ORIGINAL PAPER

Starch–Apple Pomace Mixtures: Pasting Properties and Microstructure

Andrés Felipe Rocha Parra¹ · Pablo Daniel Ribotta² · Cristina Ferrero¹

Received: 25 November 2014 / Accepted: 25 May 2015 © Springer Science+Business Media New York 2015

Abstract Apple pomace (AP) is a by-product of the juice industry that could be used as an accessible fiber source for foods. The objective of the present work was to evaluate the effect of different levels of AP on the pasting properties of composite starch systems using a rapid visco analyzer (RVA) and to relate rheological behavior to microstructural characteristics. AP was dried, ground, sieved, and sterilized before being applied. In assays at constant solid content (3 g/25 ml water), rice flour (RF) and cassava starch (CS) were mixed in equal proportions and increasing replacements with AP (0-50 %) were performed. The level of AP in starch-water dispersions had a significant influence on pasting properties such as peak viscosity (PV) and final viscosity (FV), which decreased when AP level increased, particularly when it was above 25 % (w/w). When the effect of AP addition at a constant starch concentration was analyzed, viscosity increased with the increase in total solid content. By microstructural studies (light microscopy, SEM), it was observed that fiber particles were not totally solubilized, remaining embedded in the starch paste. Water imbibing capacity (WIC) measurements indicated that AP particles were able to absorb water to a higher extent than starch. This could lead not only to less water availability in starch suspensions during gelatinization

Cristina Ferrero cferrero@biol.unlp.edu.ar but also to a certain compensation for viscosity loss due to AP particle swelling.

Keywords Fiber \cdot Cassava starch \cdot Rice flour \cdot Pasting \cdot Juice by-product

Introduction

The ingestion of dietary fiber provides many benefits for overall human health, because fiber is associated with the prevention of diseases such as chronic bowel disorders, obesity, diabetes, cardiovascular disease, and cancer (Korus et al. 2009; Al-Sheraji et al. 2011). Even people who consider their diets to be healthy and balanced rarely get enough fiber on a daily basis. Therefore, the enrichment of foods with fiber appears to be necessary, as it would contribute to covering the recommended daily intake of 25 g/day (Hager et al. 2011). Thus, a key issue in food development is to produce qualified food with high dietary fiber content (Sozer and Dalgic 2006).

Besides, starch is one of the main components widely used in the formulation of food products. Starches and modified starches are normally used to change the physical characteristics of many foods since they have gelling, thickening, adhesion, moisture retention, stabilizing, texturizing, and antistaling properties (Thomas and Atwell 1999). The knowledge of the rheological and textural behavior of starchy foods, during and after processing, is valuable for process and quality control purposes (Kaur et al. 2008).

The inclusion of fiber-rich components in a food formulation can lead to changes in water retention, thermal behavior, rheology, texture, and other physicochemical properties of the other components, particularly starches. Different studies have found that the pasting properties of starch are significantly affected by some ingredients including dietary fiber

¹ CIDCA, Facultad de Ciencias Exactas, CCT La Plata (CONICET), Universidad Nacional de La Plata, 47 y 116, CP 1900 La Plata, Argentina

² CONICET, Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, Av. Valparaíso s/n, CP 5000 Córdoba, Argentina

(Naruenartwongsakul et al. 2004; Symons and Brennan 2004; Sudha et al. 2007; Lai et al. 2011; Ronda et al. 2013; Yildiz et al. 2013). Changes in thermal properties caused by fiber addition and measured by differential scanning calorimetry have also been reported (Randzio et al. 2003).

Among natural fiber sources that are of potential interest in food development, the by-products of fruit processing industries can be mentioned. Since the development of apple processing for juice and cider production, apple pomace (AP) is generated in great quantities. After processing apples for juice extraction, two fractions are obtained: crude juice and AP. AP currently has a broad range of applications that include its use as a source of dietary fiber (Bhushan et al. 2008) since it contains 12 % dry residue, which is half fiber. Its calorie contribution is only 45 cal/100 g (Sotelo et al. 2007). Besides, AP contains different bioactive compounds such as polyphenols.

In spite of the potential advantages of using AP to improve fiber content in foods, there is scarce information about the interactions of this by-product with starch. The measurement of pasting properties and microstructural characteristics can provide insights into the behavior of starch–apple pomace systems. The thermal properties of starches, such as gelatinization characteristics and tendency to retrograde, can be studied from their pasting behavior, i.e., by observing viscosity changes in a starch suspension during programmed heating and cooling performed with a rapid visco analyzer (RVA) or a Brabender Viscoamylograph (Cappa et al. 2013).

The objectives of the present work were (a) to characterize the effect of apple pomace on the pasting parameters of cassava starch–rice flour mixtures and (b) to explain the interaction between apple pomace and starch from a microstructural point of view.

