Research Article

Thermal behaviour of wheat starch and flour at different water levels: Effect of pectins, modified celluloses and NaCl

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Rapid viscoanalyser (RVA) and differential scanning calorimetry (DSC) can be applied to study thermal transitions in starch based systems at different water levels. The effect of different hydrocolloids on wheat starch thermal transitions in the presence and absence of NaCl (2%) was evaluated in flour–hydrocolloid suspensions, starch–hydrocolloid mixtures and dough. These hydrocolloids include microcrystalline cellulose (MCC), carboxymethyl cellulose (CMC), two types of hydroxypropylmethylcellulose (HPMC F 4 M and F50), a low methoxyl pectin (LMP) and a high methoxyl pectin (HMP). The suspensions were submitted to a heating/cooling cycle in an RVA and a DSC was used to evaluate gelatinization and ALC transition in dough and mixtures. All of the suspensions containing NaCl exhibited higher hot paste stability. Furthermore, CMC and pectins showed an inhibitory effect on amylose retrogradation. Results also showed that starch thermal transitions in limited and excess water can be highly affected by hydrocolloids, particularly when NaCl is present.

Received: June 19, 2014
Revised: November 25, 2014
Accepted: November 28, 2014

Keywords:
Gelatinization / Modified celluloses / Pasting / Pectins / Wheat flour

1 Introduction

During food processing and storage of starch based foods, thermal transitions such as gelatinization, gelation and retrogradation can influence texture and appearance, thus determining the global acceptance of the final product. These phenomena are dependent on the amount of water present. When gelatinization occurs in systems with excess water, granules swell irreversibly as a result of disruption of hydrogen bonds in amorphous zones. As heating continues, the swelling assists the melting of crystalline regions and AML occurs [1, 2]. If this process persists, the swollen granules disrupt and amylose is leached, resulting in a paste [3]. Whereas when water is limited, swelling and solubilization of starch is reduced, since the effect in the amorphous regions decreases and only partial melting of crystalline regions occurs. Then, redistribution of water towards the unmelted crystalline regions facilitates their melting at higher temperatures [4].

Hydrocolloid addition enhances the possibilities of conferring particular textures to starch based foods. Besides, hydrocolloids are used as stabilizers to avoid or minimize the effects of starch retrogradation [5]. However, hydrocolloids affect starch gelatinization properties [6, 7]. Among hydrocolloids, modified celluloses and pectins are obtained from abundant natural resources and can be chemically modified to obtain particular physicochemical properties.

Different techniques allow the study of starch gelatinization at different water conditions. For systems with high water content, rapid viscoanalyser (RVA) is a widely used method that allows obtaining information about the rheological and thermal behaviour of starch pastes. Even if RVA data reflect starch behaviour in a non-concentrated medium, trends about starch behaviour in more concentrated systems can be obtained [8].

On the other hand, DSC is a technique widely used to study thermal transitions such as gelatinization, retrogradation and

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Abbreviations: ALC, amylose–lipid complex; **AML,** amylose leaching; **CMC,** carboxymethyl cellulose; **HMP,** high methoxyl pectin; **HPMC,** hydroxypropylmethylcellulose; **LMP,** low methoxyl pectin; **MCC,** microcrystalline cellulose; **RI,** retrogradation index; **RVA,** rapid viscoanalyser; T_o, onset temperature; T_c, conclusion temperature; T_p, peak temperature; T_{pa}, pasting temperature; ΔH_{AL}, enthalpy of amylose–lipid complex dissociation; η_f, final viscosity; η_{min}, minimum viscosity; η_p, peak viscosity; η_p-η_{min}, breakdown; η_f-η_{min}, setback from minimum; η_f-η_p, setback from peak

ALC dissociation in starch based systems over a wide range of water levels. Though both RVA and DSC can be applied to study starch gelatinization, temperatures are not coincident. Thus, T_{pa} has been used to estimate the T_o obtained by DSC, but it was observed that T_{pa} is always higher than T_o [9].

Thus, RVA and DSC are both widely used techniques to study starch thermal behaviour when it is submitted to heating under different water contents. Besides, the effect of other components on these transitions and the effect of the application or not of energy input can be studied by this methodology.

The objectives of the present work have been to: (a) analyse the effect of modified celluloses (microcrystalline cellulose–MCC, hydroxypropylmethylcelluloses–HPMC and carboxymethylcellulose–CMC) and two types of pectins (high methoxylpectin–HMP and low methoxylpectin–LMP) on the gelatinization and gelation behaviour of wheat flour by RVA and DSC and (b) study the effect of these hydrocolloids when the system composition is modified by the addition of NaCl.

2 Materials and methods

2.1 Materials

Commercial wheat flour (Type 000, [10]) was used. Flour composition was: protein 11.4% (Kjeldahl factor = 5.7), moisture 14.2%, lipids 1.4% and ash 0.678%. Two types of food grade hydrocolloids were employed: citrus pectins and modified celluloses. Commercial pectins (57% w/w) were: low methoxyl pectin (LMP), Genu Pectin 8001 (CP Kelco, USA) and a high methoxyl pectin (HMP), Genu Pectin 105 (CP Kelco, USA). Degree of esterification was 67% for HMP and 43% for LMP. Degree of amidation for LMP was 16% [11]. Also, four modified celluloses were used: carboxymethylcellulose (CMC, Latinoquímica Amtex S.A, Argentine) with a degree of substitution of 0.9%, microcrystalline cellulose (MCC, FMC Biopolymer, Philadelphia) which was copolymerized with 12% of CMC, and two types of hydroxypropylmethylcellulose (HPMC, Dow Chemical Company, USA) including HPMC F 4 M with 29.3% of methoxyl groups and 6.0% of hydroxypropyl groups and HPMC F 50 with 28.6% of methoxyl groups and 5.4% of hydroxypropyl groups. Distilled water and commercial salt (NaCl) were used.

