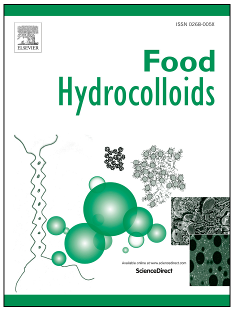

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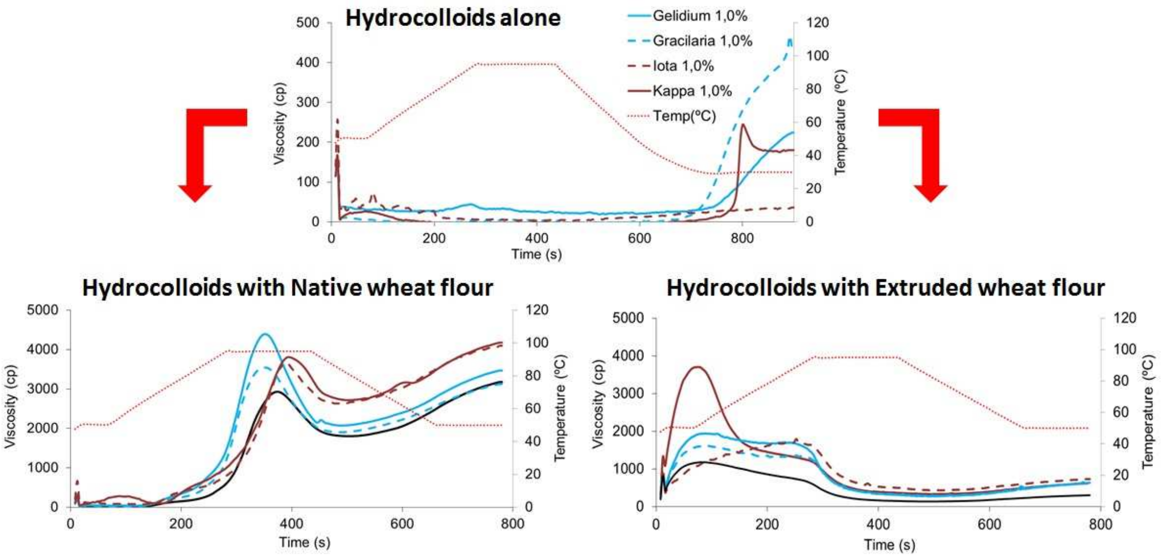
Hydrocolloids alone
Gelidium 1,0%
Gracilaria 1,0%
Iota 1,0%
Kappa 1,0%
Temp(ºC)
Viscosity (cp)
Temperature (ºC)
Time (s)
0
100
200
300
400
500
0
20
40
60
80
100
120
0
200
400
600
800
Hydrocolloids with Native wheat flour
Viscosity (cp)
Temperature (ºC)
Time (s)
0
1000
2000
3000
4000
5000
0
20
40
60
80
100
120
0
200
400
600
800
Hydrocolloids with Extruded wheat flour
Viscosity (cp)
Temperature (ºC)
Time (s)
0
1000
2000
3000
4000
5000
0
20
40
60
80
100
120
0
200
400
600
800

Influence of marine hydrocolloids on extruded and native wheat flour pastes and gels

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Abstract

Extruded and native wheat flours were combined with agars (*gracilaria* and *gelidium*) and carrageenans (κ-carrageenan and ι-carrageenan) to modify their paste and gel properties. Combinations of extruded flours with hydrocolloids produced an increase in the hydration properties (swelling volume and water holding and water binding capacities). All hydrocolloids (particularly ι-carrageenan) also produced an increase in hydration properties after combination with native flours. With regard to the pasting properties of native flours combinations, all hydrocolloids produced an increase in peak viscosity (particularly *gelidium* agar), but only agars decreased the onset temperature of gelatinization and increased breakdown, indicating a different mechanism of action. In the presence of extruded flour, the incorporation of hydrocolloids increased the cold viscosity of flours in very different ways depending on the hydrocolloid. Both native and extruded flours exhibited higher G' and G'' values and a lower tanδ after the incorporation of carrageenans, which, together with the lower dependence on frequency, would produce stiffer and more stable pastes/gels. Based on gel properties, greatest hardness with native and extruded flours was achieved by the incorporation of carrageenans. In general, carrageenans, besides producing stiffer and more stable pastes, gave rise to harder and clearer gels compared to those made with agar, for both their combination with extruded and native wheat flours. Meanwhile, pastes made with combinations of extruded flours and agar showed higher thixotropy.

