RESEARCH ARTICLE

Effect of hydrocolloids on the properties of wheat/potato starch mixtures

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The physicochemical, pasting, thermal, viscoelastic, and syneresis properties of nine formulations prepared with wheat starch, potato starch, and hydrocolloids (pectin, HPMC, arabic gum, and konjac glucomannan (KG)) were assessed. The addition of the hydrocolloids decreased the water solubility index and water absorption capacity but did not modify the swelling power of starch granules. The starch gelatinization temperature decreased in the presence of the hydrocolloids, while the enthalpy of gelatinization and gelatinization range temperature increased. Pectin and HPMC addition decreased the paste viscosity whereas KG increased and arabic gum had no effect. On the other hand, the pasting temperature was not modified by the presence of hydrocolloids. All the blends behaved as solid as the storage modulus was higher than the viscous modulus within all the frequency range assayed. Viscous characteristics were improved with the addition of pectin and HPMC. The presence of hydrocolloids increased the stability of the gelled starch mixtures to freeze–thaw cycle and no syneresis was observed in these gels stored at 4°C.

Keywords:
Hydrocolloids / Pasting / Potato starch / Rheology / Wheat starch

1 Introduction

Potato starch, which represents around 75–80% of the potato flour, is unique among other starches due to the high level of phosphorus, low gelatinization temperature as well as high water-binding capacity [1]. However, addition of the proper hydrocolloid and/or other starches can overcome some shortcomings of potato starches; for example, it can protect starch granules against shear during cooking, improve product texture/rheology, hold moisture, and protect against syneresis [2]. Thus, blends of potato starch with hydrocolloids or other starches have been assayed by some authors [3–6] to control the stability and quality of food products.

Pasting and thermal properties are one of the most important functional properties of starches. The pasting behavior is usually studied by observing changes in the viscosity of a starch system based on rheological principles. From the pasting curve, several parameters can be observed that indicate the extent of granule disintegration and the retrogradation process. The understanding of the rheological behavior of starch pastes is very important for optimizing industrial applications [7]. When the starch paste is cooled, new hydrogen bonds are established and a viscoelastic gel is formed. Processing and storage of starch based ready-to-eat foods is a challenging task as starch gels do not generally

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Abbreviations: G′, elastic modulus; **G″,** viscous modulus; **HPMC,** hydroxypropylmethylcellulose; **KG,** konjac glucomannan; **RVA,** rapid viscometer analyzer; **SP,** swelling power; **Tan(δ),** loss tangent; **Tp,** peak temperature; **WAC,** water absorption capacity; **WSI,** water solubility index; η_{peak}, peak viscosity; η_{min}, minimum viscosity or trough; η_{final}, final viscosity; η_{p-m}, breakdown or difference between peak and minimum viscosity; η_{f-p}, setback from peak or the difference between final and peak viscosity; η^*, complex viscosity

have ideal properties due to their tendency to syneresis and retrogradation. Breakdown, weakness, and rubbery are often undesirable characteristics of these gels. These shortcomings depend on starch composition characteristics (particularly amylose:amylopectin ratio), starch:water ratio, and processing temperature, which are exacerbated after freezing and thawing with detrimental effects in the texture and acceptability of the product [7].

Rheological, thermal, and syneresis properties of starch paste/gel depend on the composition and the presence of other components such as hydrocolloids that might influence these properties. Starch–hydrocolloid systems are composed of various particles suspended in mixed polymer solutions of different rheological properties. The contributions of the dispersed and continuous phases to the properties of the whole system vary with factors such as relative concentrations of starch and hydrocolloid, preparation conditions, and interactions between and/or compatibilities of the various polymer molecules present. The use of hydrocolloids to modify the properties of starch pastes or gels has been extensively studied in the literature [3, 6–10]. Most of these studies evaluated the effect of hydrocolloids on pasting and freeze/thaw stability in different starches, however, just a few of them [4, 5, 11] focused their attention on potato starch. At the moment, no information is available about the use of wheat/potato starch blends and the effect of hydrocolloids on their properties. Thus, the objective of this work was to study the effect of different hydrocolloids (pectin, HPMC, arabic gum, and konjac glucomannan (KG)) on pasting, thermal, rheological, microstructure, and syneresis properties of wheat/potato starch blends. The information on the effect of hydrocolloids on textural characteristics of wheat/potato starch gels could be important for the gelled food industry.

