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Carbohydrate Polymers 56 (2004) 65–75

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Swelling-solubility characteristics, granule size distribution and rheological behavior of banana (*Musa paradisiaca*) starch

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Received 3 July 2003; revised 15 December 2003; accepted 26 December 2003

Abstract

The rheological behavior at 25 and 60 °C together with the pasting properties of banana starch were examined through DSC, Brabender profile, swelling-solubility characteristics, granule size distribution and steady and oscillatory flow of pastes with 1–6% starch. Some of these properties and behaviors were also determined in cornstarch pastes for the purpose of comparison. The temperature of starch gelatinization was 75 °C and pastes were stable to thermal and mechanical treatment. Swelling and solubility were about 14% and 25 g/g, respectively. The median diameter D [v, 0.5] of the uncooked starch was 24.31 μm, while that of cooked starch ranged from 59 to 66 μm depending on starch concentration. The pastes exhibited non-Newtonian shear thinning behavior that could be fitted to the Cross model. Under oscillatory shear, pasted exhibited a solid-like viscoelastic behavior mainly attributed to the volume fraction of swollen granules. Pastes are a mixture of swollen and partially disrupted granules suspended in a macromolecular solution (60 °C) and in a three-dimensional network (25 °C).

Keywords: Banana; Rheology; Starch; Viscoelasticity

1. Introduction

Starch is the main reserve carbohydrate synthesized by superior plants that constitutes an essential source of energy to many living organisms, especially to man (Buléon, Colonna, & Leloup, 1990; Luallen, 1988). Starch represents an important component of a large number of agricultural products like cereals (corn, wheat, rice) whose polysaccharide content goes from 30 to 80%; legumes (bean, pea, faba) with 25–50%; tubers (potato, tapioca) with 60–90%, as well as of some tropical fruits like banana which when green may contain up to 70% on a dry basis (Guilbot & Mercier, 1985). Starch is organized in discrete particles or granules whose morphology, chemical composition and relative arrangement of macromolecules in the solid state are characteristic of the botanical source. The starch granule is made up of two different glucose polymers; amylose and amylopectin. Their proportion and physical organization inside the granule are responsible for the physicochemical and functional properties of starch as well as its susceptibility to enzyme attack which is particular to the different sources.

By modifying previously developed methods (Kim, Wiesenborn, Orr, & Grant, 1995), it has been possible to isolate starch from 'macho' banana (*Musa paradisiaca*), a non-conventional source, with a purity of 98.1% on a dry basis (Bello-Pérez, Pano, Agama-Acevedo, & Paredes-López, 1998). The blue value of the isolated polysaccharide (0.18 ± 0.006) is within those of normal cornstarch (Bello-Pérez, Agama-Acevedo, Sánchez-Hernández, & Paredes-López, 1999). However, banana starch has low stability to freezing treatments and therefore its use in frozen products is not recommended (Bello-Pérez et al., 1998). X-ray diffraction patterns, DSC behavior and gel clarity characteristics have revealed other interesting features of banana starch (Bello-Pérez, Agama-Acevedo, Sáyago-Ayerdi, Moreno-Damian, & Figueroa, 2000). In spite of its amylose content, which places banana starch within 'normal' starches, both its temperature and enthalpy of gelatinization are very different from those of normal corn

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doi:10.1016/j.carbpol.2003.12.003

and waxy starch, but are similar to amaranth starch (Bello-Pérez et al., 2000). The X-ray diffraction patterns of banana starch are of type-A, which is characteristic of cereal starches as well as starches that contain amylopectin molecules with a high proportion of short side chains (Bello-Pérez et al., 2000). Native banana starch granules are oval to ellipsoidal in shape, with sizes from 20 to 50 μm (Lii, Chang, & Young, 1982) and with an ordered radial arrangement of starch molecules, of a quasi-crystalline nature, as evidenced by their birefringence pattern.

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, Lefebvre, & Doublier, 1998). Some authors (Evans & Haisman, 1979) have proposed to interpret rheological measurements by comparison with the sedimentation behavior and the swelling characteristics of the dispersions of cooked starch, relating therefore the flow curves with the volume fraction of the swollen particles. Starch pastes can be considered as mixtures of swollen and fragmented granules embedded in a continuous phase that contains the macromolecular components leached out from the granules when starch is cooked (Doublier, 1981). Such model is useful for the qualitative interpretation of the flow behavior of starch pastes.

In this work the pasting characteristics and the rheological properties of banana starch pastes are reported together with their swelling-solubility behavior and size distribution. Although our main purpose was not to carry out a systematic comparison between banana and cornstarch, some data are included. With all this knowledge it is expected to provide useful information on the physical and functional properties of this particular type of starch that can offer further support to the consideration of banana as an alternate source of this polysaccharide and to the application of the extracted carbohydrate in the food industry as a substitute of other starches (i.e. normal cornstarch).

2. Materials and methods

2.1. Materials

Banana starch extracted from the ‘macho’ variety (*Musa paradisiaca*) according to previously reported methods (Bello-Pérez et al., 1998) was used throughout this work. Table 1 shows its composition (Bello-Pérez et al., 1998). Food grade cornstarch (Arancia Corn Products, Mexico) was used for comparison. Amylose (Sigma A0512) and amylopectin (Sigma A8515) were used to examine the wavelength of maximum absorbance. Distilled water was used throughout.

Table 1
Composition of banana starch on a dry basis (except moisture)

Moisture (%)	9.9 ± 0.24
Protein (%)	2.03 ± 0.15
Fat (%)	2.46 ± 0.3
Ash (%)	0.54 ± 0.06
Total starch (%)	98.1 ± 3.3

2.2. Starch pasting

Banana starch was cooked in a Brabender Micro Viscoamylograph (Brabender® OHG, Duisburg) at 125 rpm under the following in-sequence steps: (a) heating (1.5 °C/min) from 30 to 92 °C; (b) holding at 92 °C during 10 min; (c) cooling (1.5 °C/min) to 60 °C. Starch concentrations were 1–6% on a dry weight basis. A 5% cornstarch paste was also prepared for comparison purposes. The Viscoamylograph was used only as a cooker to prepare the pastes always under the same controlled conditions.