2.2 Methods

2.2.1 Viscoamylographic profile of flour–hydrocolloid mixtures

A rapid viscoamylograph (RVA–4, Newport Scientific Pty. LTD., Warriewood, Australia) was employed to characterize the behaviour of wheat flour–hydrocolloid suspension in the presence and absence of NaCl when submitted to a heating/cooling cycle. Modified celluloses were used at 1.5 g/100g (flour basis) and pectins at 2.0 g/100g (flour basis). Assays were performed in triplicates according to the AACC 76–21 method [12]. An exactly weighed amount of flour (3.50 g) was dispersed in 25.0 ± 0.1 ml of distilled water, stirred and placed in the RVA. When NaCl and/or hydrocolloids were used, they were dry premixed with flour (3.50 g) and then dispersed in water. Each sample was maintained at 50°C for 1 min, then heated from 50 to 95°C in 3 min 42 s, held at 95°C during 2 min 30 s, cooled from 95 to 50°C in 3 min 48 s and held at 50°C for 2 min. The paddle speed was 960 rpm for the first 10 s and then 160 rpm for the rest of the cycle. The software Thermocline for Windows was employed to calculate: paste temperature (T_{pa}), the time at which an increase in viscosity began (t_p), peak viscosity (η_p), minimum viscosity (η_{min}) or trough, final viscosity (η_f), breakdown (η_p-η_{min}), setback from minimum (η_f -η_{min}) and setback from peak(η_f -η_p).

2.2.2 Starch thermal properties studied by DSC

2.2.2.1 Dough preparation

The formulation employed was: flour 100 g, water according to farinographic absorption (Table 1) [11, 13] and salt (0 g/100 g and 2 g/100 g, flour basis). Modified celluloses were employed at 1.5 g/100 g (flour basis) and pectins at 2.0 g/100 g (flour basis). Doughs, without hydrocolloids and with and without salt, were used as control samples. They were prepared in a Brabender microfarinograph (Duisburg, Germany), and the farinographic development time of each blend was used as the mixing time for preparing the samples. Each dough sample was prepared by duplicate.

2.2.2.2 Starch extraction and model systems formulation

Doughs were prepared as described in 2.2.2.1 and wheat starch was separated from gluten according to an adaptation

Table 1. Water amount (farinographic value) used to prepare model systems and dough (water ml/100 g mixture)

Sample	Without NaCl	With NaCl
Control	58.2 ± 0.5	55.1 ± 0.1
MCC	61.3 ± 0.0	58.0 ± 0.3
CMC	63.2 ± 0.1	59.8 ± 0.0
HPMC F4 M	66.7 ± 0.7	62.5 ± 0.0
HPMC F50	64.0 ± 0.0	60.9 ± 0.4
LMP	62.1 ± 1.0	59.2 ± 0.4
HMP	60.0 ± 1.0	60.3 ± 0.5

±SD.

of the method described by Saslayan (2004) [14]. All dough was washed with tap water which was collected to separate the starch dispersed in it. This residue was centrifuged in an Avanti J-25 (Beckman Coulter, California, USA) at 12096 g during 10 min at 10°C. The obtained pellet was washed with 50% propanol and centrifuged at 12096 g at 10°C during 10 min at 30°C.

Mixtures of starch and hydrocolloid, with and without salt, were prepared by dry mixing the ingredients and adding water to obtain a homogeneous paste. Modified celluloses and pectins were employed at the same levels used in the doughs (1.5 g/100 g and 2.0 g/100 g, starch basis, respectively). Salt concentration was 2 g/100 g starch and water amounts were the same as those used for the dough systems (Table 1).

2.2.2.3 Starch thermal transitions in model starch–hydrocolloid systems and dough

Thermal transitions (gelatinization, ALC dissociation) were studied for the dough and starch model systems prepared as described above.

For dough samples, aliquots of 8–13 mg were weighed in hermetic aluminium pans and equilibrated at room temperature for at least one hour. For starch model systems about 7–11 mg were weighed and equilibrated in the same way. Samples were heated at 10°C/min up to 140°C in DSC equipment (Q100 TA Instruments, USA). As a reference, an empty pan was used and calibration with Indium was performed. Peaks corresponding to starch gelatinization and dissociation of ALC were evaluated. For each peak, onset (T_o), peak (T_p) and conclusion temperatures (T_c) were calculated as well as enthalpy value.

Amylopectin retrogradation and ALC formation were evaluated in doughs with salt. Dough samples were heated from 5 to 105°C at 10°C/min (simulating the baking process), allowed to rest until reaching a temperature of 20°C at which time half the samples were tested, while the other half were stored at 20°C for 7 days before testing. All samples were heated to 140°C before tests were performed. To improve endotherm visualization, a slower heating rate (5°C/min) was used. Onset, peak and final temperature and enthalpies of amylopectin retrogradation and ALC dissociation were measured. Besides, the retrogradation index (RI) was calculated according to the following equation:

$$\mathrm{RI}\% = \frac{\Delta \mathrm{H}_{\text{after storage}}}{\Delta \mathrm{H}_{\text{gelatinization}}} * 100$$

Moisture in each sample was determined by puncturing the pan covers and then drying at 105°C up to constant weight. Assays were performed at least in duplicate.

2.2.3 Statistical treatment

Statgraphics Plus software (StatPoint Technologies, Warrenton, VA, USA) was used to perform different statistical analyses. The effect of hydrocolloid and NaCl addition and the interaction between these factors was studied by two way analysis of variance (ANOVA). The effect of hydrocolloids on samples with and without NaCl was evaluated by one way ANOVA. To discriminate among means, Bonferroni's multiple comparison procedure was applied at 95% confidence level.

3 Results and discussion

3.1 Wheat flour–hydrocolloid systems at high water level: Analysis by RVA

The RVA profiles of flour without additives and flour with CMC, HPMC F 4 M and HMP, with and without NaCl, are shown in Fig. 1A and B, respectively. Flour with NaCl exhibited higher peak viscosities (η_p) than samples without NaCl. Day et al. [15] have studied wheat starch systems by RVA and stated that NaCl leads to lower $\eta_{p,}$ probably by reducing starch swelling. Na^+ ions would inhibit starch–water interactions, reducing the amount of water that starch can bind to. However, in our case, gluten protein can also be affected by the presence of salt, thus influencing pasting behaviour. Unfolding and more interaction between proteins and the other components could also explain the higher η_p when NaCl is added.

