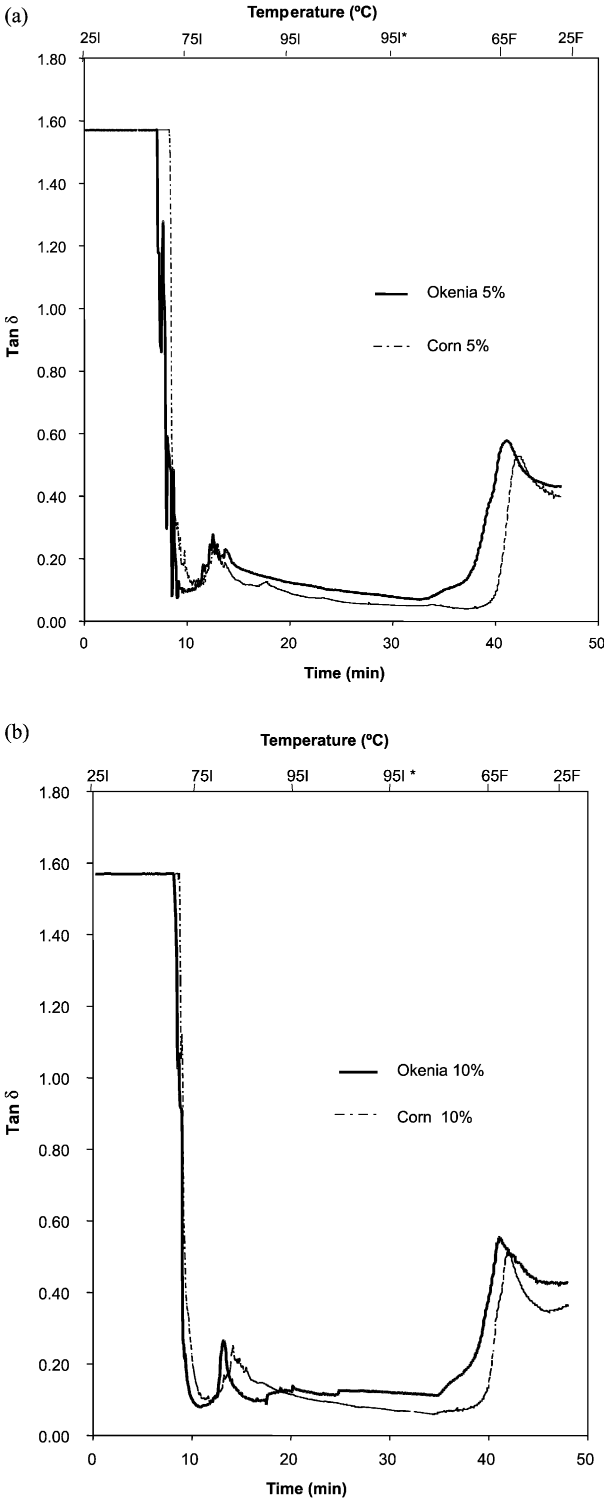

Fig. 10. Kinetics of the loss tangent of okenia and corn starch dispersions with (a) 5% (w/v), (b) 10% (w/v) total solids in function of time and temperature. I: heating stage, F: cooling stage, *isothermal for 20 min.

takes place (reversible swelling) (Lii et al., 1995). These results are consistent with those observed in the swelling profile and in the amylograms (Figs. 3 and 6), below 60 °C, there were not appreciable changes in the starch granules since the swelling is minimum and reversible. When the heating continued, it was noted at approximately 60 °C, a remarkable increment in the elastic character of the sample (rise in G', Fig. 9) which was characterized by the appearance of a peak at about 75 °C and a second one at 95 °C. This increment has been attributed to the progressive swelling of the granules (Eliasson, 1986; Rolee & Le Meste, 1997; Tecante & Doublier, 1999); in consequence, a packed system is probably being formed, augmenting the system rigidity with increase in G' values. During the isothermal stage in which the sample stayed at 95 °C, a plateau was formed and in this region, G' continued prevailing over G''. In the cooling stage a notorious decrease was observed in both moduli G' and G'', starting from 70 °C, this could be due to amylose solubilization during the heating stage, which is liberated to the dispersed phase, causing granular destruction and in consequence a change in the dynamic moduli. The initial increment in G', as well as the plateau formation is a behavior observed previously by numerous researchers (Ahmad & Williams, 2001; Clark, Gidley, Richardson, & Ross-Murphy, 1989; Eliasson, 1986; García & Walter, 1998; Tecante & Doublier, 1999). Because the relation $G' > G''$ was maintained starting from the gel formation, suggesting that the behavior of G'' was probably the same or similar as G', it was decided to only apply two way ANOVA to the values of G'. This was done randomly and in a 'single-point' way in the three evaluation stages; i.e., in the heating stage at the temperatures of 25, 60, 70, 75, 80, 85, 90 and 95 °C; in the isothermal stage where the sample stayed 20 min at 95 °C and finally, in the cooling stage at the temperatures of 70, 50 and 25 °C. The results showed that in the range from 25 to 60 °C, G' did not present significant differences when varying the botanical source or the level of solids, neither for the interaction of both (statistical data not shown), this suggests that below 60 °C the granules are not modifying its structure; however, at 70 °C, the variation of the level of solids produced significant differences in G'. It has already been mentioned that before reaching this temperature, the granules begin a swelling process suggesting that the volumetric fraction occupied for these granules is influencing the changes of G'. Over the range from 75 to 90 °C the values of G' presented significant differences for the variation of the botanical source, the level of solids and for the interaction of both factors. When reaching 95 °C, the storage modulus solely presented significant differences in its values when increasing the concentration of solids; during the isothermal period for 20 min at this temperature, it presented a significant effect for the variation of the botanical source. In the cooling stage (70–25 °C), G' exhibited a significant effect for the variation of the botanical source, for the increment in the level of solids and for the interaction of both. From the results of the application of the Tukey test, it was concluded that at 70 °C the dispersions of okenia and corn starch with 10% solids were those which produced the significant differences (not shown), being obtained this way more rigid pastes, because their elastic nature prevailed. Over the range from 75 to 80 °C, the values of G' for the dispersions of corn starch (5 and 10% solids), were significantly higher that those of okenia starch, therefore, the pastes formed by corn starch had a more elastic character. In the analysis on the increase of the solids, it was found that the values of G' for the pastes with 10% solids were significantly higher that those with 5% solids. When maintaining isothermal conditions both starch dispersions with 10% solids (95 °C, 20 min), G' showed significant differences for the botanical source, the values of corn starch being higher. In the cooling stage (70–25 °C), the dispersions of corn starch were those which produced a bigger effect in the values of G' than those of okenia.