2.3. Gelatinization

The thermal behavior was examined by DSC using a calorimeter (TA-Instruments, USA, model 2010). A mass of 2 mg of starch was placed in an aluminum pan at room temperature (20 °C) and 7 μL (7 mg) water was added to get about 70% moisture. The sealed pan was left still for 1 h at room temperature to allow complete hydration of starch. Then, the pan with the sample was placed in the calorimeter and heated (10 °C/min) from 20 to 110 °C. An empty pan was used as reference (Paredes-López, Bello-Pérez, & López, 1994). Banana and cornstarch were examined separately.

2.4. Swelling-solubility

Swelling-solubility measurements were carried out during pasting of banana starch. In the case of cornstarch only the final swelling and solubility were measured. Aliquots of the paste necessary to get a dilution containing 0.5% starch at 60 °C were taken from the cooking vessel. Samples were cooled quickly to 25 °C and 8 mL of the 0.5% dilution were centrifuged at 2000 rpm for 15 min (Leach, McCowen, & Schoch, 1959). A separate volume of 8 mL of the same 0.5% dilution was dried overnight in an oven at 100 °C for 24 h to get the mass of dry starch. The supernatant of the centrifuged portion was carefully separated from the residue. The total sugar content of the supernatant was determined by reference to a calibration curve (0–50 mg/mL of glucose) using the phenol-sulphuric method (Dubois, Gill, Hamilton, Rebers, & Smith, 1956). Solubility ($\%S$) was calculated using Eq. (1):

$$\%S = \left[\frac{m_{\mathrm{SS}}}{m_{\mathrm{DS}}}\right]100 \tag{1}$$

where m_{SS} is the mass of starch in the supernatant, calculated as the product of the concentration of total sugars in the supernatant times the volume of supernatant, and m_{DS} is the mass of dry starch in the aliquot, calculated as the product of the ratio of dry to humid mass of the residue times the volume of dilution assuming a density of 1000 kg/m^3.

Swelling was calculated according to Eq. (2):

$$G = \frac{m_R}{m_{RH}} \quad (2)$$

where m_R is the mass of wet residue and m_{RH} is the mass of dry residue. The latter was calculated as the difference between m_{DS} and m_{SS}. Values reported are the mean of quadruplicate measurements. The presence of amylose and amylopectin in both the supernatant and the residue was examined by determining the wavelength of maximum absorbance, λ_{max}. The residue, the uncooked banana and cornstarch, amylose and amylopectin, were first dissolved, separately, in 1 mol/dm^3 KOH, left at rest for 24 h for complete solubilization and then neutralized with 1 mol/dm^3 HCl (Doublier, 1981). One drop of an iodine/iodide solution was added to the supernatant and the treated residue and the absorbance as a function of wavelength measured in a spectrophotometer (Genesis 5, Spectronic Instruments, Inc., USA).

2.5. Rheological measurements

Steady shear rate sweeps were carried out at 60 °C in a rotational viscometer (Haake RV20, Germany) using the concentric cylinders fixture (MV-DIN, inside radius = 18 mm, length = 75 mm, outside radius = 21 mm). Two consecutive up and down sweeps from 0 to 700 s^{-1} were chained to a final logarithmic descent from 700 to 0 s^{-1} in a total time of 12 min. Banana and cornstarch pastes were examined following this procedure. Viscoelastic properties were determined at 25 °C in a strain rheometer (Haake CV20N, Germany) using the parallel plates fixture (gap = 1 mm). Strain sweeps were carried out to find the limit of linear viscoelasticity. In all cases, such limit never exceeded 10% strain.

2.6. Granule size distribution

The size of starch granules was determined by laser diffraction analysis (Malvern Instruments Ltd, 2000) Solid and liquid samples were analyzed using the Scirocco 2000 and Hydro 2000s modules, respectively. Measurements were run in quadruplicate at room temperature. Pastes were diluted to get a final concentration of 0.001%. The refraction index of water and starch dispersion was 1.330 and 1.335 with and absorption of 0.1 (Tecante & Doublier, 1999). It is important to point out that banana starch granules are elongated in shape but their size is referred to that of equivalent spheres. Particle size is expressed as the median diameter D [v, 0.5] and volume distribution (Malvern Instruments Ltd., 1990).

3. Results

3.1. Pasting behavior

The pasting profiles in the Brabander apparatus at different starch concentrations and in comparison with cornstarch are shown in Fig. 1a and b, respectively. A continuous increase in paste consistency with increasing starch concentration was observed. As illustrated in Fig. 1a, consistency began to increase at about 75 °C and this can be interpreted as the start of starch gelatinization. Beyond this temperature consistency increased steadily and smoothly as shown for 3–5% starch without showing a maximum. Cooling resulted in a light increase in consistency. Pastes with 6% starch exhibited a continuous increase in consistency up to 90 °C and then during the holding period consistency decreased about 10 Brabender units. However, a further increase was observed upon cooling. This behavior reveals that banana starch pastes at the concentrations and under the cooking conditions tested are stable to temperature and keep their consistency without exhibiting significant diminution. It is also concluded that cooking was homogeneous. Fig. 1b compares the behavior of corn and banana starches at a concentration of 5%. The consistency of banana starch was almost two times higher although both were stable under the conditions used.