Samples without NaCl exhibited little effect of hydrocolloid addition, except for CMC; in contrast, large differences were found among RVA profiles when NaCl was added. In the viscoamylograms of Fig. 1, the highest differences among samples were found just before and after the maximum viscosity, since at this stage starch granules are substantially hydrated. Starch pastes are described as suspensions of swollen starch granules dispersed in an amylose enriched medium [16]. Based on this fact, it was postulated that as hydrocolloids are present in the continuous phase while granule hydration proceeds, hydrocolloid concentration increases, yielding a drastic increment in the viscosity of the continuous medium [17]. Besides, hydrocolloids are also capable of enhancing adhesive interactions between gelatinized starch granules which would be responsible for an increase in viscosity [18].

In this way, differences observed between samples with and without NaCl would be related to the interactions that each type of hydrocolloid could establish with the other components in these conditions. Samples without NaCl showed viscoamylograms comparable to the control sample when MCC, HPMCs and pectins were added. CMC–flour systems showed higher viscosities, which would indicate a strong hydration and interaction with other components like

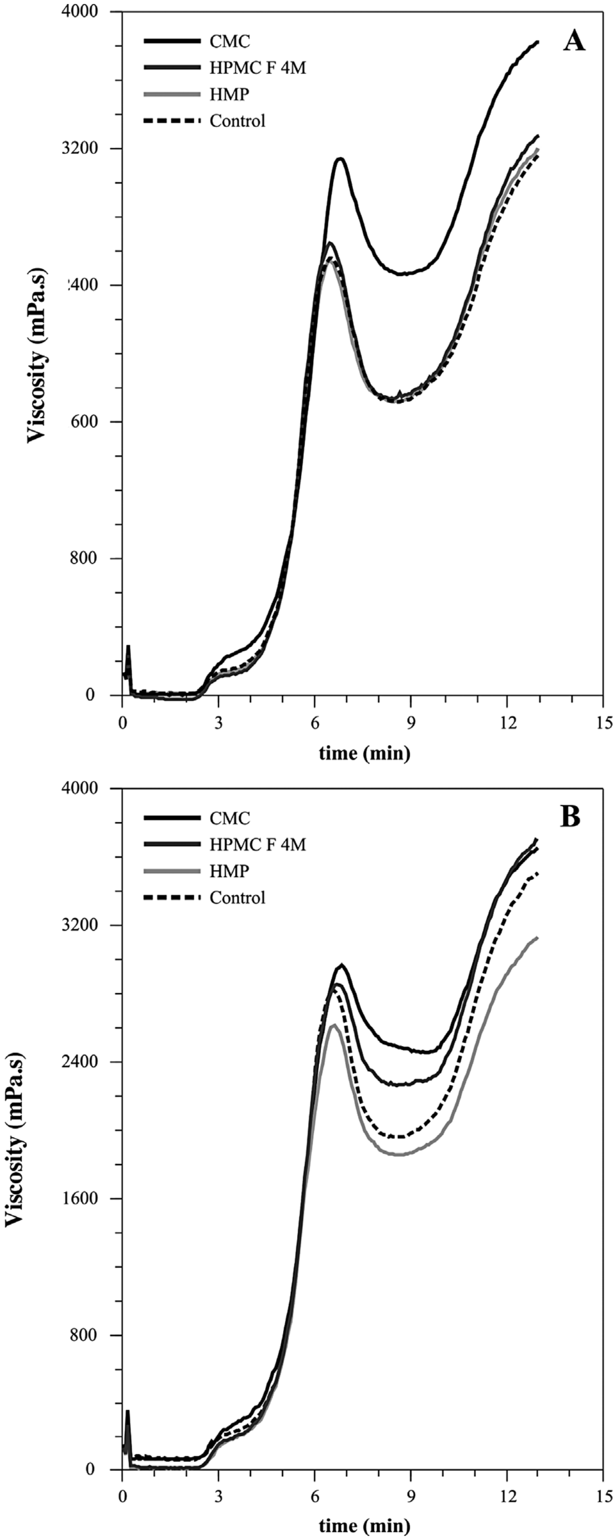

Figure 1. RVA profiles of flour–hydrocolloids mixtures (CMC, HPMC F 4 M and HMP) (A) without NaCl and (B) with NaCl (2%).

amylose and proteins. Since flour proteins are positively charged in solution, these interactions could be mainly electrostatic.

It is known that NaCl promotes hydrophobic interaction [19]. Thus, the presence of this salt in the continuous phase could promote interactions between HPMC chains and between HPMCs and proteins. Since it is well-known that HPMCs present thermogelation when submitted to a heating program [20], an increment in the viscosity with respect to the control could be expected. Nevertheless, this was verified only in the case of HPMC F 4 M, which presents a higher substitution level and a higher MW. Also, in the presence of NaCl, electrostatic shielding could occur which could explain the higher viscosity obtained when CMC and MCC (results not shown) were employed. In the last case, since MCC is copolymerized with 12% CMC, CMC would significantly contribute to system viscosity.

The effect of NaCl and hydrocolloid addition on RVA parameters and the interaction between these added components were evaluated by two-way ANOVA. The effect of both factors and their interaction between each other was found to be significant ($p < 0.05$) in all parameters. Pasting temperature (T_{pa}) is the temperature at which the starch granule starts to swell, evidenced by an increment in the viscosity. Systems consisting of flour–hydrocolloid mixtures without NaCl exhibited T_{pa} values between 66.2 and 66.9°C, whereas in the presence of NaCl, T_{pa} values ranged between 67.4 and 69.3°C. However, no significant differences were found in the pasting temperature among samples with hydrocolloids addition.

In Fig. 2 η_p, breakdown, setback from peak and setback from minimum of flour and flour–hydrocolloid mixtures without NaCl are shown. Peak viscosity is a parameter related to the starch water absorption capacity and granule fragility [21] and it showed different behaviour depending on the type of hydrocolloid used. A significant increment in η_p was observed when MCC and CMC were used, but η_p was not affected by HPMCs. On the other hand, although LMP decreased η_p with respect to the control, no significant differences were found when HMP was added. Christianson [22] postulated that the effect of hydrocolloids on η_p is due to interactions among gums, amylose and solubilized amylopectin molecules of low MW and the thickener effect of hydrocolloids. In the case of the mixture with LMP, the reduction of η_p could be attributed to a restricted granule swelling or amylose leaching. The breakdown value (η_p-η_{min}) is a measure of the degree of disintegration of starch granules and is related to paste stability to heat and shear. This parameter reached a minimum value when CMC was used, whereas no significant differences were found when the other hydrocolloids were applied. This is indicative of a higher stability, achieved when CMC is added to flour. The ability of a paste to resist heating and shear stress is an important factor for many industrial processes.

