ELSEVIER

Contents lists available at SciVerse ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng



Effect of damaged starch on the rheological properties of wheat starch suspensions

Gabriela N. Barrera ^a, Mariela C. Bustos ^a, Laura Iturriaga ^d, Silvia K. Flores ^c, Alberto E. León ^{a,b}, Pablo D. Ribotta ^{a,b,*}

- ^a Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, CC 509, 5000 Córdoba, Argentina
- ^b Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET), Argentina
- ^c Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Argentina
- d Facultad de Agronomía y Agroindustrias de la Universidad Nacional de Santiago del Estero, Argentina

ARTICLE INFO

Article history: Received 11 June 2012 Received in revised form 25 October 2012 Accepted 22 November 2012 Available online 1 December 2012

Keywords: Damaged starch Spontaneous gelatinization Flow properties Pasting

ABSTRACT

The influence of damaged starch content on particle size distribution and rheological properties of unheated starch suspensions and pasting properties were investigated. Four samples containing different amounts of damaged starch were studied. Particle size distribution curves shifted toward higher diameters, and a greater overlap of both populations of particles (A- and B-type granules) and a decrease of both peak heights were produced. The flow curves of unheated starch suspensions were fitted using the power law model. The flow behavior indexes were higher than the unit. The consistency coefficient increased with the increment of damaged starch content. Unheated starch suspensions showed time-dependent rheological behavior and were described by the Weltman model. The unheated suspensions exhibited a thixotropic behavior. With regard to the pasting process, the increment of damaged starch content produced gradual reductions in peak viscosity, final paste viscosity, breakdown and setback. Results demonstrated the importance of the presence of physically damaged granules in wheat starch rheological characteristics.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Starch is one of the most common biopolymers and is deposited as discrete granules in the amyloplasts of plant storage organs. In foods, one major use of starch is as a thickening/gelling agent. During processing, starch dispersions are subjected to combined high heating and shear rates that affect their rheological change as well as the final characteristics of the product.

Much information about starch suspensions gelatinized in different conditions has been published; the effect of temperature, time and shear rates on the rheology of gelatinized starch suspensions has been informed (Rao and Tattiyakul, 1999; Abu-Jdayil et al., 2001; Al-Malah et al., 2000; Nguyen et al., 1998). However, few studies have dealt with the flow behavior of starch suspensions without heating. (Frith and Lips, 1995) investigated the rheology of the dilatant behavior, using concentrated waxy maize starch suspensions, and reported that the dilatant transition does appear to be strongly affected by the deformability of the starch granules.

E-mail address: pribotta@agro.unc.edu.ar (P.D. Ribotta).

From an engineering point of view, the viscosity difference due to the raw material has to be carefully considered, since it may change flow regimes, processing variables and final product quality. The composition of the starting material can also cause changes in the rheological profile of starch dispersions.

Granular integrity can be affected by the mechanical action of the wheat milling process, since this operation may damage granular structure, thus producing what is called damaged starch. The level of the damage depends on wheat hardness and the conditions and technique at the milling process. The composition and architecture of starch granules regulate their susceptibility to physical damage as a function of milling time and, probably, of the magnitude of applied force (Tester, 1997). Starch damage profoundly changes starch granular structure and it influences rheological and functional properties of the starch systems (Faridi, 1990). Several studies have shown that damage induced by ball milling generates a range of fractions, which have quite different roles in starch gelatinization and swelling properties. These fractions include native granules, two forms of granule fragments and lowmolecular weight soluble material (Karkalas et al., 1992; Morrison et al., 1994; Tester et al., 1994; Morrison and Tester, 1994; Tester and Morrison, 1994).

Damage facilitates swelling of starch granules, due to destruction of the forces which prevent granules from swelling in water (Tester, 1997). Therefore, damaged starch has the ability to absorb

^{*} Corresponding author at: Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, CC 509, 5000 Córdoba, Argentina. Tel.: +54 351 4629520; fax: +54 351 4334118.

more water than native granules, native wheat starch can absorb between 39% and 87% its weight in water, while damaged starch between 200% and 430% (Berton et al., 2002). Some studies have reported that, unlike native starch, mechanically damaged starch spontaneously gelatinizes in cold water and this process is similar to gelatinization caused by heating. This spontaneous gelatinization produces a reduction on the gelatinization endotherm up to partial or complete disappearance, during heating (Morrison et al., 1994; Tester, 1997; Barrera et al., 2012). On the other hand, the higher water absorption capacity of damaged starch compared to native starch, may affect the viscosity of starch suspensions even without heating. The aim of this work was evaluated the effect of damaged starch content on particle size distribution and rheological properties of unheated starch suspensions and on starch pasting properties.