3.2. Gelatinization

Fig. 2 shows the thermal behavior of banana and cornstarch. Both starches exhibited only one endothermic peak, however, the onset temperature, peak temperature and enthalpy of banana starch were superior to those of cornstarch; $T_O = 75.46 \pm 0.36$ °C, $T_P = 80.70 \pm 0.21$ °C, $\Delta H = 16.82 \pm 0.56$ J/g for banana starch and $T_O = 66.11 \pm 0.45$ °C, $T_P = 77.71 \pm 0.30$ °C, $\Delta H = 10.45 \pm 0.36$ J/g for cornstarch. These values show that gelatinization of banana starch requires larger amounts of energy than that of cornstarch. According to the thermal profile, in both starches, gelatinization was complete at about 90 °C and occurred over a range of 15 °C. Other authors (Lii et al., 1982) studied the physical properties of banana starch isolated from fruits of different ripeness degrees and observed onset temperatures in the range 77–81 °C for a heating rate of 5 °C/min. Our onset temperature is similar and the small difference can be explained considering the different degree of ripeness. Also, our results confirm that under the pasting conditions used in this work starch was completely gelatinized.

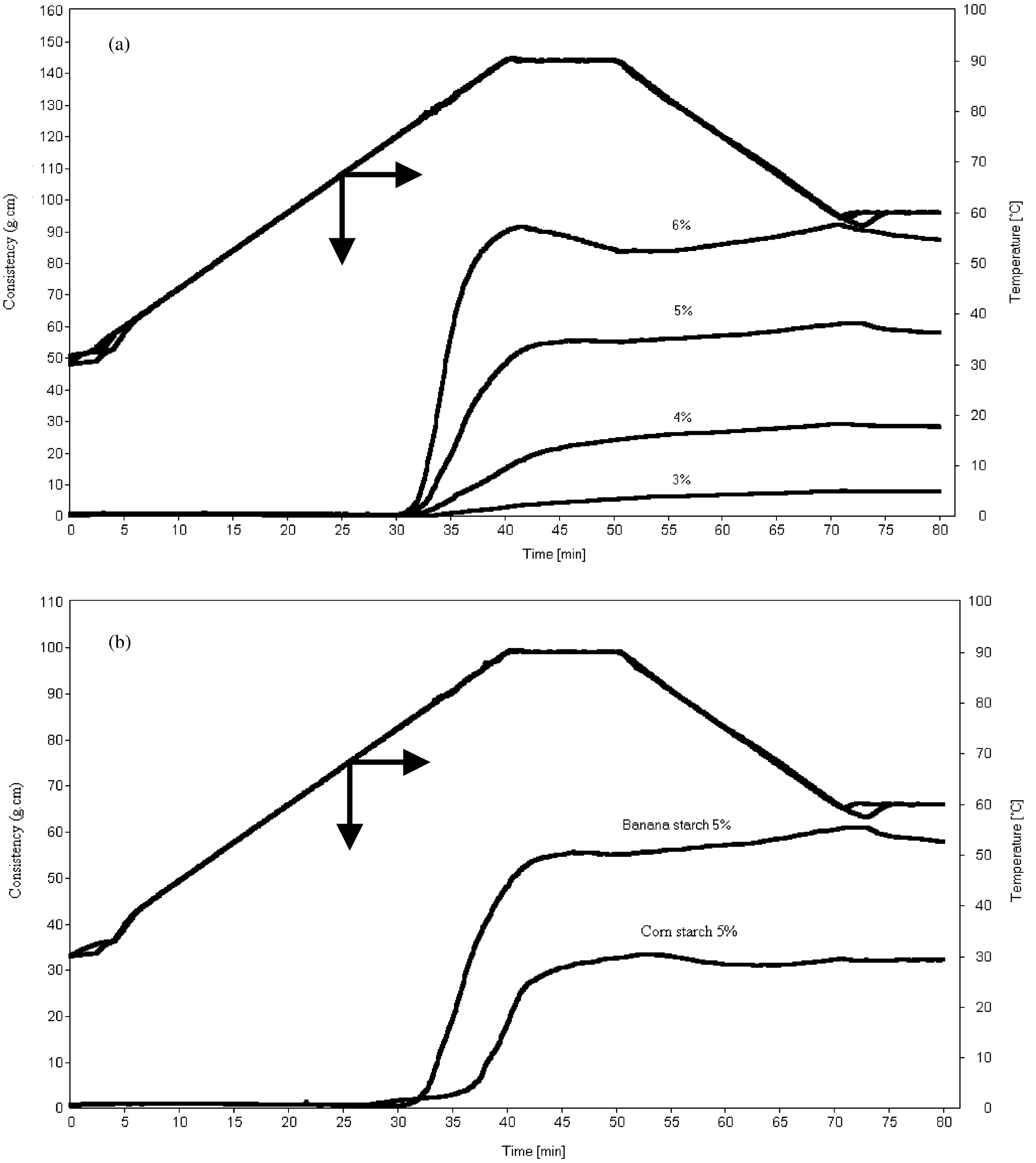

Fig. 1. Brabender profile of starch pastes. (a) Banana starch 3–6% (w/v), (b) banana and corn starch at 5% (w/v).

3.3. Swelling-solubility

Fig. 3 shows the Swelling-solubility behavior during banana starch pasting. The initial solubility (Fig. 3a) was low, but it increased considerably at about 60–70 °C owing to the start of gelatinization. Such behavior was not observed in pastes with 1% starch in which solubility was practically zero below 90 °C but increased noticeably during the holding and cooling periods. However, starch solubilization did not occur immediately because such increase was observed in the range 70–90 °C and at this latter temperature solubility remained constant, even after cooling. Pastes with 6% starch exhibited the highest solubility, while at concentrations from 1 to 5% the solubility ranged from 11 to 14% at 80 °C. As in the case of solubility, swelling increased noticeably in the range 70–90 °C, which indicates that gelatinization occurred gradually. Once at 90 °C, swelling remained essentially constant except in pastes with 6% starch. At this concentration a gradual diminution of swelling occurred during cooling possibly because of water exudation by starch granules. The final solubility and swelling of cornstarch were, respectively, 14.12±1.08% and 17.08±1.45 (g/g). These results show that while solubility was similar, banana starch swelling was about 1.5 times larger.