Keywords: agar; carrageenans; extruded flour; wheat flour; rheology; pasting properties

1 Introduction

Wheat flour is one of the most widely used ingredients both in the food industry and in cooking. Besides being the key ingredient in bread and other bakery products, where its proteins play a special role, wheat flour is used as thickening agent in numerous dishes. These thickening properties are based on the capacity of wheat starch granules to absorb water. When starch is heated in the presence of sufficient water, it eventually loses its crystalline structure, leading to an increase in the viscosity of starch pastes. This phenomenon is known as pasting. Further heating of the water-starch mixture leads to rupture of the starch granules and a fall in paste viscosity (breakdown). Finally, if a paste is cooled, hydrogen bonds develop between the amylose chains, creating a new crystalline structure that loses the absorbed water, causing a renewed increase in viscosity, a phenomenon known as retrogradation. These events constitute the basis for the use of starch and flour in the preparation of fillings, sauces, creams and dairy desserts, and other products.

Occasionally, the properties of native flours are not suitable for their use in certain products and they must be modified or supplemented with other ingredients or additives. Hydrothermal treatments can produce flours with different degrees of gelatinization, with greater thickening power after heating, or with no need for heating (Camire, Camire & Krumhar, 1990). Flours with the greatest degrees of gelatinization show notable thickening power in cold liquids. Particularly important among hydrothermal treatments that can be applied to flours for this purpose are drum drying and extrusion (Doublier, Colonna & Mercier, 1986).

Carrageenans and agar, together with alginates, are the marine hydrocolloids most commonly used in the food industry. Carrageenans are extracted from certain red seaweeds of the Rhodophyceae class, which have been extensively used in the food industry as thickening and gelling agents (Campo, Kawano, da Silva & Carvalho, 2009). The structure of carrageenan is based on a disaccharide backbone of alternating 3-linked β-D-galactopyranose and 4-linked α-D-galactopyranose units, named G and D units, respectively, in Knutsen's nomenclature (Knutsen, Mylabodski, Larsen, & Usov, 1994). Carrageenans are defined according to the position of sulphation (S) and the cyclization of the D units to form an anhydro ring (A). Carrageenans used in industry include the gelling κ-, ι-carrageenan and the non-gelling λ-carrageenan (Tischer, Noseda, Rilton de Freitas, Sierakowski & Duarte, 2006). The chemical structure of ι-carrageenan differs from that of κ-carrageenan by the presence of an additional sulphate group in the 3,6-anhydrogalactosyl residue, which makes the molecule more hydrophilic (Renn, 1997). The distinct textural properties of ι- and κ-carrageenan gels reflect the differences in their structures: ι-carrageenan gels consist of double helices with little or no aggregation, which renders them flexible and soft. In contrast, κ-carrageenan gels consist of aggregated helices,which do not gel without aggregation and the resulting gel relatively brittle and hard (Tischer, et al., 2006). Agar is extracted from seaweeds of the genera *Gelidium* and *Gracilaria* and is composed of agarose and agaropectin molecules. Agarose, responsible for the gelling properties of agar, is a linear compound formed of alternating β-D-galactopyranose and α-L-galactopyranose residues. Agaropectin has a similar structure but with a lower content of L-galactopyranose residues (Armisen, 1991). After solubilization in water, both agars and carrageenans have the property of forming reversible gels when they are cooled, and they are used extensively in the food industry as thickening and gelling agents.

Combinations of starch, or raw starchy ingredients, and hydrocolloids have been used in the food industry since the mid-twentieth century in order to achieve specific textures or to improve tolerance to certain processing conditions (heat, shear, and pH), and their interactions have therefore been studied extensively (BeMiller, 2011). Among the marine hydrocolloids, interactions between the carrageenans and starchy ingredients have received most attention. Tye (1988) observed that these interactions depend on the type of carrageenan and type of starch (native or gelatinized). Differences between the types of carrageenan have been also studied by Shi and BeMiller (2002) and by Eidam, Kulicke, Kuhn and Stute (1995), who observed that while κ-carrageenan, like other hydrocolloids, accelerated the gelation process, ι-carrageenan delayed it. However, interactions between carrageenans and wheat flour have not been investigated. Interactions between agar and flours have also received little attention and this has usually been limited to the study of interactions between agarose and different starches (Mohammed, Hember, Richardson & Morris, 1998; Lai, Huang & Lii, 1999).

Despite the particular physicochemical characteristics of extruded flours and their high potential as cold thickening agents, the properties of their pastes/gels in combination with hydrocolloids have never been studied, nor have they been compared with the pastes/gels of native flours. The objective of the present study was to investigate the effects of interactions between different types of agar (*Gracilaria* and *Gelidium*) and carrageenans (κ-carrageenan and ι-carrageenan) and wheat flours (native and extruded) on the properties of their pastes (hydration, pasting and rheological) and gels (textural and colorimetric) using Rapid Visco Analysis (RVA), hydration measurements, dynamic and steady shear measurements, and texture and colour analysis.