Materials and Methods

Materials

Crude AP was provided by the food company Jugos SA (Villa Regina, Rio Negro, Argentina). This crude by-product contains 86 % moisture. After the pretreatment, its composition on a 100 g basis, as reported in previous work, is as follows: moisture, 14.02 ± 0.06 g (according to AOAC method 964.22; AOAC 1990); protein, 4.28 ± 0.02 g (AACC 46-12; AACC 2000, with slight modifications); ash, 1.77 ± 0.02 g (AACC 8-1; AACC 2000); dietary fiber, 41.04 ± 1.02 g (determined using an enzymatic method based on AOAC method 991.43); and carbohydrates different from fiber (calculated by difference), 38.89 g. Water activity of the dried product was 0.321 ± 0.001 (Rocha Parra et al. 2015).

Rice flour (RF) (containing 82 % carbohydrate, 4.2 % protein, and 1.6 % fiber, according to supplier's information) and cassava starch (CS) (90 % carbohydrate according to supplier's information) were gluten-free grade (Kapac, Argentina).

Methods

Apple Pomace Pretreatment

The processing of apple pomace includes a minimum number of steps. As this juice by-product, which normally contains high moisture levels (>80 %), is susceptible to fast biodegradation by microorganisms, leading to changes in composition and foul smells, it is necessary to dry it up to obtain a more stable ingredient (Bhushan et al. 2008). Besides, sieving is advisable to obtain a more uniform product to be incorporated in food mixtures. Sterilization was performed to eliminate the natural microflora and avoid undesirable fermentations during food processing.

For drying crude apple pomace, a forced convection oven at 50 °C was employed (GMX 9203A PEET LAB, USA) during 24 h. Dried apple pomace was ground and sieved through a 60-mesh sieve (250 μ m) to uniform particle size (Masoodi et al. 2002, with slight modifications). The fine powder obtained was sterilized at 121 °C during 20 min to eliminate yeasts and molds (natural flora).

Water Imbibing Capacity

Water imbibing capacity (WIC) was determined by modification of Baumann's device (Torgersen and Toledo 1977). The Baumann apparatus consists of a 1-ml pipette horizontally fixed, leveled with a sintered surface, connected through a small hose, and filled with distilled water. A thin layer of material (50 mg) was dispersed on a filter paper placed on the sintered plate previously imbibed in distilled water. The extent of water absorption can be measured by the decrease in water volume in the pipette. Determinations were made at room temperature (25 °C), and the maximum volume of absorbed water (the equilibrium value) was obtained. WIC was expressed in milliliters of water per gram of material. Assays were performed at least in duplicate.

Pasting Properties

The pasting properties of RF+CS+AP blends at different concentrations were determined using a rapid visco analyzer (Perten RVA 4500; Australia). The protocol for RVA assays was performed according to Barrera et al. (2013). Solids were dispersed in distilled water (25 ml). The slurry was heated to 50 °C and stirred at 160 rpm for 10 s. Then, it was held at 50 °C for 1 min and subsequently heated up to 95 °C, held at this temperature for 2.5 min, and cooled down to 50 °C and held at this temperature for 2 min. The values measured from the pasting profile of starch–apple pomace blends were peak viscosity (PV), breakdown (B) (difference between peak viscosity and trough viscosity), final viscosity (FV), setback (S) (difference between final viscosity and trough viscosity), and pasting temperature (PaT) (temperature at which starch granules begin to swell and gelatinize due to water uptake).

Three series of experiments were conducted on the following: (a) systems with a constant amount of solids (3 g); these systems were prepared by replacement of RF+CS blend (1+ 1) with increasing AP amounts (0, 2.5, 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 % replacement); (b) systems with the same levels of RF+CS as those of samples of series (a) but without AP (RF+CS ranging from 2.7 to 1.5 g); and (c) systems with a constant amount (3 g) of RF, CS, or RF+CS blend and two different added amounts of AP (0.15 and 0.6 g) corresponding to 5 and 20 % added AP. As control samples, AP, RF, and CS (3 g solids) were evaluated. Assays were performed in duplicate.

Microstructure

Light Field Microscopy

The appearance of starch systems with and without apple pomace before and after heating was evaluated using a light field microscope (Leica DM 5000B, Wetzlar, Germany). When necessary, the samples were stained with iodine (0.2 % w/v iodine and 2 % w/v potassium iodide). Two distinct magnifications of ×40 and ×100 were applied. For these observations, the concentration of total solids was adjusted to 0.5 g to avoid crowding and to be able to distinguish details.

SEM of Stored Model Systems

For these assays, the highest concentration of apple pomace was used. Systems were prepared in the RVA at a constant amount of solids (2 % w/v) with the following solid composition: 25 % RF, 25 % CS, and 50 % AP. A RF+CS mixture was used as control. The suspension was poured while hot (50 °C) into polypropylene tubes and then cooled to room temperature (25 °C) to allow gel formation; then, the samples were stored at a refrigeration temperature (4 °C) for 7 days to observe retrogradation. After this storage period, the samples were prepared for SEM observations according to the protocol reported by Martínez et al. (2014). They were frozen in a -85 °C blast freezer and freeze-dried. The freeze-dried samples were attached to a double-sided adhesive tape mounted on SEM stubs, coated with 3-5 mA gold/palladium under vacuum and examined with a FEG SEM scanning electron microscope (Carl Zeiss Sigma, Germany).