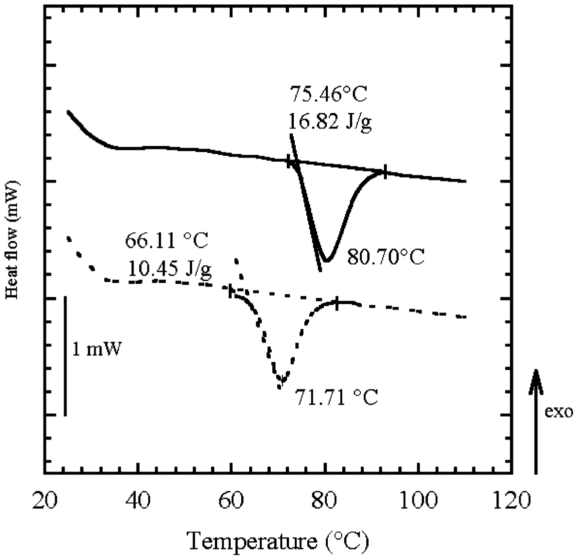

Fig. 2. DCS thermogram of banana (*Musa paradisiaca*) (continuous line) and corn (dotted line) starches.

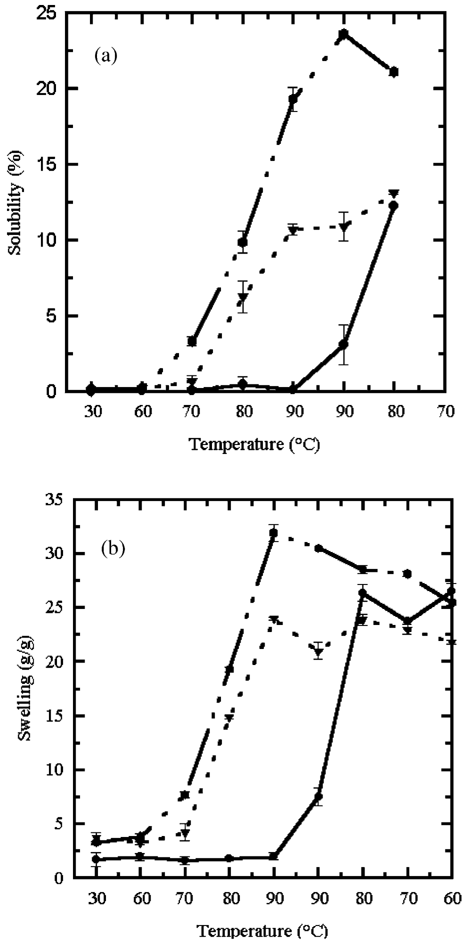

Fig. 3. Swelling-solubility behavior of banana starch during pasting: 1% (circles), 4% (inverted triangles) and 6% (hexagons).

Table 2
Wavelength of maximum absorbance, λ_{max}, of supernatant and residue of banana starch pastes at different concentrations and uncooked banana and cornstarch, amylose and amylopectin

Concentration (%)	λ_{max}	
	Residue	Supernatant
1	562 ± 0.0	616 ± 0.0
3	561 ± 1.5	616 ± 8.49
5	562 ± 1.5	613 ± 4.24
Uncooked banana starch	577 ± 1.2	
Uncooked cornstarch	586 ± 1.3	
Amylose	647 ± 0.0	
Amylopectin	545 ± 0.0	

It is important to distinguish if during gelatinization only amylose goes into the continuous phase as a consequence of leaching out from the swollen granule while amylopectin remains in the granule during the thermal treatment. To make such distinction the wavelength of maximum absorbance, λ_{max}, of the supernatant and the residue of centrifuged pastes was examined together with the corresponding of amylose and amylopectin; the results are shown in Table 2. Considering that λ_{max} from iodine spectra is 640–650 nm for amylose and 545 nm for amylopectin (Table 2), data show that both polymers were present in the supernatant. The presence of amylopectin reveals that some degradation of swollen granules actually occurred making possible its presence in the continuous phase. It seems also that small amounts of amylose remained in the granule without leaching out to the continuous phase.

Considering that starch granules are deformable particles, the swelling factor (Bagley & Christianson, 1982), cQ, corrected by starch solubility was calculated with Eq. (3) (Doublier, 1987):

$$cQ = (1 - S/100)(cG) \tag{3}$$

where c is starch concentration (g/g), S is the solubility index (%) and G is the swelling index (g/g). Fig. 4 shows the variation of cQ of swollen granules with banana and cornstarch concentration. From the linear relation shown, the cQ corresponding to 6% banana starch is superior to unity. When the volume fraction is greater than unity this quantity loses its physical meaning in suspensions of rigid particles. However, in suspensions of deformable particles $cQ > 1$ means that all the solvent has been absorbed by particles (Bagley & Christianson, 1982). Thus, 6% starch can be considered as the concentration for which granules cannot swell ‘freely’ even though they fill almost completely the total volume of the system. Below this concentration the volume fraction occupied by the granules leaves still enough space for the granules to swell freely. It is worth noting that the technique from which granule swelling was determined here does not take into account

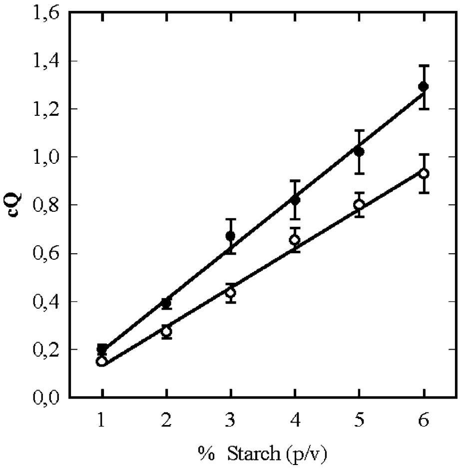

Fig. 4. Variation of *cQ* of swollen granules with starch concentration: banana (filled circles) and cornstarch (hollow circles).

the interstitial water among granules. At the same concentration the swelling factor of banana starch was superior to that of cornstarch (Fig. 4). This supports the fact that the Brabender profile (Fig. 3b) of banana starch showed higher torques during cooking. It is also clear that comparison made on the basis of an equal concentration of banana and cornstarch does not take into account the differences in swelling of the granules.