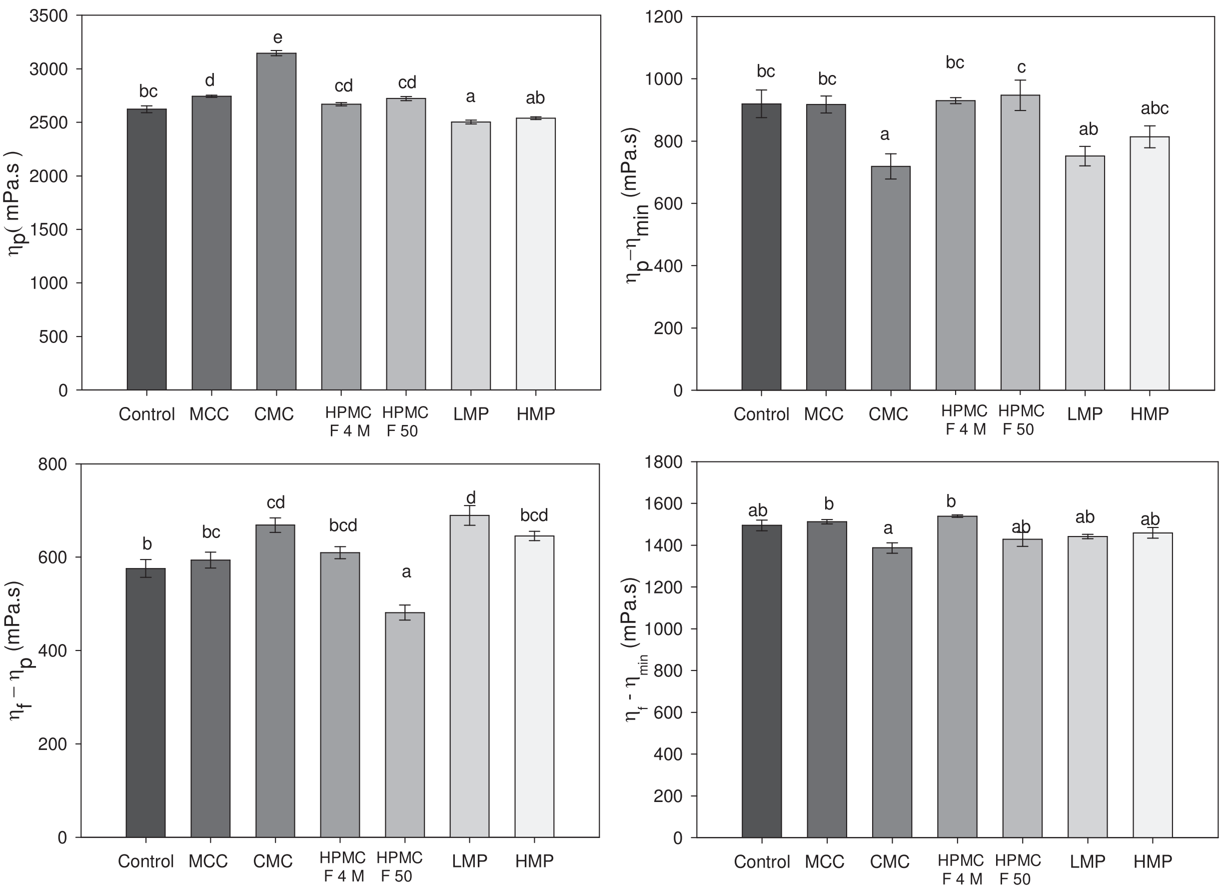

Figure 2. Viscoamylographic parameters of wheat flour–hydrocolloid blends without NaCl. Different letters indicate significant differences among samples ($p < 0.05$). Error bars indicate standard error.

During the stages of cooling and holding at 50°C, the leached amylose molecules can aggregate and junction zones are created [23]. Thus, the formed network retains water and fragmented starch granules and is responsible for the final viscosity reached by the system. The setbacks from minimum (η_f-η_{min}) and from peak (η_f-η_p) allow evaluation of the retrogradation tendency of each system. Although the setback from minimum was not affected by modified celluloses or pectins, the setback from peak was increased by CMC and LMP and decreased by HPMC F 50.

In Fig. 3, RVA parameters of mixtures with hydrocolloids and NaCl are shown. In general, salt addition led to higher η_p values than samples without it. Among samples with celluloses and NaCl, a significant increment with respect to the control was observed with CMC. On the other hand, water binding capacity of starch mixtures seems to be reduced by pectin addition since lower η_p values were obtained. Hot pastes incorporating MCC, CMC, HPMC F 4 M and LMP reached lower breakdown values. This suggests that these hydrocolloids, in presence of NaCl, promoted the stabilization of the hot paste undergoing mechanical stress. The setback from peak was increased by MCC and HPMC F 4 M and it was decreased by HMP. Finally, the setback from minimum was decreased by CMC and both pectins.

According to these results, viscoamylographic profiles were more affected by hydrocolloids in the presence of NaCl. As commented previously, this effect could be in part related to the fact that gluten proteins are hydrated and unfolded when submitted to mechanical energy and heat and they would be able to interact diversely with hydrocolloids. The retrogradation tendency of flour–hydrocolloids mixtures could be evaluated by setback from minimum, since it reflects the change in viscosity between the hot paste and the gel formed after cooling. When CMC and pectins were present with NaCl, a protective effect was observed with respect to retrogradation, but only a scarce effect was observed with HPMCs in the same environment. The latter observation is most likely due to the amylose–amylose interactions dominating the HPMC–amylose interactions, since the setback from minimum reflects a viscosity enhancement that is due to amylose chains. This could be attributed to steric hindrance or higher hydrophobicity of the HPMCs chains.