Statistical Analysis

The parameters of pasting properties were subjected to oneway ANOVA. Significant differences among means were determined using Tukey's HSD test with a confidence level of 95 %. Statgraphics Centurion XV software was used.

Results and Discussion

Pasting Properties

In Fig. 1, the pasting curves for each material (AP, CS, RF, and RF+CS) are shown. As expected, heating of RF and CS pastes led to typical amylograph curves. Particularly, the cassava starch profile showed a pronounced breakdown (3419 cP) before attaining the maximum temperature (95 °C). This behavior is related to the lack of resistance of this starch to high temperature and shearing stress. This is in agreement with the results reported by Ceballos et al. (2007) for three different cassava varieties. Cereal starches (such as that present in RF) are more resistant to heating–shearing conditions, and the breakdown was lower (B=42 cP). On the other hand, AP showed no viscosity development.

In Table 1, the mean values for pasting properties of these ingredients are shown. CS exhibited the lowest pasting temperature (67 °C); this value is in agreement with those obtained by Ceballos et al. (2007). RF pasted at 88 °C in accordance with results reported by Sandhya Rani and Bhattacharya (1995). These authors worked on different rice cultivars and reported pasting temperatures ranging from 83 to 94 °C. However, in the literature, there is no agreement on the pasting properties of RF. Cappa et al. (2013) suggested that the differences among the results reported by different authors are related to variations in sample composition (amylose content, moisture, proteins, lipids, and fiber) that can affect pasting behavior.

A higher gelatinization temperature in native starches reflects a greater internal stability of the starch granule, associated with a greater presence of crystalline zones and a higher amylose content that contributes to crystalline regions (Jenkins and Donald 1995). Thus, gelatinization temperatures of roots and tubers are lower than those of cereals due to the lower content of amylose (Alvis et al. 2008). Particularly, Swinkels (1985) reported that contents of amylose and amylopectin in CS were 17 and 83 %, respectively. Besides, the ratio between amylose molecules and amylopectin molecules in CS was 150, while maize and wheat starches had a higher amylose/amylopectin molecule ratio of 1000.

Peak viscosity is associated with the degree of granule swelling during heating. Starches with higher swelling capacity lead to higher peak viscosities (Ragaee and Abdel-Aal 2006). The highest peak viscosity corresponded to CS

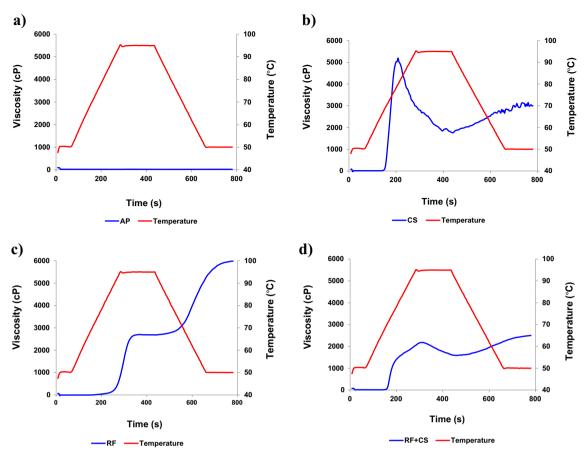


Fig. 1 Pasting curves of the different materials: a apple pomace (AP), b cassava starch (CS), c rice flour (RF), and d rice flour–cassava starch blend (1+1) (RF+CS). Red lines indicate the measured temperature

(5109 cP), followed by RF (2447 cP) and the RF+CS blend (1+1) (2164 cP). Breakdown was highest for CS (3418 cP) and lowest for RF (42 cP), indicating a greater resistance of RF to heat and shear as commented above. As expected, the blend showed an intermediate behavior (614 cP), also exhibiting a slightly unfolded peak that can be attributed to the marked difference in pasting temperatures between starches (Table 1). Final viscosities, together with setback, were higher for RF (5309 and 2904 cP, respectively). A higher setback value indicates a higher rate of retrogradation related to the higher amylose content (Thao and Noomhorm 2011).

Pasting curves for RF+CS blend (1+1) replaced with increasing AP amounts are shown in Fig. 2, and their pasting properties are listed in Table 2.

When RF+CS was substituted by AP, the curves maintained the shape, but viscosity values (PV, FV) progressively decreased, since there was less starch available for gelatinization. Besides, the fiber present in AP can reduce available water in systems. A reduction in available water would make starch granule swelling difficult, thus explaining the lower peak viscosity of pastes (Symons and Brennan 2004).

