

Thermal and Rheological Behavior of Peanut Protein Concentrate and Starch Composites

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Abstract Vegetable derivatives like peanut protein concentrates constitute an alternative for incorporation in starch-based systems. In order to assess the capacity of peanut protein concentrate (PPC) to be incorporated in starch systems, the thermo-mechanical behavior of pastes made with starches from different botanical sources (between 4.6 and 6 % w/w of corn, cassava and wheat starch), PPC (5.2–12.1 % w/w, which contributed between ~3 and ~6 % of final protein content), and sucrose (12.4–15 % w/w) was analyzed. Peanut proteins modified thermal behavior of starches as measured by the differential scanning calorimetry (DSC) technique. PPC increased the concentration of starch in the continuous phase and, consequently, the overall viscosity of the system during pasting. In addition, PPC increased the consistency of starch gels, although weaker structures were obtained. The syneresis of starch gels was reduced by PPC, which is advantageous for its incorporation in starch-based systems.

Keywords Gelatinization · Rheology · Peanut protein concentrate · Starch

Introduction

Meals obtained from soybean, rapeseed, cottonseed, sunflower seed and peanut are the most important among the sources of vegetable proteins, and represent 69, 12.4, 6.9, 5.3 and 2.8 %, respectively [1–3] of the world production of protein meal.

The protein cake residue obtained after peanut oil extraction has 40–50 % of protein and is commonly milled to elaborate peanut meals. Peanut meal constitutes a low-cost protein source, which is frequently used as animal feed, and can also be used as raw material for protein concentrates and isolates preparation [4]. Peanut protein concentrates (PPC) contain 65–70 % of proteins and can be prepared from delipidized peanut meals through various methods, such as isoelectric precipitation, alcohol precipitation and hot water extraction. All these procedures remove most of the water soluble components of peanut meals and increase the protein and fiber contents. At the same time, methods for PPC preparation enable the elimination of bitter taste compounds, trypsin inhibitors and flatulent sugars [5].

There are few studies related to the functional properties of PPC and their applications on food formulations. According to Wu et al. [6], PPC showed emulsifying and water absorption capacities and good gelling properties, although its functionality depended fundamentally on protein solubility [4]. However, the use of PPC and isolates by the food industry is limited since their functional properties are not as good as those found in other vegetable protein sources like soy. Moreover, allergy to peanut proteins is another factor explaining the less extended utilization of peanuts in food formulations. Therefore, although some studies assessed the PPC suitability for incorporation in food formulations [7], it is commonly used for animal feeding.

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In spite of these facts, the increasing need for leguminous utilization makes peanut protein derivatives an alternative for food formulation. Peanut protein digestibility is comparable to that of animal source proteins and could be used for protein fortification [8]. Besides, although methionine, lysine and threonine are limiting amino acids in low peanut protein content diets, peanut protein derivatives are rich in arginine [9]. In addition to these nutritional advantages, the peanut oil industry produces high protein content byproducts (like peanut meals), commonly used for animal feeding. Therefore, the utilization of these byproducts for food formulation can be interesting from an economic viewpoint. This is especially important in developing countries where oil and meal production are mainly concentrated [6].

In recent years, many efforts have been made in an attempt to replace, totally or partially, milk proteins with vegetable proteins in dessert-type formulas. By this means, it is possible to develop vegetable desserts with increased protein content, which can be consumed by lactose-intolerant people.

In analyzing the structure formation and mechanical properties of desserts, the study of starches/vegetable proteins systems is of great importance [10]. Physical and/or sensory properties of starch/vegetable proteins systems were studied for amaranths and buckwheat proteins [11], lupin proteins [2], pea proteins [2, 12, 13] and soy proteins [14–16]. Most of these works were carried out with protein isolates; however, protein concentrates have higher dietary fiber contents than isolates, and their preparation methods are simpler than those employed in protein isolates production [16].

Starch is used in a wide range of foods, such as milk dessert-type products and for a variety of purposes, including thickening, gelling, adding stability and replacing or extending ingredients. It has been demonstrated that the functional properties of starch depend on polymer composition, molecular structure, interchain organization, and the presence of minor constituents (lipids, phosphate ester and proteins). Therefore, starches from different botanical sources differ in their functional properties, such as thickening behavior, pasting and thermal properties, as well as availability and costs. Also, it is expected that the behavior of protein–starch composites varies as a consequence of botanical sources. The selection of a starch for a given use depends on the desired food properties and the processing conditions [12, 13, 15, 16]. Most researchers agree that, in order to increase the overall acceptance of gelled vegetable desserts, it is necessary to develop products with better sensory and physical properties. No studies assessing the usefulness of PPC as a milk replacement in starch-based systems were found. The aim of this work was to study the effect

of PPC on thermal and rheological properties of starches from different botanical sources.