3.4. Rheological behavior

Fig. 5 shows the flow behavior of banana and cornstarch pastes at 60 °C, at the same *cQ*. The shear stress vs. shear rate curve shows the non-Newtonian shear-thinning character of the pastes. Fig. 5a–c show that the extent of hysteresis decreased with the increase in *cQ* in both starches. This diminution can be attributed to the decrease of 'available' water that occurs at high starch concentrations. It is possible that when starch granules hydrate freely they are more fragile and prone to shear disruption, while those that swell partially are more resistant to rupture, reflecting thus a total absence of hysteresis (Fig. 5d). Cornstarch pastes were more viscous than banana starch pastes at the same *cQ*. A possible explanation for this lies in the shape and fragility of the swollen granules: those of banana starch are ellipsoidal and more fragile, while those of cornstarch are spherical and less fragile. Therefore, the former will exhibit less resistance to flow.

After the continuous shearing to observe the hysteresis behavior, a logarithmic shear rate descent followed. Fig. 6 shows the results from 6 to 700 s^{-1}. Owing to the presence of an incipient Newtonian plateau, the Cross model (Eq. (4)) was used to correlate viscosity with shear rate:

$$\eta = \frac{\eta_0}{1 + K\gamma^n} \tag{4}$$

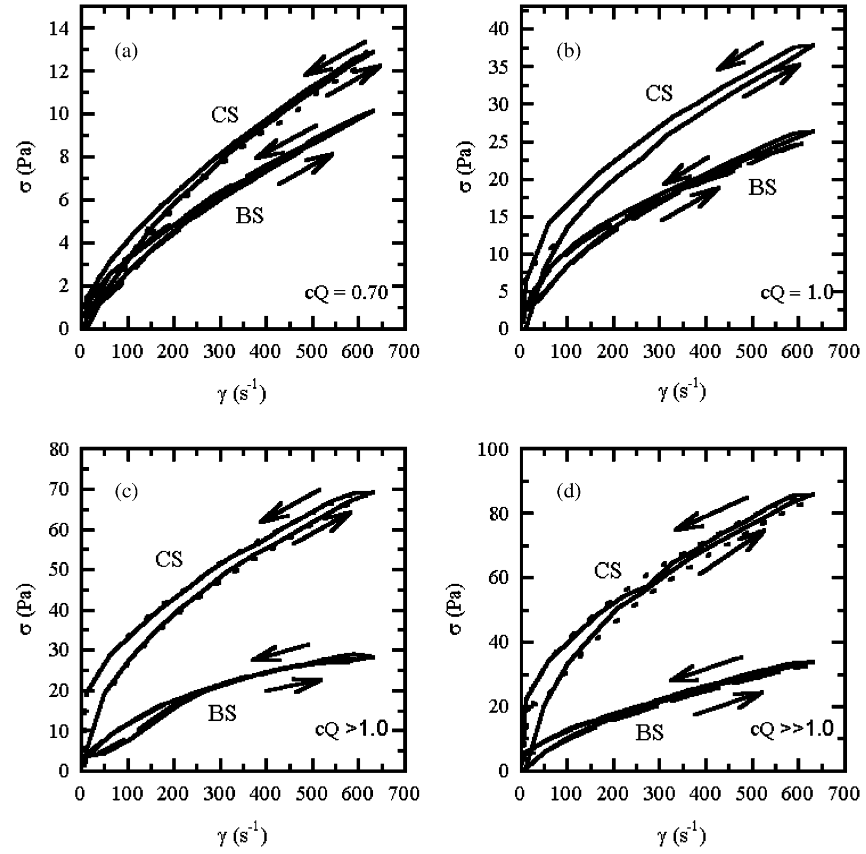

Fig. 5. Flow curves of banana (BS) and cornstarch (CS) pastes at 60 °C.

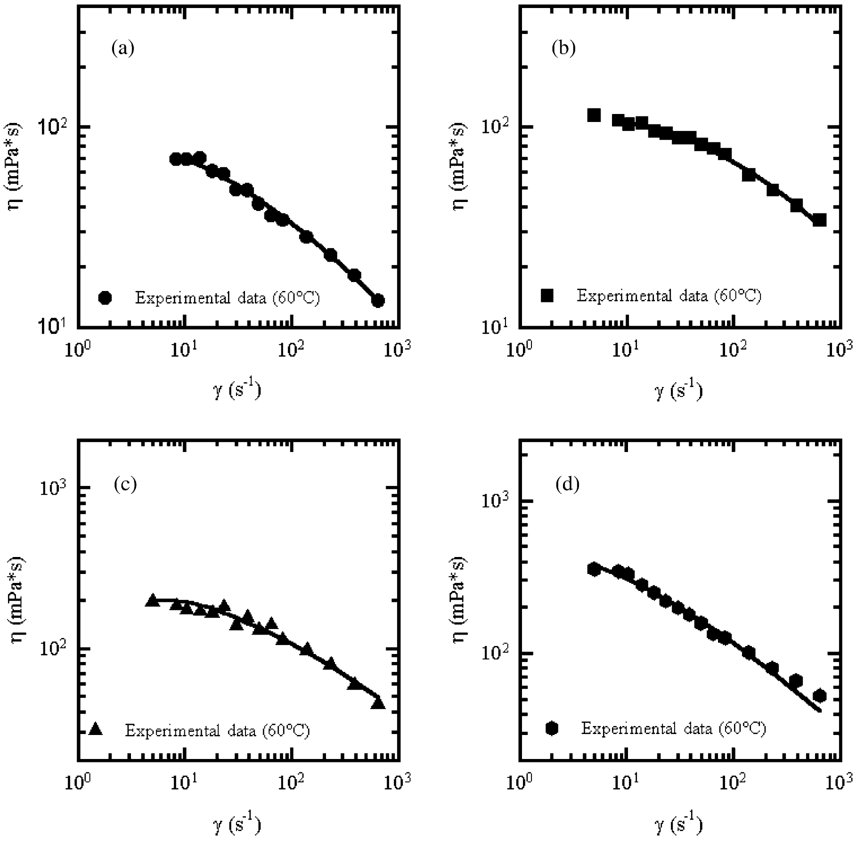

Fig. 6. Variation of apparent viscosity with shear rate of starch pastes at 60 °C. (a) 3%, (b) 4%, (c) 5%, (d) 6%.