2. Materials and methods

2.1. Samples

Unmodified (native) wheat starch (S5127 Sigma-Aldrich CAS Number 9005-25-8) was used for samples preparation. It has 10.7 g moisture/100 g and 0.18 g protein/100 g, 3.8% damaged starch (DS) and 31.1% amylose, according to AACC 44-19, 46-13. 76-30A (AACC 2000) and Megazyme amylose/amylopectin assay kit (Megazyme International, Ireland), respectively. Damaged starch was produced as described by Barrera et al. (2012). Unmodified wheat starch was milled in a Whisper Series Bench Top disk mill (Rocklabs, Auckland, New Zealand) to cause a rupture of starch granules. Temperature was monitored during the milling; it was kept under 40 °C. Four starch samples with different damaged starch contents were obtained after milling and mixing: 3.8% DS (native wheat starch from SIGMA, unmilled in mill disk), 8.4, 12.9 and 23.8% DS. The values of damaged starch were chosen according to the range of damaged starch (6.10-26.90%) generated by roller milling (Ghodke et al., 2009).

Damaged starch content was determined according to AACC 76-30A method (AACC 2000). A fungal enzyme from *Aspergillus oryzae* (A6211, Sigma Chemical Co., St. Louis, MO, USA) was used in this analysis. Analyses were performed in triplicate.

2.2. Particle size analysis

Granular size distribution of starch samples was determined by laser light scattering (Mastersizer 2000E ver. 5.20, Malvern, Worcestershire, UK). The assay was performed in two different ways. In the first case, the starch samples were transferred to the particle size analyzer dispersion tank, containing Micropore filtered water; this measure was defined as time zero (not swelled). In the second case, starch-water suspensions (6.25% w/w) were first mixed during 3 h (swelled) at room temperature. The starch suspension was transferred into the particle size analyzer dispersion tank containing Micropore filtered water, and the measure was then carried out. The instrument provides size distribution information parameters, such as volume distribution, d10, d50 and d90. De Brouckere mean diameter (D4.3) and Sauter mean diameter (D3.2). Size values designated as d10, d50, and d90 indicate that 10%, 50%, and 90% of particles are smaller than such values. De Brouckere mean diameter is the volume mean diameter of the particles, and Sauter mean diameter is the surface area weighted mean diameter of the particles. All these parameters were calculated assuming that the granules are spherical particles (Malvern Instruments, 1999).

2.3. Evaluation of leached amylose from granules

Starch suspensions (11.8% w/w) were prepared and gently agitated for 40 min at room temperature. After this time, the suspensions were centrifuged at 10,000g for 5 min and the supernatants were held at 50–55 °C for 5 min. An aliquot of 1.5 ml was used to determine the percentage of amylose and amylopectin contents leached out as consequence of spontaneous gelatinization. The amylose content was determined using the Megazyme amylose/amylopectin assay kit (Megazyme International, Ireland), according to the procedure described by Gibson et al. (1997) but the gelatinization step was avoided. Results were expressed as grams of leached amylose per 100 g of available starch.

2.4. Rheological measurements

Flow properties of the unheated starch suspensions were determined with a rheometer (AR 1000-TA Instrument, New Castle, DE 19720). Steel plate geometry (40 mm diameter) and 0.5 mm gap were used for the determinations. The starch suspensions (20% w/w) were agitated during 3 h at a fixed stirring rate which was just enough to keep the starch granules suspended. An aliquot (\sim 1 ml) of the starch suspension was poured on the rheometer bottom plate and equilibrated to 25 °C.

The geometry was accelerated uniformly from 0 to $300 \, s^{-1}$ in 3 min and the shear rate was kept constant for 10 min. After this time, the shear rate was decelerated uniformly to the rest in 3 min and immediately accelerated from 0 to $300 \, s^{-1}$ in 3 min. The starch suspensions were monitored during the shear cycle. The shear rate used for the rheological determinations did not affect measurement conditions.

In order to characterize the rheological behavior of the unheated starch suspensions the flow curves were modeled using the power-law model, which describes the data of shear-thinning and shear-thickening fluids (Rao, 1999). The model was applied to the descending segment, which starts at the higher shear rate, to minimize the starch granules sedimentation:

$$\tau = K * \begin{pmatrix} \bullet \\ \gamma \end{pmatrix}^n$$

where K is the consistency coefficient (Pa) and n is the flow behavior index (dimensionless).

Weltman (1943) model was used to describe the thixotropic behavior of unheated starch dispersions. The experimental shear stress versus shearing time data were fitted to Weltman equation:

$$\tau = A + B * (\ln t)$$

where τ is shear stress (Pa), t is shearing time (s) and A (value of stress at t = 1s) and B are constant parameters, which characterize the time-dependent behavior (Rao, 1999).