Materials and Methods

Materials

Commercial peanut flour (Nutrin S.A., Argentina) showed a fat content of 5.52 ± 0.23 % (AACC method 36-26 [17]). Since this flour is only partially delipidized and, therefore, lipolysis reactions can still occur (negatively affecting their overall quality), peanut flour was delipidized through the Soxhlet extraction method using hexane as solvent for 4 h. The composition of the delipidized peanut flour was: 53.29 ± 0.20 g/100 g protein, 6.32 ± 0.00 g/100 g moisture, 0.10 ± 0.00 g/100 g fat, 4.45 ± 0.02 g/100 g ash, and 35.84 g/100 g carbohydrates (by difference) (AACC methods [17]).

Corn (123 g kg^{-1} moisture, 4.1 g kg^{-1} protein, db) (Señor de Sipan, Argentina), cassava (156 g kg^{-1} moisture, 4.2 g kg^{-1} protein, db) (Señor de Sipan, Argentina), and wheat (112 g kg^{-1} moisture, 0.9 g kg^{-1} protein, db) (Molinos Juan Semino SA, Argentina) starches were evaluated. A commercial sugar was purchased from a local market (Ledesma, Argentina).

Preparation of Peanut Protein Concentrates (PPC)

Defatted peanut flour was dispersed (1/20 w/v) in distilled water and the pH was adjusted to 4.5 with 1.0 N HCl. The suspension was stirred for 1 h at room temperature and centrifuged at 3,000 g for 10 min. The precipitate obtained was dried at 70 °C. The dried peanut protein concentrate (PPC) was ground to a powder and sieved through a 0.2 mm sieve. The PPC presented the following composition: 57.56 ± 1.02 g protein/100 g, 8.54 ± 0.41 g moisture/100 g, 0.60 ± 0.10 g total fat/100 g, 1.98 ± 0.32 g ash/100 g, and 31.32 g carbohydrates/100 g.

Composites of PPC, Starches and Sugar

Dispersions of PPC, starch and sugar were prepared. These dispersions had the same compositions as those made in a previous work [16], taking into account the composition of commercially available milk desserts. The percent by total mass of the compounds used in each of the dispersions are shown in Table 1. The amount of PPC added to composite 5 (5.2 %) allowed us to get a protein content of ~3 %, which is similar to that currently found in commercial milk desserts in Argentina. Composite 6 (PPC 10.5 %) had a protein content of ~6 %, about twice as high as that of commercial desserts. In order to assess the effects of sucrose and

Table 1 Composites composition

Composites	PPC (%)	Starch (%)	Sucrose (%)	Water (%)
(1) Starch/water	–	6.0	–	94.0
(2) Starch/sucrose/water	–	5.1	15.0	79.9
(3) PPC/starch/water (~3 % of peanut protein)	6.1	5.6	–	88.3
(4) PPC/starch/water (~6 % of peanut protein)	12.1	5.3	–	82.6
(5) PPC/starch/sucrose/water (~3 % of peanut protein)	5.2	4.8	14.2	75.7
(6) PPC/starch/sucrose/water (~6 % of peanut protein)	10.5	4.6	13.4	71.5

Values are expressed as percentages (w/w)

PPC peanut protein concentrate

PPC on starch properties individually, composites 2, 3 and 4 were prepared. Composite 2 contained sucrose and water. Composites 3 and 4 were prepared with 6.1 and 12.1 % of PPC, respectively, which allowed us to maintain a protein content of ~3 and ~6 % in composite 3 and 4, respectively (Table 1).

Differential Scanning Calorimetry (DSC)

Dispersions were prepared by mixing solids and distilled water (Table 1), and the pH was adjusted to 6.5. Composites were stirred for 20 min at room temperature and aliquots of ~35 mg were weighed in 100 μ L aluminum DSC pans. Pans were immediately sealed to avoid sample dehydration.

Starch gelatinization was studied using a DSC823e calorimeter (Mettler Toledo, Switzerland). The equipment was calibrated with indium and zinc, and empty, sealed but pierced aluminum pans were used for reference. Samples were scanned at 5 $^{\circ}$ C min⁻¹ from 25 to 120 $^{\circ}$ C. All experiments were done at least in duplicate.

The onset temperature (T_o), the width at half-peak height ($\Delta T_{1/2}$), and the heat of phase transition (ΔH_g , in joules per gram of starch) were determined (STARe software, Mettler Toledo, Switzerland).

Pasting Profile

Apparent viscosities of composites were determined with a rapid visco-analyser (RVA) instrument (Newport Scientific, Australia). For this purpose, dispersions containing 1.21 g of starch and 25 mL of distilled water (4.62 % w/w starch) were prepared. For the analysis of viscosity profiles, dispersions containing starch, PPC and water were prepared. These composites contained 1.21 g of each starch, 25 mL of distilled water and 1.31 or 2.79 g of PPC. This allowed us to maintain mass proportions of starch/PPC at the same level of those shown in Table 1. RVA General Pasting Method was applied as described in a previous work [16]. Pasting temperature (PT), peak viscosity (PV), final viscosity (FV), breakdown (BD), and setback (SB) values were obtained (ThermoLine for Windows software, Newport Scientific, Australia). Each experiment was done in duplicate.