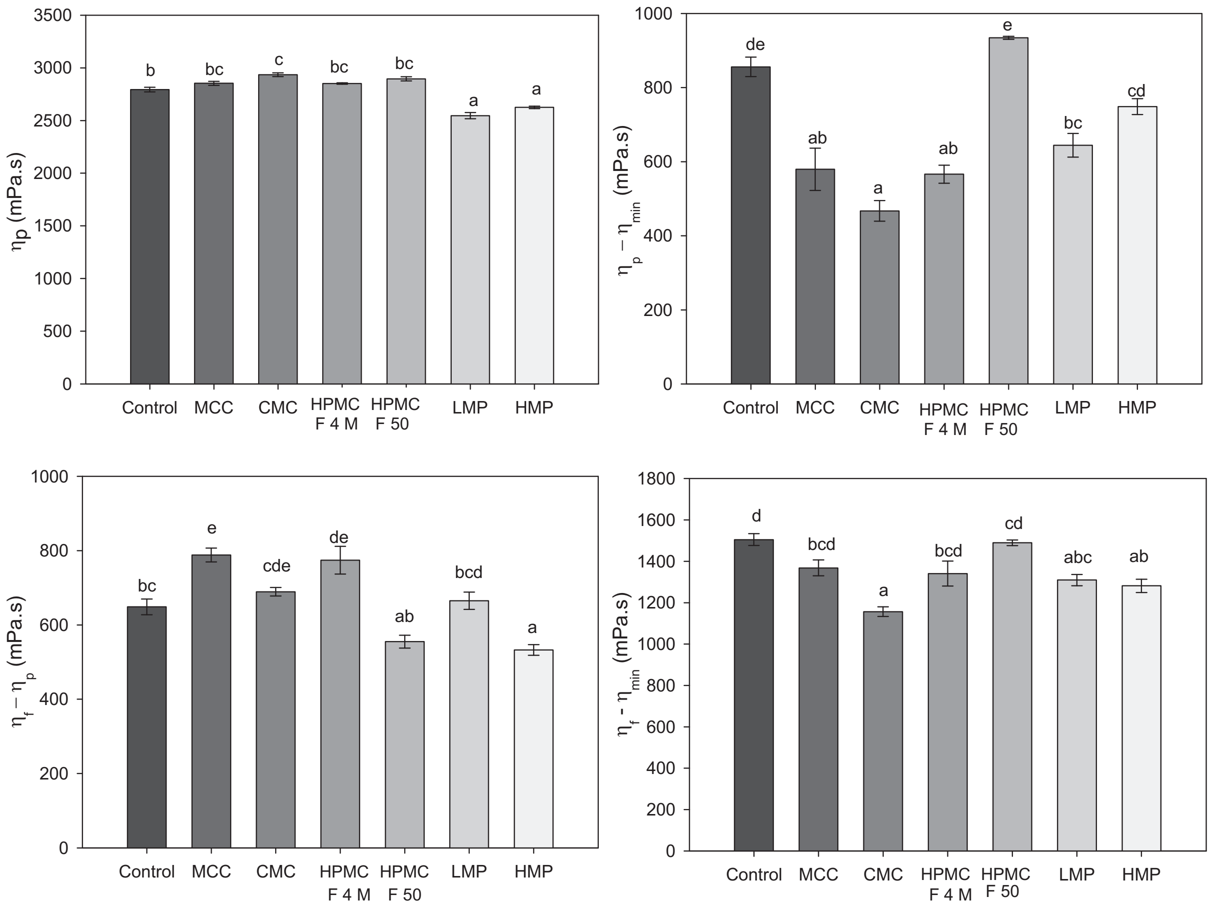

Figure 3. Viscoamylographic parameters of wheat flour–hydrocolloid blends with NaCl (2%). Different letters indicate significant differences among samples ($p < 0.05$). Error bars indicate standard error.

3.2 Wheat flour–hydrocolloid systems at low water level: Analysis by DSC measurements

3.2.1 Thermal transitions in model systems with wheat starch

To analyse the behaviour in systems without gluten proteins, wheat starch–hydrocolloid samples at low water content were assayed. Starch gelatinization exhibited two endothermic peaks and at higher temperatures a third endothermic peak associated with ALC dissociation was observed. In general, the thermogram pattern was not affected by the use of hydrocolloids while salt addition shifted the whole profile to higher temperatures.

In Table 2, ΔH, T_o, peak temperatures (T_{p1},T_{p2}) and T_c of starch–hydrocolloid blends in the presence and absence of salt are shown. A two way analysis of variance showed a significant effect ($p < 0.05$) of NaCl addition on T_o, T_{p1}, T_{p2} and T_c, whereas, hydrocolloid addition led to a significant effect on T_{p2}, T_c and ΔH.

In model systems without NaCl, neither modified celluloses nor pectins largely affected starch gelatinization. Although when CMC was used, a significant increase of ΔH was observed. In general, model systems with NaCl exhibited higher T_o, T_p, and T_c with respect to samples without it. Water mobility and its capability to act in the gelatinization process decrease when NaCl is present, thus a shift to higher temperatures is observed [24, 25]. Since NaCl competes with starch for water, the addition of salt led to a reduction in the amount of available water for the gelatinization process.

In model systems with NaCl, hydrocolloids did not largely affect gelatinization which would indicate that water levels were high enough. With the exception of MCC, all hydrocolloids led to a significant decrease in T_{p2} values with respect to the control. Besides, ΔH was significantly enhanced by HMP addition. It is interesting to remark that when NaCl and hydrocolloids are used together, the increase in T_c is lower than the increase found when NaCl is added alone (control). Probably, some type of NaCl–hydrocolloid interaction occurs which favours water availability for starch gelatinization.