2.5. Pasting profile

Pasting properties of starch samples were determined with a Rapid Visco Analyser (RVA-4), using the RVA General Pasting Method (Newport Scientific Pty. Ltd., Warriewood, Australia). The RVA parameters were obtained from starch–water suspensions. Starch samples (3.5 g) were transferred into a canister and approximately 25 ± 0.1 ml distilled water were added. The slurry was heated to 50 °C, while stirring at 160 rpm for 10 s for thorough dispersion of batter ingredients. The slurry was held at 50 °C for 1 min, and then heated up to 95 °C at a heating rate of 9.4 °C/min and a stirring rate of 960 rpm. It was held at 95 °C for 2.5 min, and finally cooled to 50 °C at a cooling rate of 11.8 °C/min. Initial pasting temperature (PT), peak viscosity (PV), final or cool paste

viscosity (CPV), breakdown (BD), and setback (SB), were obtained from the pasting curve. Analyses were performed in duplicate.

2.6. Statistical analysis

The data were statistically treated by variance analysis (ANO-VA), the means were compared by the LSD Fisher test at significance level of 0.05, and the relationship between measured parameters was assessed by Pearson test (significant levels at $p \le 0.05$) using the Infostat Statistical Software (Di Rienzo et al., 2009).

3. Results and discussion

3.1. Effect of damaged starch on granule size distribution

The size distribution of starch granules at zero time hydration and after 3 h of swelling is shown in Fig. 1. All samples, in both conditions, showed the characteristic bimodal distribution of wheat starch (Jay-Lin, 2009).

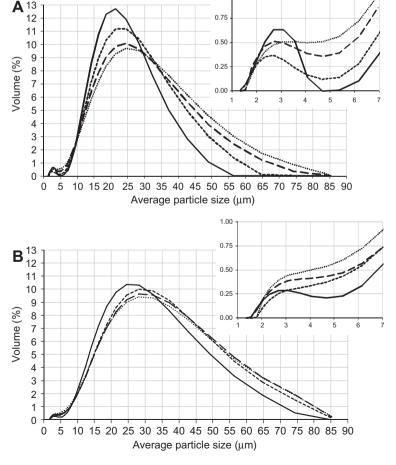
Two main fractions of starch granules, B-type $(1.3-4.4~\mu m)$ and A-type $(5.01-60.3~\mu m)$, were observed in unmilled starch sample. The gradual increment of damaged starch content caused a shift of the curves toward higher diameters, an overlap of both particle populations and a decrease in both peak heights (Fig. 1A). Parameters d50, d90 and D4.3 increased due to damaged starch effect. Parameter d50 increased from 20.2 ± 0.5 to 23.6 ± 0.9 ; d90 from

33.9 \pm 0.8 to 46.0 \pm 1.2, and *D4*.3 from 21.4 \pm 0.6 to 26.2 \pm 1.0. However, *d10* and *D3*.2 were not affected ($p \le 0.05$).

In B-type granule population, the relative volume of particles with lower diameter decreased as a consequence of the displacement of peaks produced by damaged starch influence. The diameter of the particles that represent the peak maximum increased due to damaged starch effect. The peak maximum of unmilled sample, 8.4 and 12.9 DS samples was around 2.5–2.9 μ m, while 23.8 DS sample was between 2.9 and 3.3 μ m. In general, a decrease in the % volume of particles that represent the peak maximum by damaged starch influence was observed.

In A-type granule population, the peak of particle size distribution was affected by the increase in damaged starch content; an increase in the diameter of the particles and a decrease in the relative volume associated with the maximum, were observed. The peak maximum of the unmilled sample was around 19.9–22.9 μm (21.4 μm average), while the samples with 8.4, 12.9 and 23.8 DS were between 22.9–26.3 μm (24.6 μm average). The relative volume of particles with higher diameter (40–90 μm) increased gradually when damaged starch level increased.

Starch swelling in the four samples was also evaluated after 3 h of resting time and a similar behavior was found (Fig. 1B). The swelling caused a decrease in the peak maximum of both particle size populations and a displacement of the curves toward higher diameters compared to that recorded at time zero. These effects were more pronounced in the samples with lower level of damaged starch. A greater overlap of both A- and B-particle populations was observed. The samples rich in damaged starch had a greater



1.00

Fig. 1. The percent volume distribution: (A) zero time samples and (B) samples after 3 h of swelling. The inset enlargement of low particle size shows the changes in the B-type granule population. Starch samples: 3.8 DS (-), 8.4 DS (- - -), 12.9 DS (- - -) and 23.9 DS (••••).

overlapping of both populations of particles. The d50, d10, D3.2 and D4.3 values were not modified, while d90 increased with damaged starch $(46.6 \pm 0.8 - 52.5 \pm 1.2)$ ($p \le 0.05$).