Preparation of Gels

Slurries for gel preparation were prepared in flasks as mentioned above (Table 1), and the pH was adjusted to 6.5 (which is the pH value of commercial milk desserts) and allowed to equilibrate for 20 min with continuous stirring at room temperature. The gelatinization of composites was carried out as described in a previous work [16]. Suspensions were packaged while still hot in polypropylene tubes (30 mm diameter), cooled to room temperature and kept 5 h at the same temperature. The samples were stored at 5 $^{\circ}$ C before the rheological properties, microstructure and syneresis were analyzed.

Rheological Measurements

Rheological analysis was carried out in a controlled stress RHEOPLUS/32 rheometer (Anton Paar, Germany). Cone-plate geometry (50 mm diameter and 1 $^{\circ}$ angle) and 0.5 mm gap were used for the determinations at 25 $^{\circ}$ C. Gels were kept at 5 $^{\circ}$ C for 24 h and tempered at 20 $^{\circ}$ C for 2 h before rheological measurements were carried out. Samples were carefully poured into the lower plate and allowed to rest for 3 min after taking down the upper plate. A fresh sample was loaded for each measurement. The linear viscoelastic region was determined by strain sweeps (0.01–100 %) at 1 Hz. The frequency sweeps were performed at 1 % strain over a frequency range of 0.02–15.90 Hz.

The experimental procedure allowed us to record the values of the storage modulus (G'), the loss modulus (G''), the loss tangent ($\tan \delta$), as a function of frequency.

Two fresh samples of each gel lot were measured and gels were elaborated at least in duplicate to ensure reliable results.

Scanning Electron Microscopy (SEM)

Portions of gels were fixed in glutaraldehyde and embedded in a graded acetone series to ensure full dehydration. Samples were then critical point dried. Dehydrated samples were sprinkled onto a double-sided tape attached to the specimen stubs and coated with a thin layer of gold. The images were taken using a Jeol 35 CF (Jeol Ltd, Japan) scanning electron microscopy with a 6-kV acceleration voltage.

Syneresis

Approximately 15 g of hot sample dispersions were put into 50-mL centrifuge tubes and kept at 5 °C.

Samples were analyzed after 1 and 7 days of storage. Gels were tempered at 20 °C (2 h) and centrifuged at 1,500 g for 15 min at 20 °C, (J2-MI centrifuge, Beckman Instruments, USA). After centrifugation, the free water was collected, weighed and expressed as a percentage of the total water present in the gel. Measurements were the mean of three repetitions for each duplicated gel.

Statistical Analysis

The data obtained were statistically treated by variance analysis while the means were compared by the LSD Fisher test at a significance level of 0.05, using the INFOSTAT statistical software (Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, Argentina).

Results and Discussion

Differential Scanning Calorimetry

An endotherm corresponding to the starch gelatinization was obtained from starch composite thermograms. The onset temperatures (T_o) of corn, wheat and cassava starches were 64.91 ± 0.06 , 55.21 ± 0.06 and 57.49 ± 0.09 °C, respectively (Table 2), which were similar compared to those reported in previous works [18, 19]. ΔH_g values of starches ranged between 6.16 and 9.34 J/g of starch. These values were in the range commonly found for native starches (5–20 J/g) [20].

In agreement with our results, it was previously suggested that this effect was due to the increased onset temperature (T_o) of starches as a result of the sucrose addition

[18, 21, 22]. On the other hand, sucrose addition did not affect the ΔH_g values, suggesting that the crystalline stability of starches remains the same, in spite of the sucrose occurrence.

Sucrose did not modify the width at half-peak height ($\Delta T_{1/2}$) of wheat and cassava starches, but it significantly reduced the $\Delta T_{1/2}$ of corn starch.

Peanut protein concentrate did not show a denaturation peak (result not shown), which demonstrated that peanut proteins were completely denatured as a consequence of thermal treatments during oil extraction and protein concentrate processes.

Peanut protein concentrate addition increased T_o values of the studied starches (Table 2). Similar increases were observed after addition of wheat gluten proteins, or soy protein isolate and soy protein concentrates [15, 16, 19, 23], which were related to a lower availability of starch during gelatinization.

Both protein and polysaccharides from PPC can absorb significant amounts of water. Similarly, this phenomenon seemed to be associated with the interaction between leached-out-molecules from granules and protein, and between granule surface and protein [15].

The addition of ~6 % of peanut protein (composite 4) significantly decreased the ΔH_g values of corn and wheat starch, and both the low (~3 %) and high (~6 %) proportions of protein decreased this parameter for the cassava starch. Similar results were observed with soy protein concentrate/starch systems [16], while increases in the ΔH_g values were reported after vegetable protein addition [15, 19, 23].