Hansen, Hoseney, and Faubion (1991), found that the complex modulus (G^*), the storage modulus (G') and the loss modulus (G''), of starch dispersions prepared at concentrations of 5, 7 and 10% (w/v) of total solids, presented a tendency to increase ($G^* > G' > G''$) as the concentration of starch increased; this agrees with the results found in this work, since the values of G' showed significant differences when increasing the concentration of solids. The amount of water present in these dispersions also plays an important role, because it tends to increase the molecular mobility of the polymers present (Chinachoti, Kim-Shin, Mari, & Lo, 1991), therefore, the smaller the quantity of water being formed is, the more packed the system is, presenting a bigger rigidity and as a consequence, an increase in G' values. On the other hand, Eliasson (1986), who analyzed the changes taken place on the rheological properties of wheat, corn and potato starches and waxy starch of barley, following a similar thermal profile to the one used in this work, reported that the plots of wheat and corn starch were characterized by the appearance of two peaks, the first one at 75 °C for corn starch and 65 °C for wheat starch; and the second one, around 90 to 95 °C for both starches. When continuing the heating (maximum temperature of 95 °C, isothermal for 10 min), she observed that the values of G' diminished slightly in the case of corn starch, while for wheat starch, G' increased.

Another important parameter in the description of the viscoelastic behavior of materials is $\tan\delta$, previously defined as the ratio between the viscous and the elastic component (G''/G', Fig. 10). Over the range of temperatures from 25 to 60 °C, it is observed that in both starches $\tan\delta$ presented a maximum value of about 1.57, prevailing the viscous character, i.e., the dispersion starch–water begins with a mainly liquid behavior, when the reversible swelling of the granules takes place (Lii et al., 1995). Starting from 60 °C, there is a significant decrease in the values of $\tan\delta$, when reaching 72 °C, it presented its minimum value of about 0.1. The observed change might be a consequence of the increment on G' values, as suggested by Tecante and Doublier (1999). In this area the behavior of the gels of okenia and corn starches, are similar to the one reported for weak viscoelastic gels, prevaling the elastic character (Ferry, 1980). When the heating continued, a transition was observed in the range 75–90 °C, presenting $\tan\delta$, a maximum value (about 0.2), this behavior stayed essentially constant up to 95 °C (isothermal for 20 min). A second transition was observed in the cooling stage over the range from 65 to 25 °C where $\tan\delta$, reached a maximum value of about 0.5.

Considering the ranges of peak temperature, T_p (80–82 °C) of the starch dispersions here analyzed, it is observed that they are within the range where the first $\tan\delta$ transition was observed, suggesting that this change is taking place for effect of gelatinization. The second transition that has been associated with the process of amylose gelation, could be sustained with the fact that in the amylographic profile in the stage of molecular re-association, it was observed that both starches showed a tendency to the reorganization of their molecules starting from 65 °C (cooling stage). This agrees with the work of Gómez-Aldapa (2001), who evaluated the rheological properties of corn starch, using similar heating conditions to those used in this work. The author reported that for this starch two transitions were observed, the first one in the heating stage over the range from 65 to 85 °C and the second in the cooling stage from 65 to 50 °C. He concluded that the first transition was associated with the gelatinization of the granules, since the temperature range corresponded to the range in which the gelatinization endotherm was formed, while the second transition was associated with the process of amylose gelation.

4. Conclusions

The chemical analysis of okenia starch indicated that it could be classified as normal, rather than as a waxy or a high amylose one. It had a gelatinization temperature significantly smaller ($\alpha = 0.05$), than corn starch. Melting temperature for okenia starch presented a significant increase from the 7th day of storage, but from the 14th day onwards, it was constant, while for corn starch it increased throughout the storage period. Okenia starch presented higher values of swelling capacity than corn starch while the opposite trend was observed for solubility. Okenia starch pastes showed a higher maximum viscosity, as well as a smaller tendency to the molecular dissociation and re-association than corn starch. Both starches showed a non-Newtonian behavior, samples with 5% (w/v) of total solids presented thixotropy. All starch dispersions showed changes in their rheological properties when the temperature increased, going from a more viscous system ($G'' > G'$), to a mainly elastic one ($G' > G''$), both starches originated weak viscoelastic gels. Overall, the results obtained suggest that okenia starch presents differences in its molecular structure respect to corn starch. Further research to define the molecular structure of okenia starch is needed.

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