Summarizing, granular size profiles showed a greater heterogeneity produced by damaged starch effect. Increments in damaged starch content gradually decreased the relative volume of the smallest particles and increased particle diameter and the relative volume of the biggest particles. The damage of starch granules facilitated hydration and swelling, and both events took place instantaneously. As a consequence of this, changes in particle size distribution at zero time resulted from the great water absorption capacity that damaged starch granules have (Bushuk, 1998). Rapid starch granule hydration and swelling could result from changes in the granular surface. The milling process may peel off the granular surface, affecting hydration and swelling of starch granules.

After 3 h hydration, initially observed tendencies were not modified. Particle diameter continued increasing as well as granular heterogeneity. These results demonstrate that starch samples continued absorbing water and swelling after 3 h, suggesting that undamaged starch granules were responsible for water absorption after this time. Thus, changes in size distribution during this period were caused by undamaged starch granules.

3.2. Effect of damaged starch on flow curve properties

Fig. 2 presents shear stress versus shear rate curves of the unheated starch suspensions. Results show that the relationship between shear stress-shear rate of suspensions was non-linear, indicating that the systems behave as a non-Newtonian fluid. Several researches have shown that gelatinized starch dispersions, produced by different conditions of time and temperature, are non-Newtonian fluids that could exhibit yield stress (Evans and Haisman, 1979; Christianson and Bagley, 1984; Giboreau et al., 1994).

The hysteresis loop was observed in all samples, suggesting time-dependent fluid behavior. The unheated starch suspensions exhibited thixotropic behavior due to the clockwise loops registered. Mild thixotropy has been observed in gelatinized wheat starch dispersions, characterized at low temperatures, such as 25 °C but not at 60 °C or above (Doublier, 1981; Harrod, 1989; Bagley and Christiansen, 1982). The time-dependent rheological

behavior of gelatinized starch dispersions has been attributed to structure formation by α -glucan leached into the suspending matrix on cooling to low gelling temperatures (Ellis et al., 1989).

The area of the hysteresis loop was affected by damaged starch content. The suspensions with higher damaged starch content had a larger hysteresis area than the unmilled starch and 8.4 DS samples (Table 1). The area of the hysteresis loop is a measure of the extent of thixotropy (Steffe, 1996). Thus, the fluid structure depends more on time as the damaged starch content increases in the system.

Over the range of shear rates used in this study, the power-law model described the flow behavior of each unheated starch suspension. Consistency coefficient (K) and flow behavior index (n)along with coefficients of determination (r^2) for each sample are shown in Table 2. The flow behavior index (n) values were higher than the unity, indicating that the systems exhibited a non-Newtonian shear thickening (dilatant) behavior under the investigation conditions. Several studies on wheat starch gelatinization have shown values of the power law flow behavior index (n) greater than 1.0 during the early stages of gelatinization, indicating that wheat starch could show shear-thickening behavior (Bagley and Christiansen, 1982; Dail and Steffe, 1990a, 1990b; Okechukwu and Rao, 1995). In general, the dilatant flow behavior is due to an increase in the size of structural units as a result of shear. In particular, regarding the starch-water systems, the shear-thickening behavior has been attributed to the starch granules rigid, enough to resist shear, and the high concentrations, enough to occur particle crowding (Christiansen and Bagley, 1984).

Heated starch suspensions have been described by Rao (1999). The transition of starch systems from shear-thickening to shear-thinning thixotropic flow behavior occurs progressively with increasing time and heating temperature during the gelatinization process. In this way, the starch gelatinization may be described as a transition process that transforms the rheological behavior of starch suspensions from dilatant to pseudoplastic time dependent.

Flow behavior index (n) values were not significantly affected by damaged starch; however, the consistency coefficient (K) increased due to damaged starch effect. Viscosity versus shear rate curves exhibited a change in viscosity suspensions due to damaged starch. An increase in the viscosity system resulting from damaged

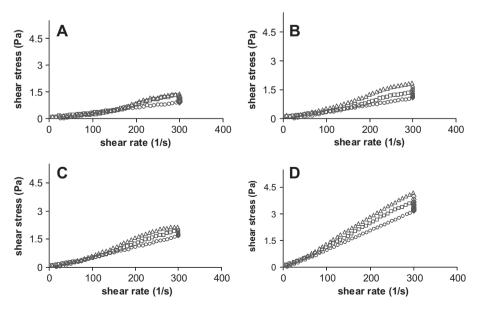


Fig. 2. Effect of damaged starch of the shear stress-shear rate curves of unheated starch suspensions: (A) 3.8 DS, (B) 8.4 DS, (C) 12.9 DS and (C) 23.8 DS. (Δ) Continuous ramp 1, (\Diamond) peak hold (\bigcirc) continuous ramp 2 and (\square) continuous ramp 3.

Table 1 Hysteresis loop area for the unheated starch suspensions.