In this model η_0 is the zero-shear or plateau viscosity, K and n are parameters determined from experimental data. Table 3 shows the values for each starch concentration with the zero-shear viscosity taken also as a regression parameter. The accuracy of the fitting was assessed with the square root of the sum of squares (Eq. (5))

$$\mathrm{SRSS} = \sqrt{\sum_{i=1}^{n} (y_i - \hat{y})^2} \tag{5}$$

where y_i is the experimental value and $\hat{y}$ is the mean of data values. A low SRSS indicates a good correlation.

Fig. 7 shows the variation of the storage, G', and the loss modulus, G'', with oscillation frequency for 4% ($cQ = 0.8$) and 5% ($cQ = 1.1$) banana starch pastes. In both cases, the storage modulus exhibited little dependence with frequency ($G' \alpha \omega^{0.12}$). Likewise, the loss modulus of the paste with 4% starch showed the same dependence with frequency ($G'' \alpha \omega^{0.12}$). If this dynamic behavior is explained on the grounds of cQ, at 4% starch there is still enough water as to allow major mobility of starch granules in the disperse phase. The amylose chains present in the continuous phase at 25 °C have presumably formed a three-dimensional network, therefore the gel behavior is expected. When starch content increased, the amount of amylose in the disperse phase increased and a more concentrated gel was formed. The system had greater moduli and can be considered more resistant to deformation. Fig. 7c shows that the elastic character of pastes with 4 and 5% starch is maintained in both systems along the frequency sweep.

3.5. Particle size distribution

Fig. 8 shows the granule size distribution of both uncooked banana starch and pastes with 1, 3 and 5% starch. Table 4 shows the median diameter D [v, 0.5] (i.e. the size at which 50% of the particles by volume are smaller and 50% are larger).

All samples exhibited a unimodal size distribution. In uncooked starch a small zone around 1–3 μm was observed. However, the major distribution was observed between 7 and 70 μm with D [v, 0.5] = 24.31 μm.

Table 3
Parameters of the Cross model of banana starch pastes of different concentrations

Concentration (%) w/v	η_0 (mPa s)	K (s^n)	n	SRSS
3	82.0	0.148	0.60	8.40
4	132.3	0.058	0.61	7.87
5	203.6	0.158	0.54	13.56
6	633.6	0.250	0.25	12.36

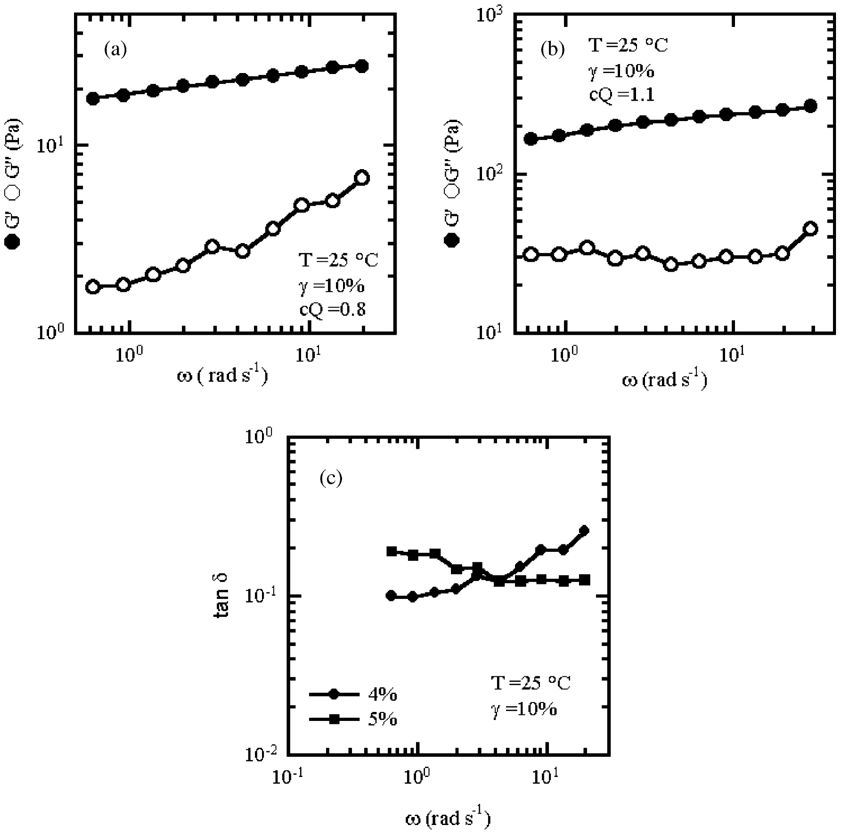

Fig. 7. Viscoelastic behavior of banana starch pastes at 25 °C. (a) 4%, (b) 5%, (c) tan δ as a function of frequency.

The distribution of 1% pastes was smooth, while that of 3 and 5% showed a slight 'shoulder' at the beginning of their corresponding ascending portion. This is may be the result of a complete hydration in 1% pastes and partial hydration in 3 and 5% pastes owing to some kind of hindrance among starch granules at larger concentrations that resulted in partial or incomplete swelling of some of them. This would mean that when the volume fraction approached unity, hydration of some starch granules was not complete enough.