PV, B, S, and FV values in the samples with 2.5 to 25 % AP were not significantly different from each other (Table 2). This

Table 1	Values for pasting
propertie	s of cassava starch (CS),
rice flour	(RF), and apple pomace
(AP)	

Material	Pasting properties					
	PV (cP)	B (cP)	FV (cP)	S (cP)	PaT (°C)	
CS	5109±84 c	3418±56 c	2940±54 b	1250±32 b	67±0.1 a	
RF	2447±252 b	42±22 a	5309±654 c	2904±381 c	88±1 c	
RF+CS (1:1)	2164±23 b	614±26 b	2462±22 b	912±2 a	69.45±0.1 b	
AP	24±1.4 a	_	21.5±0.7 a	_	-	

Mean±SD; different letters within a column indicate significant differences (p<0.05)

PV peak viscosity, B breakdown, FV final viscosity, S setback, PaT pasting temperature

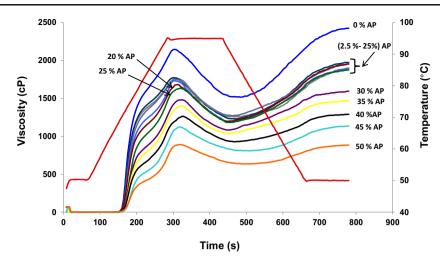


Fig. 2 Pasting curves of replacement of rice flour and cassava starch with apple pomace (AP) at different concentrations. The *red line* indicates the measured temperature

would indicate that viscosity loss due to starch replacement could be compensated by the presence of AP. However, higher levels of replacement with AP (>25 %) led to a drastic reduction in viscosities, as can be seen in PV and FV (Table 2). A diminished S indicates a reduced tendency to gelation when temperature decreases and, consequently, a reduced tendency to retrograde. A decrease in water availability due to AP addition could lead to restricted swelling and amylose leaching and, thus, to less hot and cold paste viscosities. Sudha et al. (2007) found similar results when replacing wheat starch with increasing amounts of AP. They attributed the PV decrease to a decrease of starch swelling power in the presence of AP.

To evaluate the contribution of each component (starch or AP) to the global behavior of the systems, amylograms of RF+CS blends with different levels of replacement with AP (10, 25, and 50 %) (series a) were compared with those

obtained for the same amount of RF+CS without AP (series b). Results are shown in Fig. 3. The curves of samples with 10 % AP and without AP have similar profiles, indicating that viscosity values are almost entirely related to starch, with a minor contribution of AP. In systems with 25 or 50 % replacement, a higher contribution to viscosity due to AP is observed and the systems without this component exhibited markedly lower viscosities. At higher replacements with AP (50 %), this ingredient would mainly contribute to the global viscosity, since PV of the system decreased to less than the half when AP was not included (from 899 to 284 cP).

In the other series of assays (with a constant amount of starchy ingredients, series c), the highest addition of 20 % AP (every 100 g RF+CS), led to significantly increased peak viscosity values (P<0.05) with respect to control ones in all cases (RF, CS, and RF+CS), suggesting a synergistic effect.

AP level (%)	Pasting properties					
	PV (cP)	B (cP)	FV (cP)	S (cP)	PaT (°C)	
0	2164±23 g	614±26 f	2462±52 e	912±2 f	69.5±0.1 a	
2.5	1778±25 ef	532±40 ef	1952±75 d	706±89 de	69.4±0.0 a	
5	1786±17 f	536±11 ef	1950±35 d	700±63 de	69.4±0.1 a	
10	1719±42 ef	487±11 de	1933±30 d	701±23 de	69.4±0.1 a	
15	1746±18 ef	515±29 e	1937±61 d	706±14 de	69.4±0.0 a	
20	1700±25 ef	480±8 de	1978±35 d	758±1 ef	69.8±0.6 a	
25	1665±42 e	463±15 de	1894±28 d	691±0 de	70.3±0.1 al	
30	1518±52 d	414±21 cd	1670±105 c	565±74 cd	70.2±0.0 at	
35	1425±31 d	369±4 bc	1528±85 c	472±57 bc	70.6±0.6 al	
40	1241±33 c	312±34 ab	1260±43 b	331±45 ab	70.6±0.5 al	
45	1116±12 b	296±27 ab	1124±18 b	304±33 ab	71.8±0.1 c	
50	899±11 a	256±1 a	900±23 a	257±14 a	71.4±0.6 b	

Mean \pm SD; different letters within a column indicate significant differences (p < 0.05)

Table 2 Effect of substitutionwith increasing percentages ofapple pomace (AP) on pastingcharacteristics of a blend of riceflour and cassava starch (RF+CS)

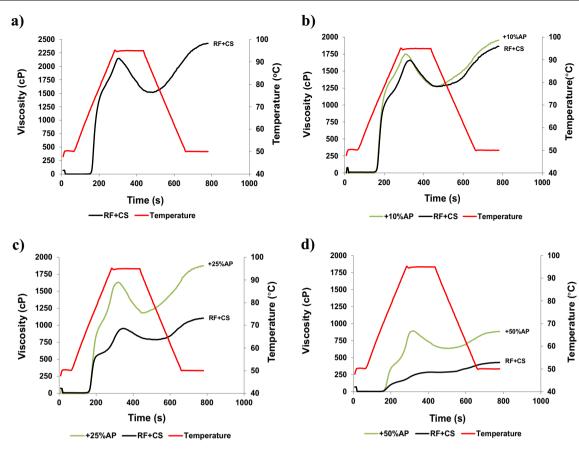


Fig. 3 Comparison among pasting curves for the RF+CS blend (1+1) with and without three different AP concentrations added (10, 25, and 50 %); **a** 3 g RF+CS. **b** Upper curve, 2.7 g RF+CS and 0.3 g AP; lower curve, 2.7 g