2 Materials and methods

2.1 Materials

Potato starch (21.8 ± 1.5% of amylose) was purchased from Windmill Trade Co. (Amsterdam, Holland). Wheat starch (23.4 ± 0.9% of amylose) was acquired from Dietary Specialties (CT, USA). Food grade citrus pectin (GENU pectin type 104, degree of amidation and esterification: 20 and 27%, respectively), and arabic gum (38.4% D-Galactose, 29.3% L-Arabinose, 14.8% L-Ramnose,12.9% D-glucuronic acid, 3.5% 4–O–Methyl glucuronic acid) were purchased from Gelfix S.A (Buenos Aires, Argentina). KG (D-mannose and D-glucose in a molar ratio of 1.6:1) was purchased from Konjac Foods (CA, USA). Hydroxypropylmethylcellulose (degree of methoxyl and hydroxypropyl substitution: 28.2 and 7.8%, respectively) was supplied by Drogueria Saporiti (Buenos Aires, Argentina).

Table 1. Formulations of 1:1 wheat/potato starch mixture with hydrocolloids

Hydrocolloid		
Type	Concentration (%)	Formulation code
–	0	F1
Pectin	1.5	F2
	3	F3
HPMC	1.5	F4
	3	F5
Arabic gum	1	F6
	2	F7
KG	1	F8
	2	F9

2.2 Formulations and sample preparation

Powder blends were prepared by combining equal parts of starches with two different concentrations of hydrocolloids. A total of nine formulations were assayed (Table 1) including a sample without hydrocolloid as a control.

2.3 Characterization of starch–hydrocolloid blends

2.3.1 Water absorption capacity, water solubility index, and swelling power

Water absorption capacity was measured by the centrifugation method reported by Du et al. [12] and was expressed as grams of water per gram of the sample on a dry basis. Water solubility index and SP were calculated as described by Reddy et al. [13]. All determinations were carried out by triplicate.

2.3.2 Thermal properties

Differential scanning calorimetry (DSC Q100 Thermal Analysis Instruments, New Castle, DE) was used to characterize thermal properties of the systems. Each powder mix (3 g) was dispersed in 25 g of water with agitation to homogenize the sample. A heating program of 10°C/min from 10 to 120°C was used.

The following parameters were determined using the Universal Analysis 2000, TA Instruments software: T_o, T_p, T_c, and ΔH (expressed as Joules/gram of starch). Gelatinization range was calculated as: $T_c - T_o$. Samples were analyzed by duplicate.

2.3.3 Pasting properties

A viscoanalyzer (RVA-4 Newport Scientific, Warriewood, Australia) was used to study the pasting properties. The assays were performed according to the AACC 71-26

method [14] by adding 3 g of each formulation to 25 g of water.

The following parameters were determined using the Thermocicline software: η_{peak}, η_{min}, η_{final}, η_{p-m}, η_{f-p}, and pasting temperature. Each assay was performed by triplicate.

2.4 Characterization of starch–hydrocolloid gels

Gels were obtained by heating the starch-hydrocolloid dispersions at 90°C for 12 min. Previous to the analysis, samples were allowed to cool to room temperature.

2.4.1 Viscoelastic properties

Dynamic oscillatory tests were performed in a RS 600 Haake controlled stress oscillatory rheometer (Karlsruhe, Germany). Each assay was performed at 25 ± 0.1°C, using a plate–plate sensor system with a 1.5 mm gap between plates. Before measurement, samples were allowed to rest 5 min between plates to relax. The following parameters were calculated using the Rheowin 3.3 software: G', G", η^*, and Tan(δ). Reported values were the average of two determinations.

2.4.2 Syneresis degree

Gels (three independent replicates) were stored at 4°C (refrigeration) or −18°C (freezing) for 24, 48, or 72 h and then thawed at room temperature for 3 h. The syneresis degree (%) was determined as described in the literature [7].

2.4.3 Confocal laser scanning microscopy

Samples were prepared as described in Section 2.2, adding 60 μL FITC (0.3 mg/mL) to the dispersions. Then samples were left in darkness to cool down for 1 h before analysis. An inverted microscope (LEICA TCS SP5, Mannheim, Germany) equipped with an Ar and He Ne lasers, was used. The excitation and emission wavelengths were 488 and 518 nm, respectively. Images were acquired using a HCX PLAPO CS 63.0×1.40/UV/oil immersion objective with a 1024×1024 pixel resolution. Software Leica Application Suite Advanced Fluorescence (LAS AF), version 2.2.1 build 4842 was employed for image analysis.