The high proportion of PPC (~6 % of peanut protein) significantly decreased the width at half-peak height ($\Delta T_{1/2}$) (with the exception of cassava starch), which could be due to the interaction between PPC and the amorphous structure of starch [24]. This could explain the decrease of heat in the phase transition: starch gelatinization is a

Table 2 Differential scanning calorimetry (DSC) parameters of composites

Composites	Corn starch			Wheat starch			Cassava starch		
	T_o (°C)	ΔH_g (J/g of starch)	$\Delta T_{1/2}$ (°C)	T_o	ΔH_g	$\Delta T_{1/2}$	T_o	ΔH_g	$\Delta T_{1/2}$
1	64.91a	9.09d	5.76d	55.21a	6.16c	6.52c	57.49a	9.34b	9.71b
2	68.89c	8.85cd	5.35c	59.72c	6.31d	6.14bc	61.94c	8.70b	9.71b
3	66.68b	8.13cd	5.06b	56.83b	5.15b	6.13bc	58.58b	6.68a	9.02ab
4	66.43b	7.51a	5.23bc	59.07c	3.38a	5.15a	58.94b	6.10a	9.48b
5	70.22d	8.56cd	5.17bc	61.65d	4.98b	5.73ab	63.93d	6.20a	8.49a
6	70.78d	7.71b	4.78a	62.42d	5.15b	5.50a	64.10d	5.92a	8.81ab

Values followed by different letters in the same column are significantly different ($p < 0.05$)

1, 2, 3, 4, 5 and 6: composites as described in Table 1

PPC peanut protein concentrate, *st* starch, *su* sucrose, *w* water

cooperative phenomenon and the expansion of amorphous regions affects the crystalline domains of starch [23].

Composites containing starch, PPC, sucrose and water had the highest onset temperature and the lowest ΔH_g values (except for composite 5 from corn starch), which indicated that sucrose and peanut protein concentrate incorporation caused a delay in starch gelatinization initiation and a decrease of heat in the phase transition.

Pasting Profile

Changes in the rheological behavior of a starch/water suspension during heating are caused by the swelling of granules and the leaching out of starch molecules, which take place in the gelatinization process and were characterized by viscosity measurements with a rapid visco-analyser (RVA) instrument (Fig. 1 and Table 3). The cassava starch slurry showed the highest viscosity followed by corn and wheat, respectively. On the other hand, cassava slurries showed lower pasting temperature than samples containing corn and wheat. Differences among starch paste behaviors are related to intrinsic factors, like amylose/amylopectin rate, molecular mass and the association between starch molecules [25].

Peanut protein concentrate (PPC) addition to wheat and corn starches decreased the pasting temperature (PT) values; however, these values were not modified in cassava samples.

Rapid visco-analyser (RVA) profiles of cassava samples showed a two step increase in viscosity during heating, that is, a change of slope before reaching the maximum viscosity was observed, which was not observed for wheat and corn (Fig. 1). A similar behavior was reported for mixtures of corn and cassava starches and soy protein isolates [26]. The two step viscosity increase was related to the thermal gelation of soy proteins after their incorporation during heating. Since peanut proteins in PPC were previously

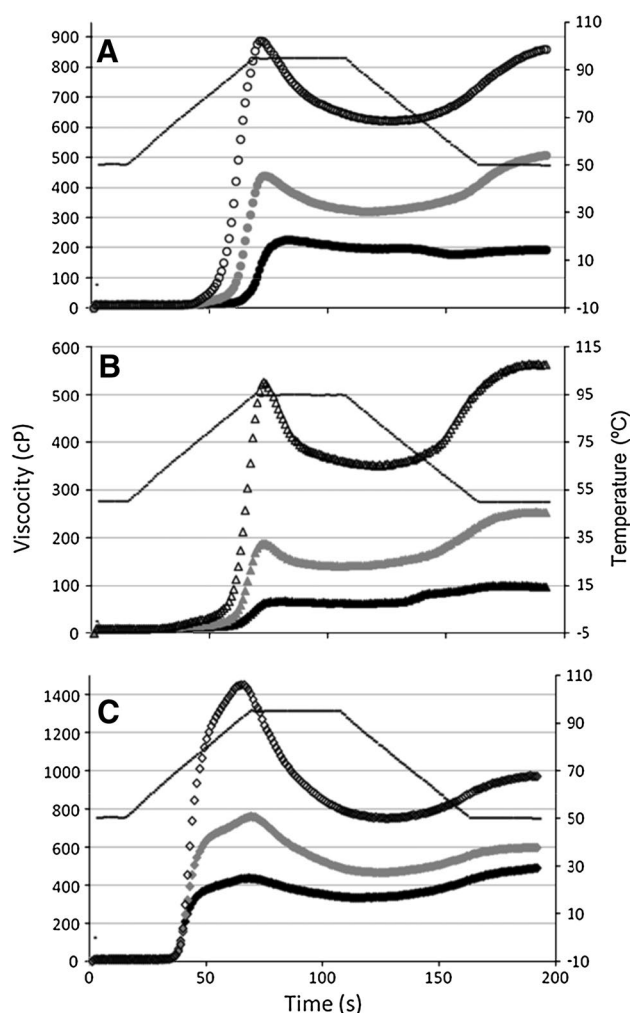


Fig. 1 Viscosgrams for corn (a), wheat (b) and cassava (c) starch. Composites as described in Table 3. Composite 1: 1.21 g starch/25 mL water (black). Composite 3: 1.21 g starch/1.31 g PPC/25 mL water (grey). Composite 5: 1.21 g starch/2.79 g PPC/25 mL water (unfilled symbol)