RF+CS. **c** Upper curve, 2.25 g RF+CS and 0.75 g AP; lower curve, 2.25 g RF+CS. **d** Upper curve, 1.5 g RF+CS and 1.5 g AP; lower curve, 1.5 g RF+CS. *Red lines* indicate the measured temperature

However, the effect of the addition of AP on pasting temperature was less pronounced and no significant differences in this parameter were found between the mixtures with and without AP (Table 3). The same tendencies were obtained by Chaisawang and Suphantharika (2006) when adding different hydrocolloids to a cassava starch suspension. Control suspensions of hydrocolloids in the absence of starch did not show viscosity development; this is in agreement with the behavior of AP in the present study.

Weber et al. (2009) proposed two possible explanations for the changes caused by hydrocolloids in starch pasting properties: (i) an association of the gum with the swollen starch or with the soluble amylose and low molecular weight amylopectin fractions of the paste and (ii) a competition of the gum

Table 3Effect of apple pomaceaddition (5 %, 20 %) on pastingcharacteristics of cassava starch(CS), rice flour (RF), and theirblend (RF+CS)

Sample	Pasting properties					
	PV (cP)	B (cP)	FV (cP)	S (cP)	PaT (°C)	
CS	5109±84 a	3418±56 a	2940±54 a	1250±32 a	67±0.1 a	
+5 % AP	5907±41 b	4118±72 a	3307±117 ab	1518±148 a	66.98±0.04 a	
+20 % AP	6627±22 c	5233±349 b	3014±30 b	1620±400 a	67±0.07 a	
RF	2447±252 a	42±22 a	5309±654 a	2904±381 a	88±1 a	
+5 % AP	2814±86 b	89±2 a	5613±144 a	2888±60 a	83.95±2 a	
+20 % AP	3416±45 c	630±31 b	5835±3 a	3049±11 a	83.95±3 a	
RF+CS	2164±23 a	614±26 a	2462±52 a	912±2 a	69.45±0.1 a	
+5 % AP	2032±54 a	654±44 a	2232±52 a	854±42 a	69.08±0.1 a	
+20 % AP	2884±54 b	955±66 b	3233±76 b	1304±87 b	69.1±0.1 a	

Mean \pm SD; different letters different letters within a column indicate significant differences (p < 0.05)

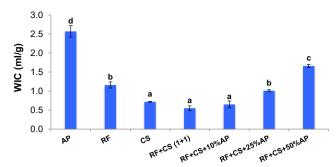


Fig. 4 Evaluation of water imbibing capacity (*WIC*) among RF+CS blend (1+1) and three different replacement levels of AP (10, 25, and 50 %)

with the starch for the free water in the system. However, these mechanisms would be limited by fiber solubility. Taking into account that most of AP solids are insoluble fiber, the first possibility would not be the main reason, but competition for water would prevail.

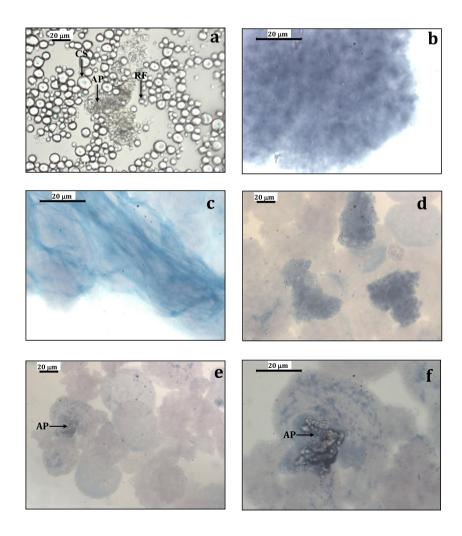
WIC Assays

To evaluate the degree of competition for water of AP with respect to starches, WIC assays were conducted. Results are

Fig. 5 Light microscopy of a RF+CS with 2.5 % AP (×40). Optical micrograph of gels stained with iodine: **b** RF (×100), **c** CS (×100), **d** RF+CS (×40), **e** RF+CS with 50 % AP (×40), and **f** RF+CS with 50 % AP (×100) (0.5 g of total solids; 2 % w/v). *Bars* correspond to 20 µm shown in Fig. 4. When comparing individual ingredients, it was observed that AP had the highest WIC value (2.57 ml/g solids) probably due to its highly hydrophilic components, mainly cellulose, pectin, and hemicelluloses (i.e., cell wall polysaccharides). On the other hand, CS and RF exhibited a lower WIC value than AP. CS had the lowest one (0.72 ml/g solids), while that of RF was the highest (1.16 ml/g solids) probably because of the significant presence of other hydrophilic components different from starch in flour, such as proteins and fiber. RF+ CS mixtures exhibited an intermediate WIC value (0.55 ml/g solids), but it was closer to CS than to RF ones.