Water molecules form a hydrogen bonded network leading to both open low density and condensed zones. Hydrophobic surfaces favour the expanded low density

Table 2. Gelatinization in starch–hydrocolloids mixtures

Sample	T_o (°C)	T_{p1} (°C)	T_{p2} (°C)	T_c (°C)	ΔH (J/g starch)
Without NaCl					
Control	52.2 ± 0.9^{a}	59.9 ± 0.2^{a}	88.1 ± 0.0^{a}	99.4 ± 0.3^{ab}	11.3 ± 0.2^{a}
MCC	52.9 ± 0.8^{a}	60.2 ± 0.1^{a}	88.3 ± 0.2^{a}	99.0 ± 1.4^{ab}	11.2 ± 0.6^{ab}
CMC	53.1 ± 0.8^{a}	60.6 ± 0.6^{a}	86.3 ± 0.3^{a}	96.8 ± 1.4^{a}	14.0 ± 0.6^{b}
HPMC F 4 M	53.1 ± 0.2^{a}	60.3 ± 0.5^{a}	88.1 ± 0.5^{a}	98.4 ± 0.5^{ab}	11.9 ± 0.6^{ab}
HPMC F 50	53.3 ± 0.3^{a}	60.5 ± 0.0^{a}	87.6 ± 1.4^{a}	97.9 ± 0.2^{ab}	11.7 ± 0.2^{ab}
LMP	54.5 ± 0.5^{a}	61.5 ± 0.9^{a}	87.9 ± 2.0^{a}	97.3 ± 0.2^{a}	11.7 ± 1.7^{ab}
HMP	54.1 ± 0.1^{a}	61.0 ± 0.3^{a}	89.7 ± 0.1^{a}	101.8 ± 1.9^{b}	10.6 ± 0.5^{a}
With NaCl					
Control	58.1 ± 0.1^{a}	67.5 ± 0.4^{a}	100.0 ± 0.9^{b}	112.5 ± 0.5^{a}	10.8 ± 0.2^{ab}
MCC	57.6 ± 0.5^{a}	66.7 ± 0.9^{a}	100.2 ± 0.5^{b}	111.1 ± 1.6^{a}	10.7 ± 0.6^{ab}
CMC	57.7 ± 0.0^{a}	67.0 ± 0.8^{a}	95.4 ± 0.3^{a}	108.7 ± 0.7^{a}	11.9 ± 0.4^{abc}
HPMC F 4 M	58.4 ± 0.6^{a}	67.5 ± 1.7^{a}	92.8 ± 0.9^{a}	108.2 ± 0.9^{a}	10.3 ± 0.0^{a}
HPMC F 50	58.5 ± 0.2^{a}	65.8 ± 0.2^{a}	93.2 ± 0.7^{a}	107.5 ± 1.1^{a}	12.1 ± 0.6^{bc}
LMP	58.0 ± 0.5^{a}	66.7 ± 0.0^{a}	95.1 ± 0.0^{a}	109.8 ± 0.7^{a}	12.1 ± 0.1^{bc}
HMP	58.2 ± 0.9^{a}	66.2 ± 0.5^{a}	93.2 ± 0.6^{a}	108 ± 1.9^{a}	12.6 ± 0.1^{c}

±SD. Different superscript letters within a column indicate significant differences within each group (without or with NaCl) ($p < 0.05$).

structure, whereas charged molecules like pectins and CMC create a zone of high density water around which a contiguous layer of low density water forms [26]. Chaotropic ions bind weakly with water and tend to be settled in areas of low density water, while highly charged kosmotropes bind more strongly with water and are located in zones of high density water. Sodium and chloride ions have an intermediate behaviour on the Hofmeister series, thus these ions could be located near both types of macromolecules. The creation of an ion gradient induced by hydrocolloids could allow higher water availability for gelatinization. So, though NaCl causes a shift to higher temperatures of gelatinization when hydrocolloids are present, there is an attenuation of this effect.

The endotherm associated with ALC (Table 3) was significantly affected by NaCl and hydrocolloid addition. Among model systems without NaCl, there were no significant differences found in the enthalpy values or onset temperature, though in the latter, a tendency to higher values was observed. The addition of CMC, HPMC F 4 M and LMP led to a decrease in peak temperature and CMC also caused a decrease in T_c. In general, model systems with NaCl exhibited higher T_o, T_p and T_c than model systems without it. The use of hydrocolloids seems to attenuate this effect, since

Table 3. Amylose–lipid complex dissociation in model systems and dough

	Model systems			Dough		
Sample	T_o (°C)	T_p (°C)	T_c (°C)	T_o (°C)	T_p (°C)	T_c (°C)
Without NaCl						
Control	107.8 ± 2.8^{a}	119.51 ± 0.4^{c}	126.7 ± 0.6^{b}	99.4 ± 1.6^{a}	112.4 ± 0.3^{a}	119.5 ± 0.6^{a}
MCC	111.1 ± 0.1^{a}	119.2 ± 0.4^{abc}	128.9 ± 1.1^{b}	98.4 ± 1.8^{a}	112.6 ± 0.2^{a}	119.4 ± 0.3^{a}
CMC	108.7 ± 0.2^{a}	117.1 ± 0.3^{a}	123.6 ± 1.8^{a}	99.3 ± 2.8^{a}	112.4 ± 0.7^{a}	119.4 ± 1.6^{a}
HPMC F 4 M	109.1 ± 1.2^{a}	118.1 ± 1.2^{ab}	125.8 ± 0.4^{ab}	98.4 ± 2.3^{a}	110.8 ± 0.5^{a}	118.3 ± 0.7^{a}
HPMC F 50	109.1 ± 1.1^{a}	118.2 ± 0.3^{abc}	126.5 ± 0.6^{ab}	96.5 ± 0.7^{a}	110.9 ± 0.7^{a}	118.6 ± 0.6^{a}
LMP	110.1 ± 1.3^{a}	117.8 ± 0.7^{ab}	125.8 ± 1.1^{ab}	100. 4 ± 1.7^{a}	113.4 ± 1.6^{a}	119.4 ± 0.9^{a}
HMP	111.2 ± 0.6^{a}	120.6 ± 0.0^{c}	128.3 ± 0.3^{b}	100.8 ± 0.6^{a}	113.6 ± 0.3^{a}	120.9 ± 0.2^{a}
With NaCl						
Control	118.3 ± 0.4^{b}	126.6 ± 0.6^{b}	134.8 ± 0.4^{b}	107.4 ± 1.3^{a}	117.0 ± 0.3^{b}	124.6 ± 0.8^{b}
MCC	118.3 ± 0.2^{b}	126.6 ± 0.7^{b}	132.5 ± 1.1^{b}	105.9 ± 0.9^{a}	116.0 ± 0.6^{ab}	122.4 ± 0.3^{ab}
CMC	113.0 ± 0.9^{ab}	124.0 ± 0.6^{a}	132.3 ± 0.0^{a}	105.8 ± 1.7^{a}	117.1 ± 0.4^{b}	124.2 ± 0.1^{b}
HPMC F 4 M	114.3 ± 2.4^{ab}	124 ± 0.1^{a}	132.6 ± 1.4^{a}	104.9 ± 1.0^{a}	115.2 ± 0.7^{a}	121.9 ± 0.9^{a}
HPMC F 50	112.9 ± 2.1^{ab}	122.7 ± 0.2^{a}	131.0 ± 1.2^{a}	105.3 ± 0.7^{a}	116.6 ± 0.2^{ab}	124.0 ± 0.2^{ab}
LMP	113.9 ± 0.0^{ab}	123.8 ± 0.4^{a}	132.8 ± 0.5^{a}	105 ± 1.0^{a}	115.9 ± 0.6^{ab}	122.4 ± 0.4^{ab}
HMP	111.6 ± 0.1^{a}	122.6 ± 0.5^{a}	131.5 ± 0.3^{a}	105.5 ± 0.3^{a}	116.3 ± 0.4^{ab}	122.7 ± 1.3^{ab}