2.5 Data analysis

An analysis of variance of data was performed and the least significant differences were calculated to compare the means at a level of 95% using the Fisher test. All results were processed by using the Infostat software (Córdoba National University, Córdoba, Argentina).

3 Results and discussion

3.1 Physicochemical characterization of starch–hydrocolloid blends

3.1.1 Water-related properties

Table 2 shows the values of WSI, WAC, and SP obtained for the formulations. The water solubility index indicates the solubility of the molecular components of the mixture. In this system, potato starch has the main contribution to this parameter probably due to the weak internal organization, as a result of negatively charged phosphate ester groups within the starch granules [15] (values of the WSI of potato starch and wheat starch separately are not shown). Results in Table 2 show that the WSI was higher in F1 and decreased with the addition of hydrocolloids, especially with KG (F8 and F9). The water solubility index depends on the interactions between water and the polymer chains of starch. As this interaction has an electrostatic nature, any other molecule, like a hydrocolloid, might interfere decreasing its solubility.

During food processing, the water absorption capacity of the ingredients influences functional and sensory properties [12]. Results in Table 2 show that the addition of hydrocolloids slightly decreased the WAC values of the mixtures, except for the sample with 2% of arabic gum in which no significant differences ($p < 0.05$) with F1 was observed.

The swelling power measures the tenacity of the bonds in the crystalline portion of the starch granule, showing how fast the starch will cook [13]. The effect of different hydrocolloids on the granule swelling has been described extensively in the literature. Some authors [16, 17] found that granules became more swollen or granule swelling was reduced [18, 19] or found a specific inhibition of potato starch granule swelling by anionic hydrocolloids [5]. Huang [9]

Table 2. Water solubility index (WSI), water absorption capacity (WAC), and swelling power (SP) of wheat/potato starch mixtures with hydrocolloids

Sample	WSI (%)	WAC (g/g)	SP (g/g)
F1	17.54^{a}	2.35^{a}	14.56^{a}
F2	12.47^{b}	$2.03^{b,c}$	13.77^{a}
F3	11.29^{b}	1.89^{c}	12.24^{a}
F4	13.31^{b}	$1.98^{b,c}$	13.76^{a}
F5	11.51^{b}	$2.05^{b,c}$	12.19^{a}
F6	10.81^{b}	2.07^{b}	12.56^{a}
F7	9.77^{b}	$2.15^{a,b}$	13.57^{a}
F8	8.27^{c}	$1.99^{b,c}$	14.21^{a}
F9	8.03^{c}	1.84^{c}	13.33^{a}

Values in the same column with the same letter are not significantly different ($p < 0.05$).

reported little if any change in SP, agreeing with results shown in Table 2.

3.1.2 Thermal analysis

Peak temperature of the mixture control (F1) decreased with the addition of hydrocolloids (Table 3) except for 3% HPMC and 1% KG samples (no significant differences were observed, $p < 0.05$). The T_p values for samples F8 and F9 were similar to those reported in the literature [20] for potato starch/KG mixtures. However, the T_o and T_c values were lower and higher, respectively, than results reported by the same authors who found that T_p increased for KG contents from 0 to 1%. In the present work, the results showed that increasing the concentration of this hydrocolloid from 1 to 2% did not modify significantly ($p < 0.05$) the T_p.

Samples with 2% of arabic gum (F7) showed onset peak shifted to higher values suggesting that this hydrocolloid delayed the onset of starch gelatinization. On the other hand, the T_c increased with the addition of HPMC, arabic gum, and KG suggesting that gelatinization process is slower when these hydrocolloids are added to the mixture.

Results in Table 3 show that ΔH was lower in the control sample (F1) and slightly increased with the addition of hydrocolloids. A possible explanation for this fact is that during gelatinization, water migrates toward the starch granule, however, the hydrophilic nature of hydrocolloids delayed water migration increasing the energy required for the process.

The gelatinization range refers to the temperature limits over which all the granules are fully swollen. This range varies in different starches and could be affected by other components in the mixture. Results in Table 3 showed that the hydrocolloids used in this study increased the gelatinization range probably by delaying water migration toward the starch granule.