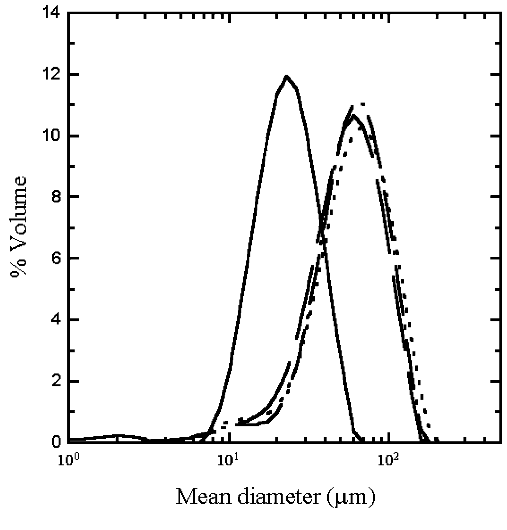

Fig. 8. Particle size distribution of uncooked starch (continuous line) and pastes with 1% (dashed line), 3% (dashed-dotted line) and 5% (dotted line) starch.

4. Discussion

Starch cooking in the presence of an excess of water results in noticeable changes in granule structure that can be traced in different ways. The Brabender curves (Fig. 1) show an increase in consistency at about 75 °C with this temperature being practically independent of starch concentration. This initial increase can be ascribed to the progressive swelling of starch granules that occurs upon heating. The further increase in paste consistency is due to the smooth change from a liquid medium with uncooked

Table 4
Median diameter of uncooked banana starch granules and starch pastes at different concentrations

Concentration% (w/v)	*D* (*v*, 0.5)
Uncooked starch	24.31
1	59.64
3	64.06
5	66.27

suspended particles to a system of swollen deformable particles suspended in a more viscous medium. The swollen granules can be closely or loosely packed depending on the cQ they occupy which in turn depends on starch concentration (Fig. 4). The temperature at which consistency began to increase (75 °C) was very close to the onset temperature (75.46 °C) recorded in DSC tests. This latter temperature sets the point of melting of crystallites in the granules. It is expected that as melting goes on swollen granules become softer. However, the Brabender profiles show that banana starch is stable to the combined thermal and shearing treatment. The DSC profile also shows that the melting process reached its peak temperature at 80.70 °C and that it was completed at approximately 90 °C. Therefore, under the pasting conditions used in this work it is possible to affirm that banana starch was completely gelatinized. This affirmation is also supported by the results of the swelling-solubility measurements from which it can be observed that both quantities began to increase at about the above-mentioned temperatures.

During starch gelatinization partial separation of amylose and amylopectin can also occur. It is well documented in the literature that in mixtures of purified samples of each component partial separation takes place, at 70–90 °C, because of the thermodynamic incompatibility between such macromolecules (Kalichievsky & Ring, 1987). Considering this, it is expected that in a starch paste the separation occurs outside the granule when both the amylose leached out from it and the partially solubilized amylopectin are found in the continuous phase. Inside the granule separation can hardly occur (Keetels, van Vliet, & Walstra, 1996). Pasting can also result in granule disruption besides granule swelling. A swollen starch granule can be considered as an amylopectin matrix where the chains of this macromolecule can be entangled (Keetels et al., 1996). Under certain thermal and mechanical conditions disentanglement can occur giving rise to a gradual breakdown of the amylopectin matrix and therefore to granule disruption. Fig. 9a shows that in the case of banana starch, some granule disruption actually occurred under the pasting conditions used here, while cornstarch granules remained essentially intact. Therefore it is expected that in banana starch pastes, the continuous phase is constituted of amylose and small amounts of amylopectin (see Table 2), while the disperse phase is formed by swollen, partially swollen and disrupted granules. Laser diffraction measurements show, however, that the behavior of the population of granules, of which $D[v, 0.5]$ is a characteristic, points to the existence of a system with a large fraction of swollen granules instead of a system of soluble starch with granule fragments.

At 60 °C, temperature at which the steady flow behavior of starch pastes was examined, amylose in the continuous phase is in a random coil conformation. The rheological properties of the pastes are mainly determined by the swollen granules instead of the liquid medium as amylose does not form viscous solutions at such temperature (Alloncle, Lefebvre, Llamas, & Doublier, 1989). The lack of significant hysteresis even at high starch concentrations can be taken as an indication of low interaction among starch granules. The mechanical stability of banana starch pastes is remarkable in comparison with starches from other sources which exhibit large hysteresis loops upon shearing (Doublier, 1987). Likewise, the smooth variation of apparent viscosity (Fig. 6) with shear rate opposite to the high shear thinning character of corn and wheat starches also supports this affirmation. In this work, the rheological behavior of banana and cornstarch pastes was compared on the basis of cQ instead of starch concentration because cQ, being an index of the swelling behavior, describes more appropriately the physical state of the systems. Besides, as shown in Fig. 4, at the same concentration, different starches have different swelling factors.