Table 3 Peanut protein concentrate (PPC) effect on pasting properties of corn, wheat and cassava starches

Composites	PT	PV	FV	BD	SB	
Corn starch	(1) St/water	95.4e	225c	192b	47b	14a
	(3) St/PPC/water	88.9c	439d	506e	119d	186f
	(5) St/PPC/water	83.4b	888g	859h	268f	239i
Wheat starch	(1) St/water	95.0e	68a	98a	6a	36b
	(3) St/PPC/water	92.3d	189b	253c	48b	112c
	(5) St/PPC/water	88.9c	526e	563f	175e	212g
Cassava starch	(1) St/water	69.4a	434d	486d	102c	154e
	(3) St/PPC/water	70.15a	759f	595g	295g	131d
	(5) St/PPC/water	70.25a	1450h	967i	701 h	218h

Values followed by different letters in the same column are significantly different ($p < 0.05$). 1: 1.21 g starch/25 mL water, 3: 1.21 g starch/1.31 g PPC/25 mL water, 5: 1.21 g starch/2.79 g PPC/25 mL water

St starch, PT peak temperature (°C), PV peak viscosity (cP), FV final viscosity (cP), BD breakdown (cP), SB setback (cP)

denatured, it is expected that this phenomena is caused by the intrinsic characteristics of cassava starches, independently of the PPC addition.

PPC addition caused a steady increase in peak viscosity (PV) values for all studied starches. Besides, breakdown (BD) and setback (SB) values were also increased as a consequence of the PPC addition.

Similar results were shown for soy protein addition to corn, wheat and cassava starches [14, 15, 17]. Increases in overall viscosity of starch pastes were also reported when studying the effect of amaranth and buckwheat proteins on corn starch [11], and when analyzing casein/starch and casein hydrolysates/starch pastes [27].

The dispersed phase of a starch paste (mainly composed of gelatinized starch granules, amylopectin rich granules) is more important than the continuous phase (leached out molecules of starch) in determining its rheological properties [28]. Nevertheless, the continuous phase can also contribute to the overall viscosity of a starch paste [29].

PPC retained 3.92 g of water/grams of proteins, which suggests that the overall increase in viscosity could be due to the increase of starch in the continuous phase [30]. On the other hand, the added peanut proteins could interact with the dispersed phase causing an increase in the paste viscosity [31]. From our DSC results, it was suggested that PPC can interact with amorphous regions of starch. As a consequence, there could be a synergistic effect between starch molecules leached out of the granules during gelatinization and PPC, which can increase the viscosity of the dispersed phase [11]. When studying whey protein/starch systems, it was found that interactions between proteins and starch were more important than granule swelling in determining the viscosity of the mixtures [32]. Interactions in the continuous phase can increase the viscosity and, at the same time, prevent disintegration and implosion of starch granules, increasing the volume of swelled granules and, as a consequence, the paste viscosity [33].

Rheological Analysis

Starch forms viscoelastic gels, which have both solid-like (elastic) and liquid-like (viscous) behaviors. Since the starch molecules in gels have no permanent bonds, strong associations between molecules contribute to G' , whereas weaker bonds (which have shorter relaxation times) contribute to G'' [20].

Figure 2 shows storage modulus (G') vs frequency plots of corn, wheat and cassava starch composites. Table 4 shows the rheological parameters of analyzed samples obtained at 1 Hz. Samples showed higher storage modulus (G') than loss modulus (G'') throughout the whole range of frequency, which indicated that gels were fundamentally elastic.