Sample	Hysteresis loop (Pa s ⁻¹)	
3.8 DS	59.2 a	
8.4 DS	131.4 ab	
12.9 DS	184.5 b	
23.8 DS	178.4 b	

Different letters within columns mean significant differences at $p \le 0.05$.

Table 2 Power law parameters.

Fitted parameters	Power-Law	Power-Law model parameters			
	3.8 DS	8.4 DS	12.9 DS	23.8 DS	
K (Pa)	0.0013 a	0.0014 a	0.0022 b	0.0058 с	
n	1.16 ab	1.18 b	1.17 ab	1.11 a	
r^2	0.98	0.99	1.00	1.00	

Different letters within columns mean significant differences at $p \le 0.05$.

starch presence was observed (Fig. 3). The effects registered in consistency coefficient (K) and viscosity could be explained in terms of the cold gelatinization suffered by starch damaged granules. Damaged starch granules have the ability to hydrate spontaneously in cold water, and this process is very similar to the gelatinization caused by heating (Morrison et al., 1994). Therefore, damaged starch granules can absorb water, swell and leach out amylose and amylopectin, which could cause an increase in the viscosity of the system.

Tester (1997) proved that fractions of insoluble material are produced as a result of granule damage: native starch granules; fragments of native granules containing the native granule ordered structure which do not readily hydrate in cold water; granule fragments which have lost ordered structure and can hydrate in cold water to form gels; and soluble material (soluble fragments of amylopectin). Our findings are in agreement with (Tester, 1997) since it appeared that the physically damaged granules facilitated the leaching out of amylopectin.

The amylose/amylopectin proportion in the leached material during the hydration and swelling of the starch granules at room temperature were determined. The amount of leached material during cold gelatinization was affected by damaged starch content. The leached material increased when damaged starch content rose, and an increment of more than 100% of leached material was recorded (Table 3). Physical damage facilitated hydration and swelling of starch granules; therefore, a higher number of starch granules could spontaneously gelatinize. Consequently, the

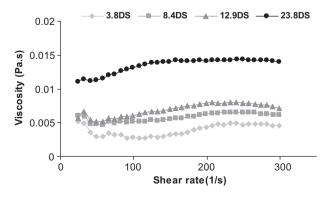


Fig. 3. Effect of damaged starch content on viscosity of the unheated starch samples.

Table 3Leached amylase and leached material during the cold gelatinization of the starch granules.

Sample	Amylose (%)	α-Glucan leached (%)
3.8 DS	83.9 с	0.14 a
8.4 DS	26.0 b	0.31 b
12.9 DS	20.5 ab	0.54 c
23.8 DS	17.9 a	1.18 d

Different letters within columns mean significant differences at $p \le 0.05$. α -Glucan leached correspond to leach out amylose and amylopectin.

material which partially diffuses out of damaged granules increased in the suspension.

The amylose/amylopectin proportion in the leached material during cold gelatinization was modified by starch damage. In the leached material, the amylose proportion decreased by damaged starch content (Table 3). These results indicated that the material leached during cold gelatinization becomes proportionally richer in amylopectin when damaged starch content increases in the system.

Therefore, taking into account the results of granular size profile, flow behavior and leached out material, it is possible to assume that changes on the rheological behaviors of the unheated starch suspensions caused by damaged starch were related to the extent of starch granule swelling and the amount and proportion of leached amylose and amylopectin. The spontaneous gelatinization experienced by damaged starch granules resulted in suspensions of swollen starch granules in a macromolecular solution. The size of swollen starch granules is greater at higher damaged starch proportions, and the suspensions become richer in leached material, especially in the amylopectin fraction. In this way, increments in damaged starch content result in a larger volume fraction occupied by swollen granules that contribute to viscosity. Therefore, the viscosity of the unheated starch suspensions increases. Besides, polymer chains in the macromolecular solution are in contact with each other, which also contribute to the increase of the viscosity. The raises in amylopectin fraction are especially related to viscosities increments due to the size and structure differences of this molecule compared to amylose polymer.

Leached material has the ability to form structure into the suspending matrix. Thus, unheated starch suspensions rich in damaged starch have a more structured matrix. Consequently, the changes in fluid structures and increments in the extent of thixotropy were caused by the differences in the swollen granules and the suspending matrix.

Tested starch suspensions showed a dilatant thixotropic behavior. From this, it is possible to conclude that the system behaved as a mixture between starch suspensions behavior in the early stages of gelatinization and gelatinized starch pastes.

3.3. Effect of damaged starch on time-dependent flow properties

When a thixotropic material is sheared at a constant shear rate a progressive breakdown of the structure is caused (Abu-Jdayil and Mohameed, 2004).