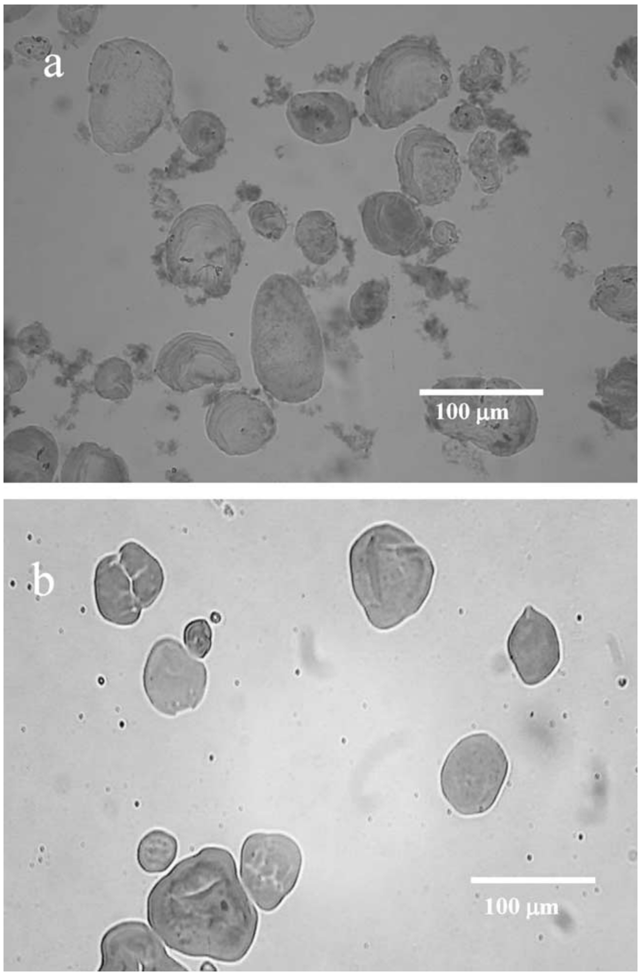

Fig. 9. Micrograph (10×) of: (a) banana (*Musa paradisiaca*), (b) cornstarch paste.

When starch cools to ambient temperature the amylose in the continuous phase forms a three-dimensional network resulting in a gel (Miles, Morris, & Ring, 1985a). In amylose solutions gelation occurs by a phase separation into polymer-rich and polymer-deficient regions followed by crystallization in the former phase (Miles et al., 1985a). Phase separation occurs over a short-time scale, while crystallization does it over a long-time scale. Although some authors have proposed a gelation mechanism involving aggregation of interchain double helices (Gidley, 1989), all of them agree that the minimum amylose concentration at which this polymer forms gels is about 1% (Clark, Gidley, Richardson, & Ross-Murphy, 1989; Doublier & Choplin, 1989; Gidley, 1989; Kalichievsky, Orford, & Ring, 1986; Miles et al., 1985a). However, depending on amylose concentration and degree of polymerization different states going from precipitates to gels and mixtures of both can be observed (Gidley & Bulpin, 1989).

At 25 °C, it is expected to found a three-dimensional amylose network in the continuous phase of the banana starch pastes. However, in our particular case it is possible to observe (Fig. 9) that the system is complex because it is formed by a disperse phase of amylose and amylopectin, intact swollen granules as well as partially swollen and broken granules. However, when $cQ = 1$, assuming that banana starch has 25–28% amylose, the calculated amylose concentration in the continuous phase is 1.2% w/v which is above the minimum required for amylose gelation. Thus, analyzing the rheological behavior of pastes at 25 °C, it can be observed that the depicted behavior is characteristic of a gel (Ferry, 1970); G' is significantly greater than G'', both moduli are not strongly dependent on frequency and the phase angle is low. Unlike ‘true’ gels, starch pastes at 25 °C resisted relatively large strains; frequency sweeps were carried out at 10% strain well within the zone of linear viscoelasticity. Nevertheless, gels prepared from purified amylose also exhibit such resistance to strain and in fact their dynamic viscoelastic behavior has been examined at the same strain amplitude that the one used in this work for starch pastes (Tecante & Doublier, 2002). All the precedent evidence points to the existence of an amylose network, but unfortunately it is not possible to separate the contribution of the disperse phase (starch granules) from that of the continuous phase (amylose network). On the basis of the mechanical spectra shown in Fig. 7a and b, one may surmise, however, that although at 4% ($cQ < 1$) and 5% ($cQ > 1$), a typical gel behavior is observed, such behavior points to the reinforcement of the amylose gel by the starch granules (containing amylopectin) embedded randomly in the amylose network (Carnali & Zhou, 1995; Miles, Morris, Orford, & Ring, 1985b), where the rheological behavior is attributed to the amylose gel formed rather than to the hydrated amylopectin molecules (starch granules). Additionally and observing that tan δ (Fig. 7c) remains practically constant or with a slight decrease for $cQ > 1$, the system can be considered to be composed of an amylose network reinforced with the starch granules that act as a filler in the gel (Eliason, 1986). This contribution depends on cQ, as well as on the compressibility and adhesion between the continuous and the disperse phase (Carnali & Zhou, 1995). In this case, the rheological behavior does not depend on particle size (Okechukwu & Rao, 1995), but on cQ and its corresponding concentration of amylose and amylopectin during pasting. Also, in a system as complex as this, the possibility exists of co-precipitation and co-crystallization of amylose with amylopectin to the interior of starch granules as an alternate process to starch gelatinization (Miles et al., 1985b).

Knowing that native banana starch has a type-A X-ray diffraction pattern (Bello-Pérez et al., 2000) with a high proportion of short chains, then according to the phase diagram (Gidley & Bulpin, 1989) it is possible that the formation of the amylose gel for this type of starch is that corresponding to an amylose with a moderate degree of polymerization (DP 200–600) and an essentially monodisperse distribution with fast gelling (Clark et al., 1989) at amylose concentrations greater than 1% in the aqueous phase ($cQ > 1.0$). However, further research is needed to clear this point for banana starch.

Other additional factors influencing amylose gelation, such as ionic strength and thermal history have been found (Doublier & Choplin, 1989). In this work, pastes were cooked at 92 °C and this temperature produces a large number of nuclei in the system (Doublier, Coté, Llamas, & Charlet, 1992) leading to gel formation because nucleation induces a rapid crystallization without any chain included in different crystals, which is in favor of the fact of having a moderate degree of polymerization.

5. Conclusions

The gelatinization temperature of banana starch is 75 °C, with granules stable to cooking but without avoiding rupture of some of them and without affecting noticeably their rigidity. Gelling of amylose and the rigidity of the resulting gel depend on cQ and therefore on amylose and amylopectin concentration. Results suggest that the amylose network formed during paste gelation, is constituted essentially of chains with moderate DP (200–600), with monodisperse distributions and a rapid gelling time. It is considered that the system formed at 25 °C, follows the model of structure of a gel reinforced by hydrated starch granules.

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