2 Materials and methods

2.1 Materials

Native wheat flour (11.73% moisture, 69.09µm particle size, 11.02% protein, 6.18% free sugars and 5.89% damaged starch) was supplied by Harinera Castellana (Medina del Campo, Valladolid, Spain). Hydrothermally modified wheat flour (11.20% moisture, 99.37µm particle size, 8.74% protein, 44.80% free sugars and 38.09% damaged starch) was provided by Harinera Los Pisones (Zamora, Spain), which performed the extrusion treatment using a Bühler Basf single screw extruder (Bühler S.A., Uzwil, Switzerland). The length to diameter (L/D) ratio for the extruder was 20:1. Wheat flour was extruded at a maximum barrel temperature of 160ºC with a feed rate of 500kg/h. The moisture content of this flour was 17% and the screw speed was 453rpm. The extruded product was dried by convection air and then ground with a compression roller to a particle size below 200 microns. Flours were stored in airtight plastic containers at 4°C until analysis.

Gelidium agar RG-ST and *Gracilaria* agar RGM-900 were supplied by (ROKO, Galicia, Spain). κ-carrageenan Ceamgel 1860 (with potassium chloride) and ι-carrageenan Ceamvis 3383 were supplied by (Ceamsa, Pontevedra, Spain)**.**

2.2 Methods

Samples used in the different tests were prepared by addition, in order to compare a 100% flour paste/gel to one made with 100% flour with a 7.14% and a 10.71% of hydrocolloid addition (flour basis) for pastes and gels making respectively. Hydrocolloid powder and flour were mixed and added jointly to water; the suspension was then heated.

2.2.1. Hydration properties

Hydration properties include swelling volume (SV), water holding capacity (WHC) and water binding capacity (WBC) (Nelson, 2001). Swelling volume (SV), or the volume occupied by a known weight of the mix, was evaluated by adding 100ml of distilled water to 5g (±0.1g) of flour with 0.357g (±0.001g) of hydrocolloid and allowing it to hydrate for 16h. Water holding capacity, defined as the amount of water retained by the sample without being subjected to any stress, was determined on the same suspension used to evaluate swelling; the hydrated solid was weighed after removing the excess of water and values were expressed as grams of water per gram of solid. Water binding capacity (WBC), or the amount of water retained by the sample after it has been centrifuged, was measured as described in method 56-30 (AACC, 2012), using 5g (±0.1g) of flour mixed with 0.357g (±0.01g) of hydrocolloid before the addition of distilled water. Hydration properties were analysed twice.

2.2.2. Pasting properties

Pasting and paste properties of the normal and extruded flours were determined in the presence and absence of the hydrocolloids using a Rapid Visco Analyser (Model RVA-4C, Newport Scientific Pty. Ltd., Warriewood, Australia).

The flour-only slurry was prepared by dispersing 3.5g (±0.1g) of the flour in 25g (±0.1g) of distilled water. When hydrocolloids were used, the mix of flour (3.5±0.1g) and hydrocolloid powder 0.25g (±0.01g) were thoroughly dry blended prior to slurrying in water. The slurries were then poured into aluminium canisters and stirred manually using plastic paddles for 20s before pouring into the RVA machine. The heating and cooling cycles were programmed following general pasting method 61.02.01 (AACC, 2012). The slurry was held at 50ºC for 1 min, then heated to 95ºC and held at that temperature for 2 min 30 s. It was subsequently cooled to 50ºC and held at that temperature for 2 min, while maintaining a rotation speed of 160 rpm. When pasting and paste properties of the hydrocolloids alone in distilled water were performed, pastes were cooled to 30ºC and held at that temperature for 2min 30s in order to assist the gelation process of the hydrocolloids. All measurements were performed in duplicate.

2.2.3. Rheological measurements

Dynamic viscoelastic and steady flow properties of the freshly prepared pastes of flour alone and flour–hydrocolloid mixtures obtained from pasting in the RVA were performed using a rheometer (Haake RheoStress 1, Thermo Fischer Scientific, Scheverte, Germany) with a titanium parallel serrated plate geometry sensor PP60 Ti (60 mm diameter, and 3 mm gap). The sample was placed into the rheometer which was stabilized at 50ºC and was covered with Panreac vaseline oil (Panreac Química S.A., Castellar del Vallés, Spain) to avoid drying. The pastes were rested for 500s before the test was started. Two dynamic viscoelastic measurements were made: (1) deformation sweeps at a constant frequency (1 Hz) to determine the maximum deformation attainable by a sample in the linear viscoelastic range, and (2) frequency sweeps over a range of 0.01–100 Hz at a constant deformation within the linear viscoelastic range. The storage modulus (G’), loss modulus (G’’) and loss factor ($\tan \delta = G''/G'$) as a function of frequency (ω) were obtained.