±SD. Different superscript letters within a column indicate significant differences within each group (without or with NaCl) ($p < 0.05$).

a tendency to lower T_o was observed. Also, with the exception of MCC, hydrocolloid use results in the decrease of T_p and T_c with respect to the control. On the other hand, ΔH_{AL} values were not affected by hydrocolloid presence.

3.2.2 Thermal transitions in dough

The effect of hydrocolloid addition on starch gelatinization was also studied in wheat dough. The transition is more complex to study in doughs, since additional interactions are established among the starch, hydrocolloids and flour components [27].Two endotherms were obtained for doughs with and without NaCl, during the gelatinization transition. In Table 4 gelatinization parameters for both types of doughs are shown. The two-way ANOVA showed that both the type of hydrocolloid and the presence of NaCl, led to a significant effect ($p < 0.05$) on T_0, T_{p1}, T_{p2} and T_c.

In doughs without NaCl, the addition of hydrocolloids led to insignificant differences in gelatinization parameters. Although, when HPMC F4M was added, a trend towards lower T_c and higher ΔH was found. On the other hand, for all hydrocolloid addition cases including NaCl, a significant decrease in T_c and a tendency to lower T_{p2} and higher ΔH were observed, as was the case in the model systems.

From the comparison between the results obtained for the model systems and the doughs (Tables 2 and 4) arises the effect caused by the presence of flour proteins. Doughs without NaCl exhibited higher T_o and T_{p1} and lower ΔH than similar model systems. Several authors have stated that gluten affects gelatinization since water can migrate from starches to proteins [28–30].

On the other hand, doughs exhibited lower T_{p2} and T_c values than model systems. This could be attributed to the rapid collapse of the gluten network covering the starch granules after the onset of gelatinization. Such a collapse would reduce the stability conferred by the gluten network [30]. The gelatinization range for the model systems without NaCl was between 42.8 and 47.7°C, whereas for the dough it was between 34.9 and 38.5°C. The model systems containing NaCl presented a gelatinization range between 49.0 and 54.4°C, while the dough was between 36.9 and 40.6°C. Thus, a narrower gelatinization range was obtained for doughs, showing that starch gelatinization is facilitated. A comparable behaviour was observed between model systems and doughs with salt. So, in general, doughs exhibited higher onset and T_{p1}values and lower T_{p2}, T_c and ΔH than the model systems.

Amylose–lipid complexes are of interest to the food industry since they are able to modify the properties and functionality of starch [21]. Regarding the ALC transition, the two-way ANOVA showed that the presence of NaCl led to a significant effect on T_o, T_p and T_c and also on ΔH_{AL}, whereas the addition of hydrocolloids significantly affected and ΔH_{AL}. In general, the dissociation of ALC in dough was not affected by hydrocolloid addition, whereas a shift to higher temperatures was observed when NaCl was added (Table 3). However, doughs with NaCl and CMC, HPMC F 4 M, LMP or HMP addition showed an increase of ΔH_{AL}.

3.2.3 Thermal transitions during storage

Amylopectin retrogradation and ALC dissociation after 0 and 7 days of storage were determined. The addition of neither LMP nor HMP significantly affected amylopectin retrogradation in crumb like samples since no significant differences were found with respect to the control. The retrogradation index (RI) for the control was 37.2, while both samples with pectins exhibited RI = 38.4. In a previous work

Table 4. Gelatinization in wheat dough with modified celluloses and pectins

Sample	T_o (°C)	T_{p1} (°C)	T_{p2} (°C)	T_c (°C)	ΔH (J/g starch)
Without NaCl					
Control	57.7 ± 0.5^{abc}	66.2 ± 0.0^{ab}	86.6 ± 0.8^{ab}	95.3 ± 1.2^{ab}	7.8 ± 0.6^{a}
MCC	57.5 ± 0.2^{ab}	66.6 ± 0.1^{ab}	84.8 ± 0.3^{ab}	94.4 ± 0.0^{ab}	8.3 ± 0.1^{a}
CMC	58.2 ± 0.6^{abc}	67.3 ± 0.9^{ab}	86.1 ± 0.8^{ab}	94.7 ± 0.5^{ab}	7.5 ± 0.6^{a}
HPMC F 4 M	56.6 ± 0.5^{a}	65.1 ± 0.0^{a}	84.1 ± 1.1^{a}	91.5 ± 0.2^{a}	8.7 ± 0.3^{a}
HPMC F 50	58.7 ± 0.3^{bc}	67.8 ± 0.6^{b}	85.7 ± 0.2^{ab}	94.9 ± 0.4^{ab}	7.7 ± 0.5^{a}
LMP	59.7 ± 0.2^{c}	68.1 ± 0.6^{b}	87.5 ± 0.3^{b}	96.5 ± 1.9^{b}	7.3 ± 0.5^{a}
HMP	58.9 ± 0.6^{bc}	67.9 ± 0.4^{b}	87.6 ± 0.4^{b}	97.4 ± 0.3^{b}	8.0 ± 0.9^{a}
With NaCl					
Control	62.3 ± 0.7^{b}	72.7 ± 1.2^{a}	92.4 ± 0.5^{a}	102.9 ± 0.8^{d}	6.9 ± 0.8^{a}
MCC	61.0 ± 0.7^{ab}	71.2 ± 0.2^{a}	90.5 ± 0.4^{a}	98.2 ± 0.3^{ab}	8.2 ± 0.6^{ab}
CMC	59.8 ± 0.5^{a}	72.4 ± 0.8^{a}	92.4 ± 0.3^{a}	100.1 ± 0.8^{c}	8.6 ± 0.4^{ab}
HPMC F 4 M	60.8 ± 1.0^{ab}	71.6 ± 0.4^{a}	89.6 ± 0.6^{a}	98.0 ± 0.6^{a}	8.5 ± 0.8^{ab}
HPMC F 50	60.8 ± 0.7^{ab}	71.1 ± 1.2^{a}	90.8 ± 0.9^{a}	99.9 ± 1.0^{bc}	7.8 ± 0.3^{ab}
LMP	61.0 ± 0.7^{ab}	72.4 ± 0.5^{a}	90.6 ± 1.6^{a}	98.9 ± 0.5^{abc}	8.9 ± 0.6^{b}
HMP	61.8 ± 0.8^{ab}	71.9 ± 0.4^{a}	90.8 ± 0.8^{a}	98.7 ± 0.4^{abc}	7.5 ± 0.5^{ab}