Table 3. Thermal properties of wheat/potato starch dispersions with different hydrocolloids expressed as gelatinization onset (T_o), peak (T_p) and conclusion (T_c) temperatures, enthalpy of gelatinization (ΔH), and gelatinization range

Sample	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	Gelatinization range (°C)
F1	$56.38^{a,b,c}$	67.70^{d}	75.43^{a}	10.20^{a}	19.05^{a}
F2	55.67^{a}	66.29^{b}	77.11^{b}	11.19^{b}	21.44^{b}
F3	$56.03^{a,b}$	$66.55^{b,c}$	77.43^{b}	11.20^{b}	21.40^{b}
F4	57.23^{c}	$66.60^{b,c}$	80.49^{c}	11.41^{b}	23.26^{c}
F5	$56.45^{a,b,c}$	$66.97^{c,d}$	80.55^{c}	$12.59^{b,c}$	$24.10^{c,d}$
F6	$56.98^{b,c}$	$65.70^{a,b}$	80.61^{c}	$12.63^{b,c}$	$23.63^{c,d}$
F7	58.21^{d}	65.12^{a}	80.72^{c}	11.74^{b}	22.51^{c}
F8	$56.00^{a,b}$	$66.81^{c,d}$	80.75^{c}	12.79^{c}	24.75^{d}
F9	$56.72^{b,c}$	$66.47^{b,c}$	79.80^{c}	$11.94^{b,c}$	23.08^{c}

Values in the same column with the same letter are not significantly different ($p < 0.05$).

3.1.3 Pasting properties

Figure 1 shows the pasting behavior of wheat/potato starch mixtures with or without hydrocolloids. Samples with KG (F8 and F9) showed the highest peak viscosity (Fig. 1a). An increase in the peak viscosity in starch samples with hydrocolloids was previously reported by other authors [7, 10, 17, 21]. A possible explanation for this fact is the interaction between the hydrocolloid and the leached amylose and low-molecular weight amylopectin from the starch granule [7]. Konjac glucomannan is a polysaccharide with a low degree of branching which could favor thermodynamically compatible interactions with amylose. On the other hand, HPMC showed the lowest value of peak viscosity, probably derived from their methyl and hydroxypropyl groups which could be responsible for the lower interaction with amylose. Another possible explanation is that during heating, HPMC loses water faster than KG decreasing its hydrodynamic volume and viscosity. Whatever the reason, this fact renders an adverse effect on starch pasting, consequently retarding the paste formation and viscosity increase during pasting. Some authors [22, 23] also reported the same effect using xanthan gum. With respect to the formulations containing pectin and arabic gum, they showed no significant differences ($p < 0.05$) in the peak viscosity compared to the control sample F1 (Fig. 1a).

The breakdown parameter represents the extent of disruption of the swollen granules when heating and shear forces are applied. In the case of the formulations with pectin and arabic gum, these hydrocolloids did not modify the breakdown of the sample. Comparing to the control (F1), significant differences ($p < 0.05$) were observed with HPMC and KG at both concentrations (Fig. 1c). The latter would increase the starch granule fragility. On the other hand, HPMC would exert a protective effect on the granules disruption delaying the leaching of amylose. Funami et al. [24] also reported that hydrocolloid addition inhibited amylose leaching.

Figure 1d shows that the final viscosity was higher in samples with KG (F8 and F9) and lower in samples with pectin (F2 and F3) and HPMC (F4 and F5). As it was described above, KG would facilitate the starch granule disruption releasing the amylose and, thus, increasing the final viscosity. Results reported in the literature [25] indicate that final viscosity increments might be due to the leach and aggregation of amylose. On the other hand, arabic gum showed no significant differences ($p < 0.05$) in the final viscosity with the control sample (F1).

During cooling of starch paste, leached amylose molecules rapidly aggregate and then the formation of amylose junction zones is responsible for the setback [26]. The presence of other components might influence the viscous properties of the system by altering the aggregation and junction zones of the amylose. Setback significantly