As expected, when replacement of RF+CS with AP was performed, the WIC value progressively increased from 0.65 up to 1.66 ml/g solids. This would indicate that AP water absorption could be favored over starch absorption. Linlaud et al. (2009) found that replacing wheat starch with increasing levels of different hydrocolloids (xanthan gum, galactomannans, pectin) progressively increased WIC. In the same trend, Correa et al. (2012) found that the addition of maximum level of pectin on wheat starch increased WIC values.

These results are in agreement with the behavior observed in RVA assays. The enhanced ability of AP to absorb water



could decrease the available water for starch swelling. The restriction to starch swelling, particularly at high AP contents, would contribute to decreasing system viscosity. Yildiz et al. (2013) proposed that the addition of insoluble dietary fiber in a food matrix caused an uneven distribution of water by competition with starch, which affected starch swelling capacity.

Microstructure

In Fig. 5, the micrographs obtained with a light microscope before and after gelatinization are shown. In Fig. 5a, the relative sizes of native starch granules and AP particles can be seen. Particle size (expressed as Sauter diameter) followed a bimodal distribution, with 0.84 μ m in diameter for the principal population and 241.03 μ m in diameter for the minor one (Rocha Parra et al. 2015). With respect to starch granules, it can be seen that RF starch granules are smaller than CS ones. According to Thomas and Atwell (1999), the rice starch diameter ranges from 1 to 3 μ m, while cassava starch varies from 4 to 35 μ m.

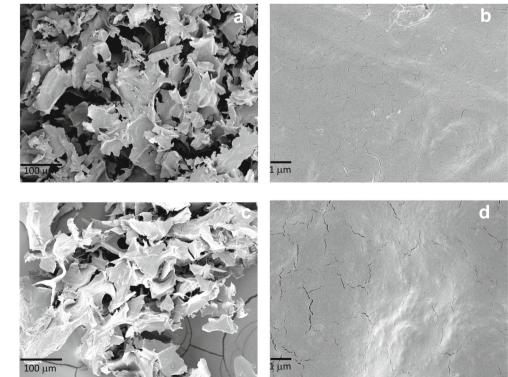
After gelatinization, RF (Fig. 5b) and CS (Fig. 5c) showed a very different network structure. RF gel exhibited a continuous aggregated matrix formed by small swollen granules that were uniformly dyed by iodine. In cassava gel, granules could yet be visualized as discrete structures, not quite disintegrated, with surrounding filaments of blue-stained amylose. Ribotta and Rosell (2010) found that cassava granular structure could be completely disintegrated by stirring during the pasting process, forming a continuous dispersed phase of amylose/amylopectin. Karam et al. (2006) also observed that starch granules in gels of cassava starch have lost their integrity and the amylose matrix could be well distinguished by staining with iodine.

In binary systems of starches, a good integration of both starch networks is largely dependent on the possibility of cogelatinization, as reported by Karam et al. (2006). In the present work, RF+CS (Fig. 5d) showed two distinct types of regions: those formed by swollen cassava starch granules (slightly dyed) and those with agglomerated rice starch granules (darker blue). The formation of this heterogeneous structure could be explained by the differences in pasting temperatures. Since the pasting temperature of CS was lower than that of RF, CS granules would begin to swell and gelatinize before RF, capturing water. So, this swollen and expanded dispersion of cassava starch would confine the smaller rice granules to rice-rich zones.

AP particles do not swell to the same extent as starch granules, and in the major population of particles, their sizes were lower than those of cassava granules. When AP was included in the system of RF+CS (Fig. 5e, f), it formed (as rice starch granules did) into aggregates randomly distributed and immersed in a more continuous CS matrix. From these observations, the RF+CS+AP-gelatinized suspensions could be described as a relatively predominant matrix of CS where AP and rice granule aggregates are imbedded.

SEM

Fig. 6 Scanning electron micrographs of model systems: **a** 50 % rice flour and 50 % cassava starch (×200); **b** 50 % rice flour and 50 % cassava starch (×10,000); **c** 50 % apple pomace, 25 % rice flour, and 25 % cassava starch (×200); and **d** 50 % apple pomace, 25 % rice flour, and 25 % cassava starch (×10,000)



The last part of the RVA profile and particularly FV reflects the rheological behavior of starch systems during cooling and

allows prediction of their behavior during storage. To evaluate the interactions among the main components during storage, the model systems based on RF, CS, AP, and water were prepared for SEM assays as described previously.

Figure 6a, b shows the appearance of the system obtained from the mixture of both starchy ingredients without AP, after storage. It can be observed that the gelatinized starch is forming an open network structure, with solids agglomerated under the shape of "sheets." With a higher magnification (Fig. 6b), small cracks on the surface of these sheets are visible.

In starch pastes replaced with 50 % of AP (Fig. 6c, d), a more aggregated structure can be observed and the surface of the sheets also looks different, exhibiting larger cracks (Fig. 6d). Lai et al. (2011) found that in mixtures of gelatinized rice starch and dietary fiber, the latter had the ability to hold water around starch granules, accelerating the reassociation of starch molecules. Sasaki et al. (2004) found that when wheat starch was mixed with water-insoluble protein (WIP) (waterinsoluble fractions of non-starch polysaccharides), it showed significantly higher swelling power than starch alone, indicating that WIP has a high capability to hold water around starch granules, accelerating the reassociation of starch molecules.