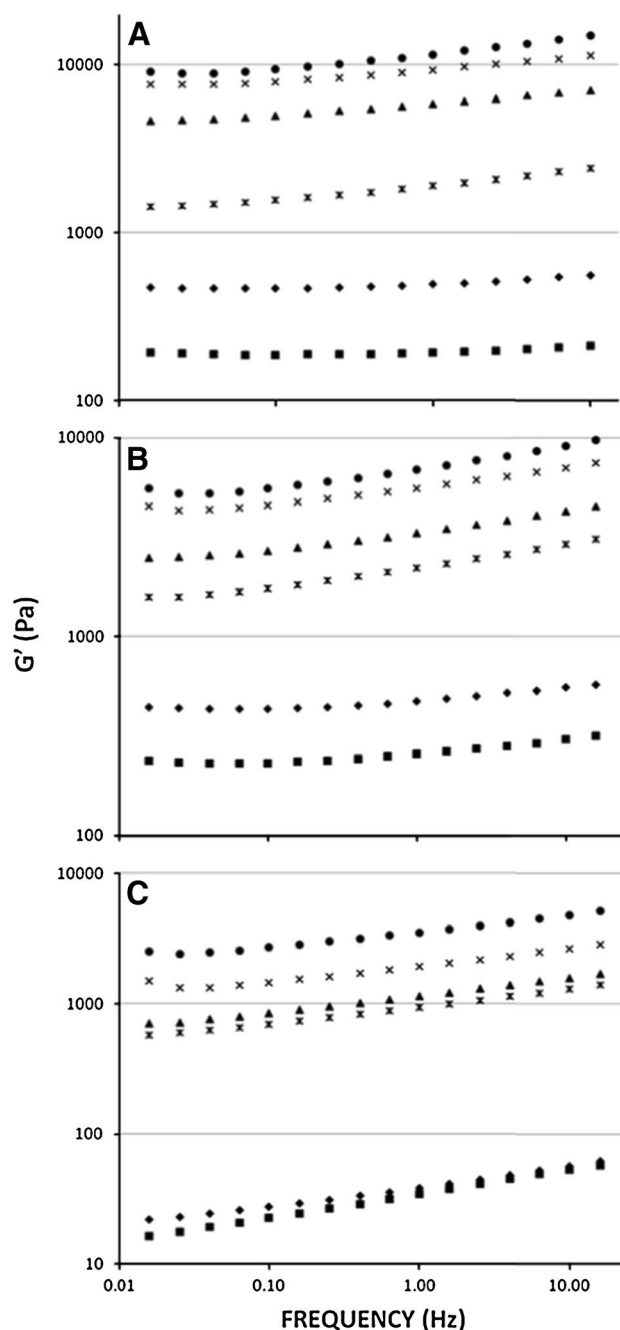


Fig. 2 Storage modulus (G') vs frequency plots for corn (a), wheat (b) and cassava (c) starches. Starch/sucrose/water (filled squares), Starch/water (filled diamonds), PPC (0.069)/starch/sucrose/water (asterisks); PPC (0.069)/starch/water (filled triangles), PPC (0.147)/starch/water (cross symbols), PPC (0.147)/starch/sucrose/water (filled circles)

G' values were independent of the frequency in corn starch samples with and without sucrose (Fig. 2a). In addition, G' values for wheat starch and wheat starch/sucrose samples remained almost independent at low frequencies and showed a slight dependence at higher frequencies

Table 4 Rheological parameters at 1 Hz of analyzed samples

Composites	Corn starch			Wheat starch			Cassava starch		
	G'	G''	$\tan \delta$	G'	G''	$\tan \delta$	G'	G''	$\tan \delta$
1	494a	37a	0.08a	470a	52a	0.11a	38a	10a	0.26ab
2	172a	11a	0.06a	224a	24a	0.10a	33a	10a	0.31d
3	5860c	1018c	0.17b	3756c	846c	0.23b	1180b	310b	0.26ab
4	9333d	2040 cd	0.22c	5580d	1350d	0.24bc	2440c	654c	0.27b
5	2463b	502b	0.20c	2206b	518b	0.23b	936b	246b	0.26ab
6	11503e	2748d	0.24 cd	6879e	2129e	0.31d	3519d	1232d	0.35e

Values followed by different letters in the same column are significantly different ($p < 0.05$) 1, 2, 3, 4, 5 and 6: composites as described in Table 1

G' storage modulus (Pa), G'' loss modulus (Pa), $\tan \delta$ loss tangent

Table 5 Syneresis values (%) of gel samples

Composites	Corn starch	Wheat starch	Cassava starch
After a 1-day storage			
1	1.35b	1.22bc	0.03a
2	4.33e	3.88ef	0.00a
3	1.03a	1.00bc	0.01a
4	0.12a	0.61a	0.00a
5	1.42b	0.84ab	0.00a
6	0.23a	0.83ab	0.03a
After a 7-day storage			
1	5.98f	2.37d	0.13a
2	5.83f	4.20f	0.00a
3	3.52de	1.63cd	0.02a
4	0.25a	0.95bc	0.02a
5	4.07e	2.63d	0.00a
6	3.30d	2.13d	0.01a

Values followed by different letters in the same column are significantly different ($p < 0.05$). 1, 2, 3, 4, 5 and 6: composites as described in Table 1

(Fig. 2b). These behaviors suggest that molecular rearrangements within the network were reduced over the time scale analyzed. Therefore, the gels formed can be considered as strong gels.

Figure 2c showed that cassava and cassava/sucrose gels had a steady increase of G' values with increasing frequency. These results suggested the existence of relaxation processes within these samples, which can be then considered as weak gels [34].