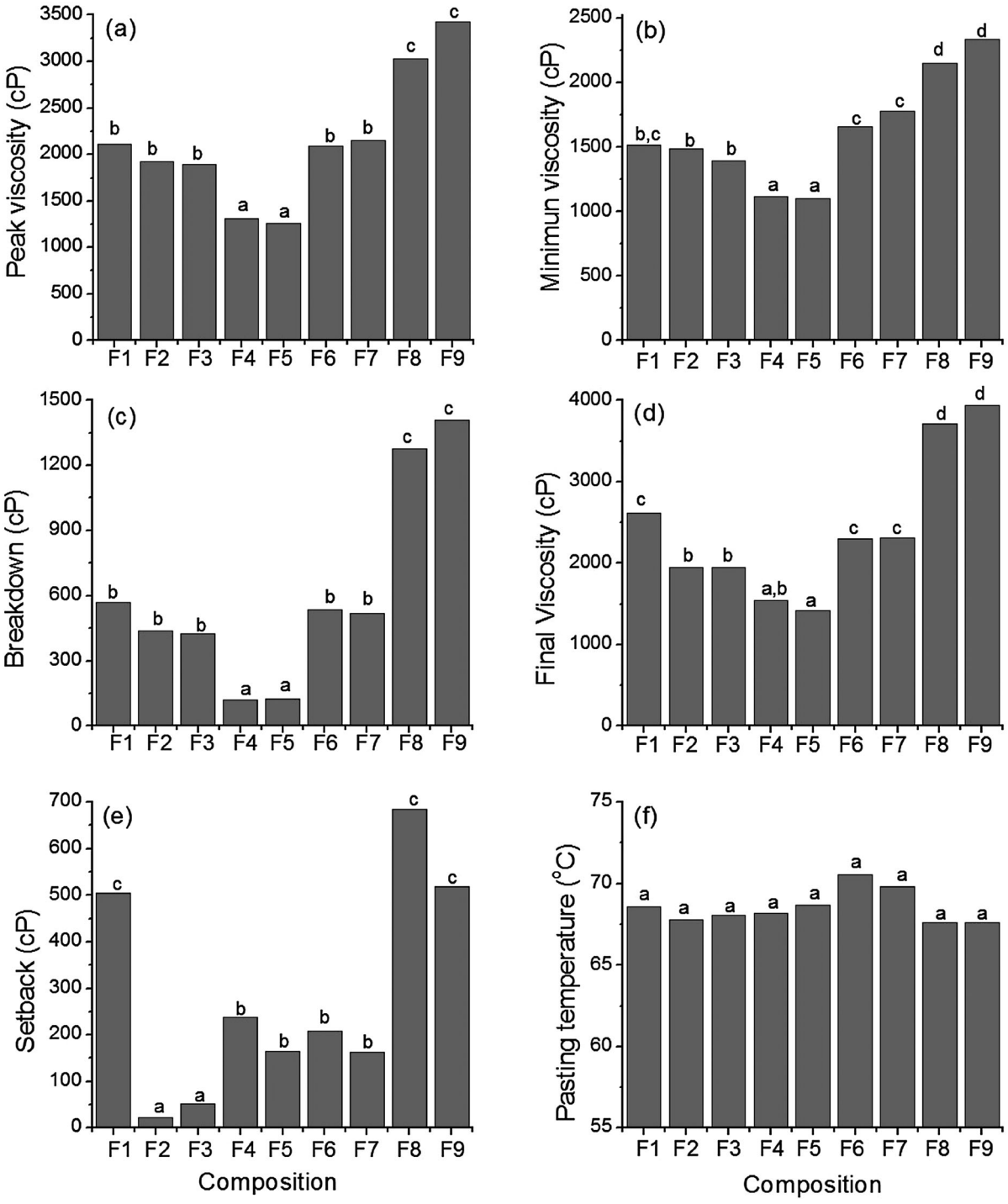

Figure 1. Pasting properties of wheat/potato starch dispersions with hydrocolloids. Values in the same graph with the same letter are not significantly different ($p < 0.05$).

decreased ($p < 0.05$) with the addition of pectin, HPMC, and arabic gum (Fig. 1e), suggesting that the increase in the viscosity due to gelation was lower. Other authors [8] also found a decrease in the setback of tapioca starch gels with increasing xanthan concentration. On the contrary, KG showed no significant differences ($p < 0.05$) with the control samples (F1) in the setback values indicating the same increase in the viscosity due to gelation. This result agrees with those obtained by Song et al. [19] for rice starches with guar gum and gellan gum.