In the present work, the marked ability of AP to hydrate could also enhance the effective concentration of starch and promote aggregation, though this fact would not be reflected in an enhanced FV (Fig. 2) due to lower starch concentration.

Conclusions

Apple pomace addition to cassava starch-rice flour mixtures modified the rheological profile, as obtained using a RVA. When AP replaced starch ingredients, lower viscosities (PV, FV) were obtained. AP is a fiber-rich ingredient and has a marked ability to capture water as demonstrated by water imbibing capacity (WIC) measurements. This behavior could lead to the reduction of available water in these systems, thus affecting starch gelatinization (less starch granule swelling and lower hot paste viscosity) and gelling behavior (lower cold paste viscosity). Besides, the restriction in water availability caused by the hydration of AP could promote aggregation of starch during storage. However, when AP was added to a constant amount of CS+RF blend, viscosity markedly increased, suggesting a synergistic effect.

AP particles remain mostly insoluble during heating, and no viscosity development was found using a RVA. Microscopy studies on CS+RF+AP pastes revealed that they are not uniform systems, exhibiting a predominant CS matrix where aggregated gelatinized RF and AP particles are embedded. CS begins to gelatinize first and thus governs paste structure formation, inducing aggregation of smaller particles such as RF and AP ones. SEM studies suggested an influence of AP on structure changes during storage.

The present study shows that AP, a by-product of the juice industry, has a potential ability to be used in starch-based formulations to enhance the level of dietary fiber. However, and depending on the amount of AP added, it can cause important changes on the microstructure and pasting properties of starch-based systems.

Acknowledgments The authors want to acknowledge Universidad Nacional de La Plata (Argentina), Universidad Nacional de Córdoba (Argentina) and CONICET for financial support, and the company Jugos SA (Rio Negro, Argentina) for apple pomace (AP) donation.

References

- AACC International. (2000). Approved methods of the American Association of Cereal Chemists (10th ed.). St. Paul: The Association.
- Al-Sheraji, S. H., Ismail, A., Manap, M. Y., Mustafa, S., Yusof, R. M., & Hassan, F. A. (2011). Functional properties and characterization of dietary fiber from Mangifera pajang Kort. fruit pulp. *Journal of Agricultural and Food Chemistry*, 59(8), 3980–3985.
- Alvis, A., Vélez, C. A., Villada, H. S., & Rada-Mendoza, M. (2008). Physicochemical and morphological analyses of yam, cassava and potato starches and determination of their viscosity. *Información Tecnológica*, 19(1), 19–28.
- AOAC. (1990). Official methods of analysis. In Association of Analytical Chemists. Washington, DC: AOAC.
- Barrera, G. N., Bustos, M. C., Iturriaga, L., Flores, S. K., León, A. E., & Ribotta, P. D. (2013). Effect of damaged starch on the rheological properties of wheat starch suspensions. *Journal of Food Engineering*, 116(1), 233–239.
- Bhushan, S., Kalia, K., Sharma, M., Singh, B., & Ahuja, P. S. (2008). Processing of apple pomace for bioactive molecules. *Critical Reviews in Biotechnology*, 28(4), 285–296.
- Cappa, C., Lucisano, M., & Mariotti, M. (2013). Rheological properties of gels obtained from gluten-free raw materials during a short term aging. *LWT - Food Science and Technology*, 53(2), 464–472.
- Ceballos, H., Sánchez, T., Morante, N., Fregene, M., Dufour, D., Smith, A. M., & Mestres, C. (2007). Discovery of an amylose-free starch mutant in cassava (Manihot esculenta Crantz). *Journal of Agricultural and Food Chemistry*, 55, 7469–7476.
- Chaisawang, M., & Suphantharika, M. (2006). Pasting and rheological properties of native and anionic tapioca starches as modified by guar gum and xanthan gum. *Food Hydrocolloids*, 20(5), 641–649.
- Correa, M. J., Pérez, G. T., & Ferrero, C. (2012). Pectins as breadmaking additives: effect on dough rheology and bread quality. *Food and Bioprocess Technology*, 5(7), 2889–2898.
- Hager, A., Axel, A., & Arendt, E. (2011). Status of carbohydrates and dietary fiber in gluten-free diets. *Cereal Foods World*, 56, 109–114.
- Jenkins, P. J., & Donald, A. M. (1995). The influence of amylose on starch granule structure. *International Journal of Biological Macromolecules*, 17(6), 315–321.
- Karam, L. B., Ferrero, C., Martino, M. N., Zaritzky, N. E., & Grossmann, M. V. E. (2006). Thermal, microstructural and textural characterisation of gelatinised corn, cassava and yam starch blends. *International Journal of Food Science and Technology*, 41, 805– 812.