Cassava gels showed higher $\tan \delta$ and lower G' values than corn and wheat starch samples ($p < 0.05$), which indicated that cassava gels have a larger viscous component and less consistency. A less efficient gel structure network with more free water was related to cassava samples. The RVA results suggested that cassava starch had a lower resistance to thermo-mechanical treatments than corn and

wheat starches. This could lead to a greater leaching out of amylose molecules during gelatinization, which causes higher viscous component values of the gels. In addition, the weaker structure of cassava gels could be related to relaxation processes taking place in its amylose network.

Sucrose did not significantly affect G' , G'' or $\tan \delta$ values of corn and wheat starch gels. For cassava gels, the sucrose addition increased the $\tan \delta$ values (Table 4), suggesting a decrease in the solid-like properties of the system.

Peanut Protein Concentrate addition at the two levels (~3 and ~6 % of peanut proteins, composites 3 and 4, respectively) produced an increase in both G' and G'' values. The addition of a high proportion of PPC (12.1 %) increased ~19, ~12 and ~64 times the G' values of corn, wheat and cassava starch samples, respectively. In addition, G'' values increased up to ~55, ~26 and ~65 times compared to corn, wheat and cassava starch gels. Therefore, gels that are more consistent were obtained with the addition of PPC to the starches.

In analyzing the effect of the concentrate on $\tan \delta$ values, PPC showed an increase in these parameters in corn and wheat starch gels (causing a decrease in the elastic component), while $\tan \delta$ values of cassava gels were not affected by PPC, which could be due to the already highly viscous matrix showed by the gels composed of cassava starch.

The G' values of composites 6 were higher than those of composites 4 for all starches. However, a different effect was observed in samples with the lowest proportion of PPC (composites 3 and 5, Table 4). Therefore, it seemed that sucrose effect depends on the PPC levels or water availability.

The G' values of all gels containing PPC showed a steady increase with frequency (Fig. 2). The frequency dependence of the storage modulus in PPC/starch gels indicates a gel network, which can suffer breakdown processes at the junction zones within the studied frequency range [36]. Therefore, despite the increase in consistency caused by PPC, gels showed a weaker gel structure. This can also