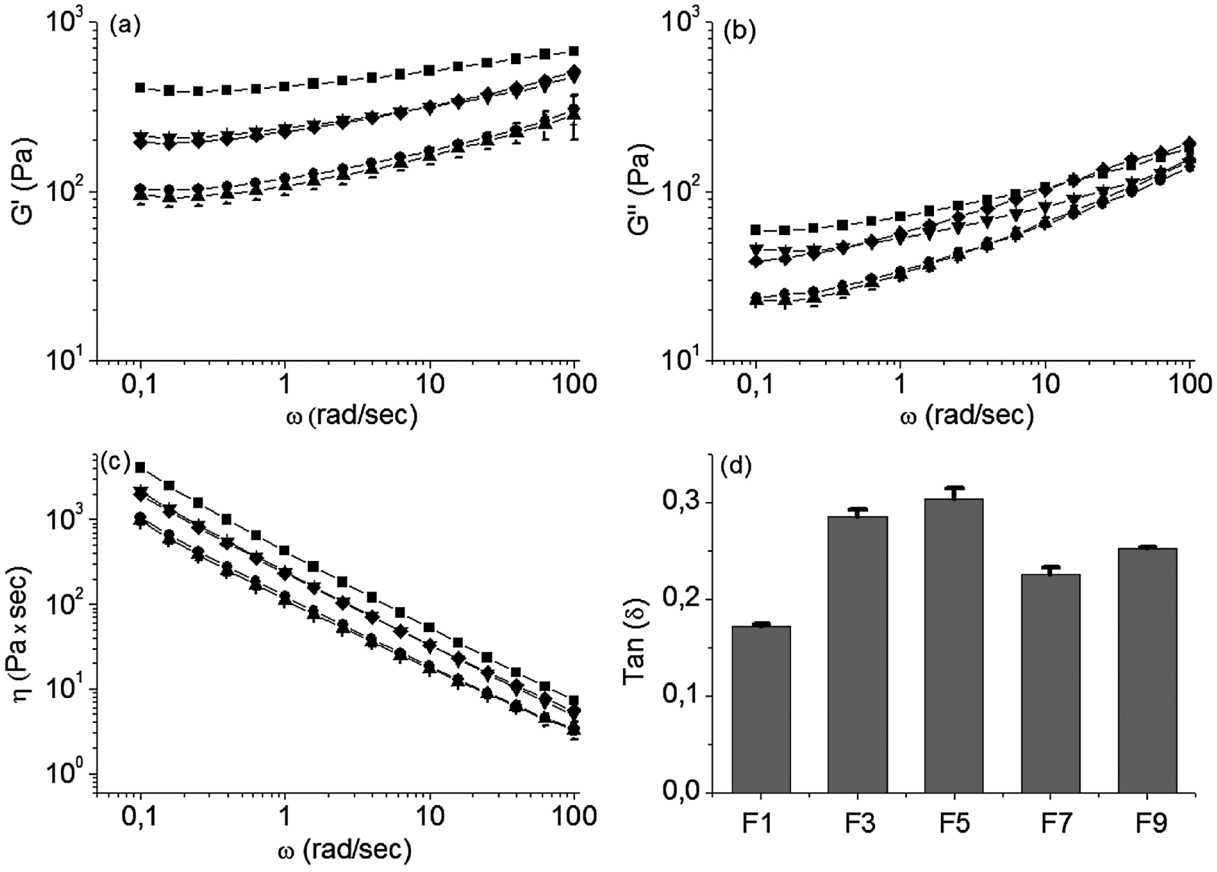

Figure 2. Elastic modulus (G′) (a), viscous modulus (G″) (b), complex viscosity (η) (c), and loss tangent (Tan(δ)) (d) at 1 rad/s of wheat/potato starch gels with different hydrocolloids. ■: F1, ●: F3, ▲: F5, ▼: F7, ◆: F9.

The pasting temperature did not change significantly ($p < 0.05$) with the addition of hydrocolloids (Fig. 1f). Similar results were reported in the literature [24, 27] with pectin/HPMC and arabic gum on the pasting behavior of wheat starch. On the other hand, Rojas et al. [28] found an increase in the pasting temperature in systems composed by pectin or HPMC and wheat flour.

Several authors [29–31] reported that modifying the amount of hydrocolloids changed the RVA parameters such as breakdown, setback, and final viscosity of starch pastes. However, the results of the present work showed that pasting properties of wheat/potato starches were similar independently of the hydrocolloid concentration used in the mixture.