The thixotropic behavior of starch suspensions at a constant shear rate was described by the Weltman model (Weltman, 1943). Constants A and B were obtained after fitting the equation of the Weltman model to experimental data. Constant A is associated with the yield point, and constant B is related to the extent of thixotropy. Table 4 shows calculated Weltman parameters and coefficients of determination (r^2). The B constant took negative values due to the suspensions presented a thixotropic behavior (Rao, 1999). The time-dependent flow properties of starch suspensions were affected by damaged starch. Constants A and B

Table 4The parameters of the Weltman model.

Sample	A (Pa)	B (Pa)	r^2
3.8 DS 8.4 DS 12.9 DS 23.8 DS	1.21 a 1.92 ab 2.61 b 4.49 c	-0.04 a -0.14 b -0.16 b -0.19 b	0.53 0.90 0.94 0.90
23.0 03	4.45 C	-0.15 b	0.50

Different letters within columns mean significant differences at $p \le 0.05$.

obtained for unmilled starch suspension were 1.21 Pa and −0.004 Pa, respectively. The increment of damaged starch content in the system caused an increase in A and B parameters. The effect in A was interpreted as an increment in the yield point of the fluid. Damaged starch presence caused an increase in the minimal stress necessary to achieve the state of motion of the suspensions. The starch suspensions yield stress increased due to the increment of starch granule's volume and leached material during spontaneous gelatinization. Since yield stress is a measure of the strength of a network of interacting particles, the increments in this parameter might be related to a more structured system, which is associated to the increments in the amylopectin fraction. The impact in B was associated to a change in the rate of structure loss of the system. Consequently, it is suggested that the fluid lost structure faster when damaged starch content increased in the system. The unheated starch suspensions became more structured but these structures were weaker when they were sheared due to damaged starch presence.

3.4. Effect of damaged starch on pasting behavior

When a starch–water suspension is heated above the gelatinization temperature, an increase in viscosity of the starch heating system is produced. Gelatinized starch is an amylose network where swollen granules are immersed (Copeland et al., 2009). Starch pastes, regarded as composite materials in which a continuous phase is interspersed with particles (swollen granules), have properties that are dependent on a number of factors, including the rheological properties of the continuous phase, the volume fraction and deformability (rigidity) of the particles, and the interactions between the dispersed and continuous phases (Biliaderis, 2009).

Results indicated that damaged starch content affected pasting parameters of starch suspensions. Sample viscosity profiles revealed that increments of damaged starch content produced slight but significant increments in the initial pasting temperatures. On the other hand, peak viscosity (PV), final paste viscosity (CPV), breakdown (BD) and setback (SB) gradually decreased when damaged starch content increased (Table 5). The increment of damaged starch content from 3.8% to 23.8% produced a 32.1%, 30.4% and 33.1% reduction of PV, BD and SB, respectively.

It seemed that damaged starch granules swelled to a high degree and consequently were weaker during cooking and shear stress. Probably, gelatinized damaged granules are broken more

Table 5 Pasting parameters.

Sample	Pasting parameters				
	PT	PV	CPV	BD	SB
3.8 DS	77.6 a	380.3 d	476.5 d	58.7 c	154.9 с
8.4 DS	78.4 ab	343.3 c	439.5 c	54.0 bc	150.1 c
12.9 DS	80.0 bc	305.1 b	387.3 b	46.9 ab	129.2 b
23.8 DS	80.4 bc	259.2 a	321.9 a	40.8 a	103.6 a

Different letters within columns mean significant differences at $p \le 0.05$. PT: Initial pasting temperature (°C), PV: peak viscosity (cP), CPV: final hot paste viscosity (cP), BD: breakdown (cP), and SB: setback (cP).

easily and are more deformable than less damaged granules. Therefore, damaged starch granules do not fully contribute to viscosity increment during suspension heating. The effect of damaged starch on the viscosity profile could be comparable to the effect of decreasing starch concentration: the higher degree of free water and lower proportion of swollen granules occupying the space at lower starch concentration contribute to lower viscosity (Rasper, 1980). The concentration of native starch decreased as a consequence of the enrichment of damaged starch. In this way, increments in damaged starch content result in a smaller volume fraction occupied by native starch granules that may contribute to viscosity during heating and shearing. In a previous work, (León et al., 2006) found that RVA pasting properties in wheat flour were influenced by the amount of damaged starch. Changes in viscosity profiles of the starch pastes could be influenced by the spontaneous gelatinization that damaged granules of starch undergo in cold water.

Breakdown and setback were influenced by the height that peak viscosity reached. However, reductions on breakdown and setback caused by damaged starch could also be due to changes in the characteristics of the pastes formed. At peak viscosity, swollen granules and fragmented starch granules are immersed in the amylose network.

The viscosity of the gel at the end of the test depends on leached amylose concentration, occupied volume by the swollen granules, stiffness of the dispersed granules and attractive forces between granules and continuous phase. Reductions in cold paste viscosity values could be associated with differences in the characteristic of the formed paste. The presence of higher damaged starch involves a larger level of granule disintegration and, consequently, a smaller occupied volume fraction of the dispersion and a continuous phase enriched amylopectin. But also, the stiffness of the dispersed granules could be modified as a consequence of the damage.