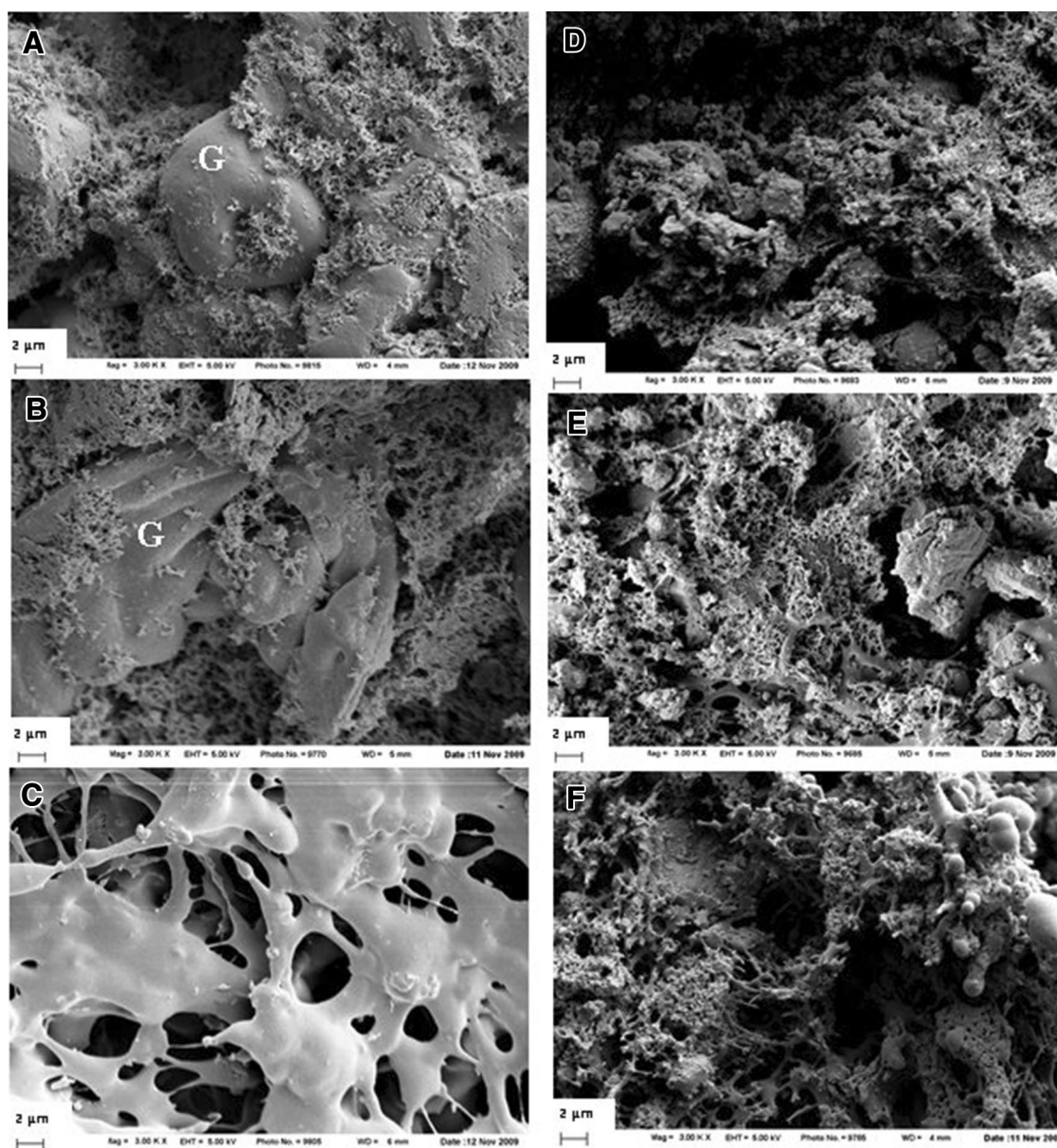


Fig. 3 Scanning electron microscopy of corn (a), wheat (b) cassava (c), corn/PPC (d), wheat/PPC (e) and cassava/PPC (f) starch gels. *G* starch granule. Composites 1 (starch/water) and 4 (starch/PPC/water) as described in Table 1

be observed by the increase in $\tan \delta$ values and, therefore, in the viscous component produced after the PPC addition.

Since protein in PPC is denatured and cannot form a gel structure under heating, it could be expected that starch and PPC were arranged in a two-phase system. Therefore, the observed rheological behavior for PPC/starch pastes and gels could be a consequence of the mutual exclusion between PPC and starch. Mutual exclusion could increase the effective concentration of both polymers, and influence the water partition between the two phases [17, 37]. This could explain the increases in consistency caused by PPC (which could be observed both in the increased viscosity

values measured by RVA, and in the raising of G' and G'' values of gels) without a reinforcement of the continuous gel matrix, as indicated by the frequency dependence of the storage modulus.

Syneresis

Table 5 shows the syneresis values of starch gels. Water separation was assessed after 1 and 7 days of storage at 5 °C. Corn and wheat starch samples (composite number 1 at 1 and 7 days of storage, Table 5) increased the percentage of released water with storage time. It was suggested

that the separation of water is related to the development of junction zones as a consequence of the interaction between leached amylose and amylopectin chains [38]. On the other hand, cassava samples (samples number 1 at 1 and 7 days of storage, Table 5) showed little or no syneresis, which is in accordance with the results previously reported in the literature [13, 26].

The addition of sucrose increased the amount of water released (composites 1 and 2 after a 1-day storage), which is in agreement with previous results [35, 39]. The opposite effect was shown as a consequence of the PPC addition (composites 1, 3 and 4 after a 1-day and 7-day storage). As mentioned above, PPC had a high water retention capacity and could, therefore, produce an increment of water retention of starch gels. Similar results were previously found when studying the effect of soy protein concentrates on starch [15, 17]. The authors suggested that this effect was due to an increase in starch-protein interactions.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs of starch and starch/PPC gels are shown in Fig. 3. Corn and wheat gels presented round-shape granules (G), which acted as rigid fillers in the continuous phase (Fig. 3a, b) after gelatinization. On the other hand, cassava gels did not present a granular structure (Fig. 3c), showing a complete lack of granular integrity, in agreement with previous results [26, 40]. This finding was in accordance with the results obtained through RVA analysis of starch pastes, which revealed that cassava starch had a lower resistance to thermo-mechanical processes (lower breakdown) than corn and wheat starches.

For all starches, the gel structure appears more compact than the structure of gels without PPC (Fig. 3d–f). PPC changed the ultrastructure of the gels, it appeared that peanut material adhered to the granule and mixed with the leached out material, obstructing the continuous starch matrix, accounting for a more irregular gel network. Cassava starch/PPC gels (Fig. 3f) showed a more regular arrangement than corn and wheat samples, which could be attributed to the completely disintegrated granules of cassava starch.

Conclusions

Cassava starch pastes show lower stability than corn and wheat starches against shear under heating. Our results obtained with starch/PPC mixtures suggested that PPC interacted with amorphous regions of starch granules and modified the water availability for starch. Besides, PPC could affect the continuous phase of starch pastes and increase paste viscosity values. The consistency of gels was increased, although weaker structures were obtained.

In addition, syneresis from starch gels was reduced by high proportions of PPC (~6 % of peanut protein), which is favorable for its incorporation into the starch-based systems.

Taking these results into account and the analysis of thermo-mechanical properties of starch pastes, it is suggested that PPC and starch form a two-phase system. It can be concluded that vegetable derivatives like PPC constitute an alternative for incorporation into starch-based systems.

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