3.2 Characterization of wheat/potato starch gels with hydrocolloids

3.2.1 Viscoelastic properties

Figure 2 shows the dynamic spectrum of wheat starch/potato starch gels prepared with different hydrocolloids. Only the highest content of each hydrocolloids were plotted as no significant differences were observed with the lower amount. Results indicated that G' was higher than G" for all samples within all the frequency range assayed. Both moduli showed dependence with frequency evidencing a weak gel structure [32]. The addition of hydrocolloids decreased G' and G",

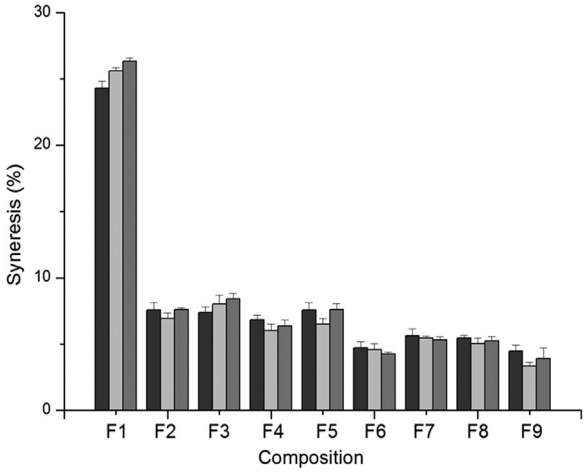

Figure 3. Effect of different storage times at −18°C on the syneresis of wheat/potato starch gels with different hydrocolloids. Storage time: (■): 24 hs, (■): 48 hs, (■): 72 hs.

especially with the addition of pectin and HPMC coinciding with the low values of peak viscosity. BeMiller [2] suggested that the presence of hydrocolloids would lead to amylose network defects, reducing the paste viscosity and weakening the gel. On the other hand, no significant differences were observed in the G' value of samples with arabic gum or KG. Results reported in the literature showed different behavior of the starch–hydrocolloid system. Some authors [16, 33] reported an increase in G' whereas others [31, 34] reported an increase in both moduli. On the other hand, Kaur et al. [35] showed that G' and G" decreased with the addition of cassia gum to potato starch. Funami et al. [24] also found a decrease in G' of wheat starch/arabic gum gels, coinciding with results showed in Fig. 2.

Tan(δ) is related to the overall viscoelastic response and can be considered as an indicator of the structural organization of a material [36]. Values of $\mathrm{Tan}(\delta) > 1$ indicate that the viscous behavior predominates, whereas values of $\mathrm{Tan}(\delta) < 1$ indicate that the elastic or solid behavior dominates in the sample. Results in Fig. 2d suggest that all samples analyzed behave as solid. Samples containing pectin and HPMC (F3 and F5, respectively) were slightly more viscous than the others. Results reported in the literature [20] also found an increase in the Tan(δ) when KG was added to potato starch. This result agrees with those observed with the RVA parameters but in general, both moduli and complex viscosity did not accurately reflect the trends observed with RVA. This fact could be explained taking into account that pasting parameters are measured under heating during the rotational stress applied. On the contrary, viscoelastic parameters were measured at 25°C, condition