- Kaur, L., Singh, J., Singh, H., & McCarthy, O. J. (2008). Starch-cassia gum interactions: a microstructure—rheology study. *Food Chemistry*, 111(1), 1–10.
- Korus, J., Witczak, M., Ziobro, R., & Juszczak, L. (2009). The impact of resistant starch on characteristics of gluten-free dough and bread. *Food Hydrocolloids*, 23(3), 988–995.
- Lai, P., Li, K. Y., Lu, S., & Chen, H. H. (2011). Physicochemical characteristics of rice starch supplemented with dietary fibre. *Food Chemistry*, 127(1), 153–158.
- Linlaud, N. E., Puppo, M. C., & Ferrero, C. (2009). Effect of hydrocolloids on water absorption of wheat flour and farinograph and textural characteristics of dough. *Cereal Chemistry*, 86(1900), 376–382.
- Martínez, C. S., Ribotta, P. D., Añón, M. C., & León, A. E. (2014). Effect of amaranth flour (*Amaranthus mantegazzianus*) on the technological and sensory quality of bread wheat pasta. *Food Science and Technology International*, 20(2), 127–135.
- Masoodi, F. A., Sharma, B., & Chauhan, G. S. (2002). Use of apple pomace as a source of dietary fiber in cakes. *Plant Foods for Human Nutrition (Dordrecht, Netherlands)*, 57(2), 121–128.
- Naruenartwongsakul, S., Chinnan, M., Bhumiratana, S., & Yoovidhya, T. (2004). Pasting characteristics of wheat flour-based batters containing cellulose ethers. *LWT - Food Science and Technology*, 37(4), 489–495.
- Ragaee, S., & Abdel-Aal, E. S. M. (2006). Pasting properties of starch and protein in selected cereals and quality of their food products. *Food Chemistry*, 95(1), 9–18.
- Randzio, S. L., Flis-Kabulska, I., & Grolier, J.-P. E. (2003). Influence of fiber on the phase transformations in the starch-water system. *Biomacromolecules*, 4(4), 937–943.
- Ribotta, P. D., & Rosell, C. M. (2010). Effects of enzymatic modification of soybean protein on the pasting and rheological profile of starchprotein systems. *Starch - Stärke*, 62(7), 373–383.
- Rocha Parra, A. F., Ribotta, P. D., & Ferrero, C. (2015). Apple pomace in gluten-free formulations: effect on rheology and product quality. *International Journal of Food Science and Technology*, 50, 682– 690.
- Ronda, F., Pérez-Quirce, S., Angioloni, A., & Collar, C. (2013). Impact of viscous dietary fibres on the viscoelastic behaviour of gluten-free formulated rice doughs: a fundamental and empirical rheological approach. *Food Hydrocolloids*, 32(2), 252–262.

- Sandhya Rani, M. R., & Bhattacharya, K. R. (1995). Rheology of riceflour pastes: relationship of paste breakdown to rice quality, and a simplified Brabender viscograph test. *Journal of Texture Studies*, 26, 587–598.
- Sasaki, T., Kohyama, K., & Yasui, T. (2004). Effect of water-soluble and insoluble non-starch polysaccharides isolated from wheat flour on the rheological properties of wheat starch gel. *Carbohydrate Polymers*, 57(4), 451–458.
- Sotelo, R., Giraudo, M., Aeberhard, C., Sánchez Tuero, H., Mancuello, B., Lencina, G., & Pardo, L. (2007). Reciclo de pulpa de manzana para la producción de alimentos (Barra Energética Fibroproteica). *Mundo Alimentario*, 26–30.
- Sozer, N., & Dalgic, A. C. (2006). Modelling of rheological characteristics of various spaghetti types. *European Food Research and Technology*, 225(2), 183–190.
- Sudha, M. L., Baskaran, V., & Leelavathi, K. (2007). Apple pomace as a source of dietary fiber and polyphenols and its effect on the rheological characteristics and cake making. *Food Chemistry*, 104(2), 686–692.
- Swinkels, J. J. M. (1985). Composition and properties of commercial native starches. *Starch - Stärke*, 37(1), 1–5.
- Symons, L. J., & Brennan, C. S. (2004). The effect of barley B-glucan fiber fractions on starch gelatinization and pasting characteristics. *Journal of Food Science*, 69(4), 257–261.
- Thao, H. M., & Noomhorm, A. (2011). Physiochemical properties of sweet potato and mung bean starch and their blends for noodle production. *Journal of Food Processing and Technology*, 02(01), 1–9.
- Thomas, D. J., & Atwell, W. A. (1999). *Starches* (Eegan Press handbook series). St. Paul: Eagan.
- Torgersen, H., & Toledo, R. T. (1977). Physical properties of proteins preparations related to their functional characteristics in comminuted meat systems. *Journal of Food Science*, 42, 1615–1620.
- Weber, F. H., Clerici, M. T. P. S., Collares-Queiroz, F. P., & Chang, Y. K. (2009). Interaction of guar and xanthan gums with starch in the gels obtained from normal, waxy and high-amylose corn starches. *Starch-Starke*, 61, 28–34.
- Yildiz, Ö., Yurt, B., Baştürk, A., Toker, Ö. S., Yilmaz, M. T., Karaman, S., & Dağlıoğlu, O. (2013). Pasting properties, texture profile and stress-relaxation behavior of wheat starch/dietary fiber systems. *Food Research International*, 53(1), 278–290.