4. Conclusion

The granular size profile was affected by damaged starch content. A greater heterogeneity and granule size was recorded, confirming the greater water absorption capacity of the damaged starch granules compared to native granules.

The rheological characteristics of unheated suspensions were studied. Flow tests showed that the unheated suspension exhibited a combined flow behavior between the starch suspensions in the early stages of gelatinization and the gelatinized starch pastes. Unheated starch suspensions presented a dilatant thixotropic flow behavior. The presence of damaged starch resulted in an increase in the thixotropic behavior and consistency coefficient of the unheated starch—water systems.

The time-dependent rheological behavior of unheated starch suspensions was modified by damaged starch. An increase in the minimal stress necessary to achieve the state of motion in the fluid and in the thixotropic coefficient was recorded.

In general, the changes in rheological profile of the unheated starch suspensions were related to an increase of the granule size and the leaching out of starch material as a consequence of granule damage.

Clear differences on pasting properties were observed due to damaged starch increase. Lower viscosity values were found due to the disintegration of the gelatinized damaged starch granules during the cooking and shearing. Damaged starch granules do not contribute to viscosity increment and the characteristics of the continuous phase containing immersed granules were changed by damaged starch.

The results of this study demonstrate the influence of damaged starch content on the rheological profile of non-heated and heated starch dispersions, which could be useful in flow regimes studies, processing variables and final product properties.

Acknowledgments

The authors would like to acknowledge Consejo Nacional de Ciencia y Técnica, Secretaría de Ciencia y Tecnología, Universidad Nacional de Córdoba and Ministerio de Ciencia y Tecnología of Córdoba for financial support.

References

- Abu-Jdayil, B., Mohameed, H.A., 2004. Time-dependent flow properties of starch-milk-sugar pastes. Eur. Food Res. Technol. 218, 123–127.
- Abu-Jdayil, B., Azzam, M.O.J., Al-Malah, K.I.M., 2001. Effect of glucose and storage time on the viscosity of wheat starch dispersions. Carbohydr. Polym. 46, 207– 215
- Al-Malah, K.I., Azzam, M.O.J., Abu-Jdayil, B., 2000. Effect of glucose concentration on the rheological properties of wheat-starch dispersions. Food Hydrocolloids 14, 491–496.
- AACC, 2000. Approved Methods of the American Association of Cereal Chemists (AACC), ninth ed. St. Paul, MN, The Association, USA.
- Bagley, E.B., Christiansen, D.D., 1982. Swelling capacity of starch and its relationship to suspension viscosity: effect of cooking time, temperature and concentration. J. Texture Stud. 13, 115–126.
- Barrera, G.N., León, A.E., Ribotta, P.D., 2012. Effect of damaged starch on starch thermal behavior. J. Int. Starch/Stärke. http://dx.doi.org/10.1002/star. 201200022.
- Berton, B., Scher, J., Villieras, F., Hardy, J., 2002. Measurement of hydration capacity of wheat flour: influence of composition and physical characteristics. Powder Technol. 128, 326–331.
- Biliaderis, C.G., 2009. Structural Transitions and Related Physical Properties of Starch. In: BeMiller, Whistler (Eds.), Starch: Chemistry and Technology. Academic Press, pp. 293–359).
- Bushuk, W., 1998. Interactions in Wheat Doughs. In: Hamer, Hoseney (Eds.), Interactions the Key to Cereal Quality. American Association of cereal chemists. Inc. St. Paul MN, USA, pp. 1–16.
- Christiansen, D.D., Bagley, E.B., 1984. Yield stresses in dispersions of swollen deformable cornstarch granules. Cereal Chem. 61, 500–503.
- Copeland, L., Blazek, J., Salman, H., Chiming Tang, M., 2009. Form and functionality of starch. Food Hydrocolloids 23, 1527–1534.
- Dail, R.V., Steffe, J.F., 1990a. Dilatancy in starch solutions under low acid aseptic processing conditions. J. Food Sci. 55, 1764–1765.
- Dail, R.V., Steffe, J.F., 1990b. Rheological characterization of crosslinked waxy maize starch solutions under low acid aseptic processing conditions using tube viscometry techniques. J. Food Sci. 55, 1660–1665.
- Di Rienzo, J.A., Casanoves, F., Valzarini, M.G., Gonzalez, L., Tablada, M., Robledo, C.W., 2009. Infostat Statistical Software 2009. Universidad Nacional de Córdoba, Argentina, Facultad de Ciencias Agropecuarias (Infostat group).
- Doublier, J.L., 1981. Rheological studies on starch. Flow behavior of wheat starch pastes. Starch/Stärke 33, 415–420.
- Ellis, H.S., Ring, S.G., Whittam, M.A., 1989. A comparison of the viscous behavior of wheat and maize starch pastes. J. Cereal Sci. 10, 33–34.
- Evans, I.D., Haisman, D.R., 1979. Rheology of gelatinized starch suspensions. J. Texture Stud. 10, 347–370.