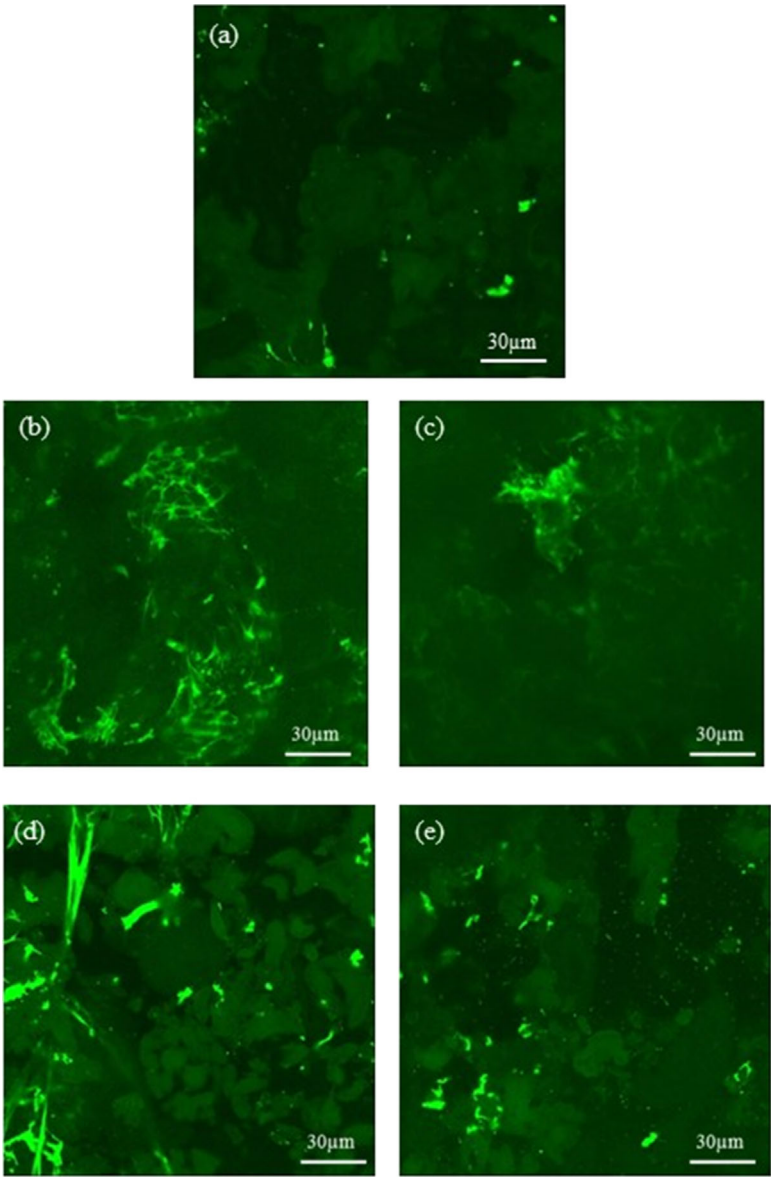

Figure 4. Confocal laser scanning microscopy images of wheat/potato starch gels with different hydrocolloids. (a): F1, (b): F3, (c): F5, (d): F7, (e): F9.

at which new and more molecular bonds stabilize the gel network [7].

3.2.2 Syneresis degree

Starch retrogradation, which is a major problem for the food industry, can be effectively retarded by refrigeration and freezing. However, after storage, syneresis usually occurs affecting the quality of the product. On the other hand, hydrophilic hydrocolloids usually hold water preventing the syneresis in the host system. Results in Fig. 3 show that the presence of hydrocolloids increased the stability of the gelled starch mixtures to freeze–thaw cycle and no syneresis was observed in these gels stored at 4°C (results not shown). In addition, no significant changes were observed in the syneresis of gels stored at −18°C at different times, however, samples containing arabic gum or KG showed slightly lower values than those containing pectin or HPMC.

3.2.3 Microstructure analysis

Figure 4a shows a discontinuous and glutinous network of starch leached out components when the gels are analyzed by confocal laser scanning microscopy. Disruption of starch granules after thermal treatment resulted in a smooth structure in gels with pectin (Fig. 4b) and HPMC (Fig. 4c) which favor the smooth flow of the dispersed phase. This fact would explain the low values of G' and G" observed in Fig. 2 and also the lowest peak viscosity of HPMC observed in Fig. 1. On the contrary, gels with arabic gum (Fig. 4d) and KG (Fig. 4e) showed non-homogeneous dispersions of unevenly swollen starch granules. As described above (Table 3), these hydrocolloids delayed starch gelatinization. In addition, the enhanced fluorescence zones showed in Fig. 4b–e could be due to the presence of hydrocolloids which are non-uniformly spread throughout the gel. Probably, the higher affinity of the dye for the hydrocolloids is responsible for this observation. According to Hu et al. [37], hydrocolloids like carrageenan can cover the surface of the intact starch granule, however, Funami [24] found that arabic gum form aggregated structures in wheat starch gels. The black zones observed could be due to microsyneresis, which would induce the formation of rich in solvent pockets [38].

4 Concluding remarks

Different pastes and gel characteristics were obtained with the wheat/potato starch–hydrocolloid combinations studied. This behavior is very important for optimizing industrial processing applications and could be useful for the commercial manufacture of gelled desserts with different textures. The most significant effect was the reduction in consistency of the composite system when hydrocolloids were added, especially with pectin and HPMC. Besides, functional properties like water solubility index and water absorption capacity were reduced in the presence of hydrocolloids.

The refrigeration of the formulations at different times did not affect the gel stability and the apparent freeze–thaw stability was increased by the addition of hydrocolloids. Due to the complexity of the systems is probably that contribution of different competing mechanism, which varies with each hydrocolloid, is probably responsible for the starch–hydrocolloid paste/gel behavior.

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