±SD. Different superscript letters within a column indicate significant differences within each group (without or with NaCl) ($p < 0.05$).

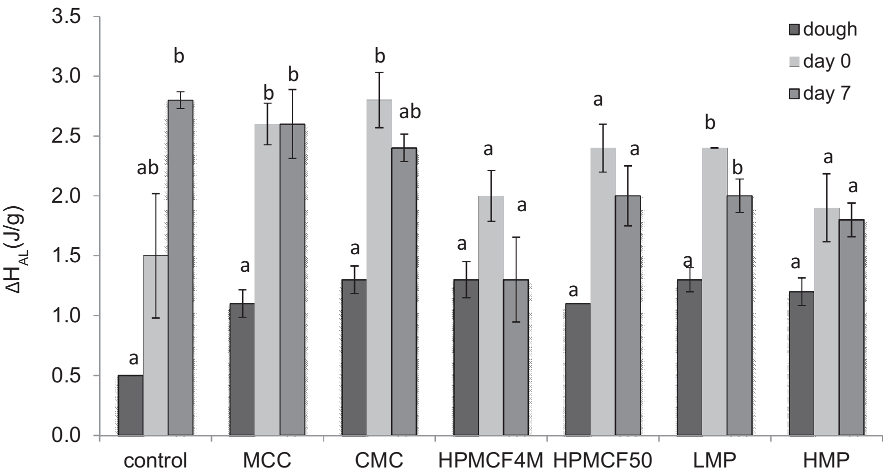

Figure 4. Enthalpy values of amylose–lipid complex dissociation in raw dough, dough after baking (crumb) (day 0) and crumb after storage (day 7). Different letters indicate significant differences among each type of sample ($p < 0.05$). Error bars indicate standard error.

[31] amylopectin retrogradation in samples with modified celluloses was studied, showing little effect from hydrocolloids. Breads with HPMC F 4 M after 7 days of storage exhibited the highest RI (59.3), whereas no significant differences were found for samples with 1.5% HPMC F 50, MCC or CMC respect to control (RI = 37.2). Thus, the incidence of hydrocolloids on amylopectin retrogradation seems to be low. Since amylopectin remains inside the granule till after the baking, hydrocolloid incidence on retrogradation could be in relation with the effect on the surrounding matrix.

The dissociation of ALC was studied after the simulated baking and 7 days of storage at room temperature (Fig. 4). RI positively correlated with ΔH_{AL} at the seventh day of storage. During storage, the amount of ALC was not significantly modified by hydrocolloids, though a tendency to lower values was observed in some cases (HPMC F 4 M, HPMC F 50, HMP). Purhagen et al. [32] found the same effect in breads stored for seven days and they attribute the decrease in enthalpy to a change in the structure of the ALC that resulted in a less detectable form.

4 Conclusions

Viscoamylograms (RVA) showed that hydrocolloids have a more marked effect on pasting and gelation of starch when NaCl is present. In this case, lower breakdown values were obtained with MCC, CMC, HPMC F 4 M and LMP suggesting a lesser degree of disintegration of starch granules and higher paste stability to heat treatment and mechanical stress. Besides, CMC and pectins showed an inhibitory effect on amylose retrogradation.

Gelatinization under limited water conditions studied by DSC showed a shift to higher temperatures when NaCl was added to starch or wheat flour samples. However, in both samples the addition of hydrocolloids minimizes or compensates this effect since T_c in samples with hydrocolloids was lower than the control. In general, a narrower gelatinization range was observed in doughs and a higher ΔH was found in the model systems. Finally, ALC transitions in absence of salt showed little effect of hydrocolloids, while when NaCl and hydrocolloids were added, lower T_c and higher enthalpy values were obtained.

Starch thermal transitions were modified by hydrocolloid addition in different manners depending on water amount, degree of granule disruption and the presence of NaCl and other flour components like proteins. A more pronounced effect was observed in water excess and stirring (RVA), probably related to the greater granule disruption and the leach of amylose that lead to more interaction among components than in DSC assays. Both in RVA assays and DSC assays, samples without NaCl exhibited little effect of hydrocolloid addition indicating that this salt would act as a promoting agent on starch–hydrocolloid interactions.

The authors would like to thank Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for the funds and fellowships granted, the University of La Plata (UNLP) for the economic support and Dow Chemical Co. and Latinoquímica Amtex (Argentina) for gum donations. The authors are thankful to Dr. Carla Brites from the Instituto Nacional de Investigação Agrária e Veterinária (INIAV)–Unidade Tecnologia Alimentar (Oeiras, Portugal) for her kind support on RVA assays. The authors want to thank to Christopher Young, Facultad de Ingenieria UNLP, for his kind revision of English use in our work.

The authors have declared no conflict of interest.

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