- Faridi, H., 1990. Applications of Rheology in the Cookies and Cracker Industry. In: Faridi, Faubion (Eds.), Dough Rheology and Baked Product Texture. Van Nostrand Reinhold, New York, pp. 363–384.
- Frith, W.J., Lips, A., 1995. The rheology of concentrated suspensions of deformable particles. Adv. Colloid Interface Sci. 61, 161–189.
- Ghodke, S.K., Ananthanarayan, L., Rodrigues, L., 2009. Use of response surface methodology to investigate the effects of milling conditions on damaged starch, dough stickiness and chapatti quality. Food Chem. 112, 1010–1015.
- Giboreau, A., Cuvelier, G., Launay, B., 1994. Rheological behavior of three biopolymer/water systems with emphasis on yield stress and viscoelastic properties. J. Texture Stud. 25, 119–137.
- Gibson, T.S., Solah, V.A., McCleary, B.V., 1997. A procedure to measure amylose in cereal starches and flours with Concanavalin A. J. Cereal Sci. 25, 111–119
- Harrod, M., 1989. Modelling of flow properties of starch pastes prepared by different procedures. J. Food Process Eng. 11, 257–275.
- Jay-Lin, J., 2009. Structural Features of Starch Granules II. In: BeMiller, Whistler (Eds.), Starch: Chemistry and Technology. Academic Press, pp. 193–227.
- Karkalas, L., Tester, R.E., Morrison, W.R., 1992. Properties of damaged starch granules. I. Comparison of a micromethod for the enzymic determination of damaged starch with the standard AACC and Farrand methods. J. Cereal Sci. 16, 237-251
- León, A.E., Barrera, G.N., Pérez, G.T., Ribotta, P.D., Rosell, C.M., 2006. Effect of damaged starch levels on flour-thermal behaviour and bread staling. Eur. Food Res. Technol. 224, 187–192.
- Malvern Instruments, 1999. Operators guide: Man.0247 Issue 2.0. Worcestershire. Malvern Instruments Ltd., United Kingdom.
- Morrison, W.R., Tester, R.F., 1994. Properties of damaged starch granules. IV. Composition of ballmilled wheat starches and of fractions obtained on hydration. J. Cereal Sci. 20, 69–77.
- Morrison, W.R., Tester, R.F., Gidley, M.J., 1994. Properties of damaged starch granules II. Crystallinity, molecular order and gelatinisation of ball milled starches. J. Cereal Sci. 19, 209–217.
- Nguyen, Q.D., Jensen, C.T.B., Kristensen, P.G., 1998. Experimental and modelling studies of the flow properties of maize and waxy maize starch pastes. J. Chem. Eng. 70, 165–171.
- Okechukwu, P.E., Rao, M.A., 1995. Influence of granule size on viscosity of cornstarch suspension. J. Texture Stud. 26, 501–516.
- Rao, M.A., Tattiyakul, J., 1999. Granule size and rheological behavior of heated tapioca starch dispersions. Carbohydr. Polym. 38, 123–132.
- Rao, M.A., 1999. Rheology of Fluid and Semisolid Foods: Principles and Applications. Aspen Publishers, Inc., Gaithersburg, Maryland, Chapter 2: Flow and Functional Models for Rheological Properties of Fluid Foods.
- Rasper, V., 1980. Theoretical Aspects of Amylographology. In: Shuey, Tipples (Eds.), The Amylograph Handbook. American Association of Cereal Chemists St. Paul, Minnesota, pp. 1–6.
- Steffe, J.F., 1996. Rheological Methods in Food Process Engineering, second ed. Freeman Press, East Lansing, USA.
- Tester, R.E., Morrison, W.R., 1994. Properties of damaged starch granules. V. Composition and swelling of fractions of wheat starch in water at various temperatures. J. Cereal Sci. 20, 175–181.
- Tester, R.F., 1997. Properties of damaged starch granules: composition and swelling properties of maize, rice, pea and potato starch fractions in water at various temperatures. Food Hydrocolloids 11, 293–301.
- Tester, R.F., Morrison, W.R., Gidley, M.J., Kirkland, M., Karkalas, J., 1994. Properties of damaged starch granules. III. Microscopy and particle size analysis of undamaged granules and remnants. J. Cereal Sci. 20, 59–67.
- Weltman, R.N., 1943. Breakdown of thixotropic structure as a function of time. J. Appl. Phys. 14, 343–350.