Steady-flow tests were also performed on freshly prepared paste samples at 50ºC to obtain shear rate versus shear stress data. The plate was programmed to increase the shear rate from 0.06 to 500s^{-1} (up curve) over 400s immediately followed by a reduction from 500 to 0.06s^{-1} over 400s (down curve). Data from the up curve of the shear cycle were used to characterize the flow of the paste samples and to estimate the power law parameters by application of the equation $\sigma = K.\gamma^{n}$, where σ is the shear stress (Pa), γ is the shear rate (s^{-1}), K is the consistency coefficient (Pa.s^{n}), and n is the dimensionless flow behaviour index. In addition, the area between the up and down curves was calculated in order to obtain the thixotropic behaviour of samples. All measurements were made in duplicate in both rheological tests.

2.2.4 Gel preparation

Hydrocolloid gels were made using a 1L beaker, dispersing 9g (±0.1g) of hydrocolloid and 84g (±0.1g) of flour into 600g of distilled water. Hydrocolloid solutions were heated to boiling (95ºC) on a heater plate at a constant stirring speed in order to achieve sufficient hydration and homogenous dispersions. Samples were held at boiling temperature for 15 min. During heating, the beaker was cover with plastic film with small orifices to avoid water loss due to evaporation. Hydrocolloid solutions were poured into cylindrical containers (35 mm internal diameter, 65 mm height), then allowed to rest at room temperature for 25min and were stored in a fridge at 4ºC for 24 hours to achieve gel stabilization. Each gel was made in triplicate.

2.2.5 Gel texture and colour

Samples (≈25g) were taken from the fridge and maintained at room temperature (≈25ºC) for 1 h prior to colour and texture measurement. Texture measurements of the prepared gels were performed at room temperature (≈25ºC) using a TA.XT2i Texture Analyzer (Stable Micro Systems Ltd., Surrey, UK) equipped with Texture Expert version 1 software for Windows; a 5kg load was used for force calibration. One compression cycle was applied using a 25mm-diameter cylindrical probe (P25a) at a constant crosshead velocity of 0.5mms^{-1} to a sample depth of 10mm, followed by a return to the original position. The force-time curve thus obtained was used to calculate the values of the texture attributes: hardness (the peak force observed during the compression cycle) and breaking strain (strain to reach the highest value of force).

Gel colour was measured using a Minolta CN-508i spectrophotometer (Minolta Co., Ltd, Osaka, Japan). Results were expressed in the CIE L*a*b* colour space and were obtained using standard illuminant D65 with the 2° standard observer. Colour and texture determinations were performed in triplicate.

2.2.6 Statistical analysis

Differences between the parameters for the gels were studied by analysis of variance (one-way ANOVA). Fisher’s least significant difference (LSD) was used to describe means with 95% confidence intervals. The statistical analysis was performed using the Statgraphics Plus V5.1 software (Statpoint Technologies, Inc., Warrenton, USA).

3. Results and discussion

3.1. Hydration properties

The hydration properties of the flours and of their mixtures with hydrocolloids are shown in table 1. In general, extruded flours and their combinations showed a higher WHC, SV and WBC; the differences were significant for all combinations except those with ι-carrageenan. Camire et al. (1990) proposed that the rupture of starch granule integrity that occurs during gelatinization in the extrusion process, leads to a poorly ordered molecular phase with hydroxyl groups made available to bind water molecules. This mechanism would explain the higher WHC, SV and WBC of mixtures of hydrocolloids and extruded flours.

In general, hydrocolloids increased the WHC, SV and WBC of non-treated flours, and this increase was greater with carrageenans than with agar, particularly with ι-type carrageenan. A number of authors have already observed higher SV values in starch-carrageenan-water pastes (Tecante & Doublier, 1999; Techawipharat, Suphantharika & BeMiller, 2008). According to Christianson, Hodge, Osborne and Detroy (1981), the addition of hydrocolloids can considerably increase the shear forces exerted on the swollen granules in the shaking phase compared with the forces present in starch–water suspensions. This can enhance water uptake (increasing swelling), granule breakdown and the amount of material exuded into the continuous phase.

In the case of agar, significant differences of the WBC values were only observed with non-treated flour, with highest values being obtained with agar from *gracilaria* seaweeds. When combined with extruded flours, agar did not modify the hydration properties of the flours, whereas carrageenans increased WHC but not WBC, and only ι-carrageenan increased SV.

The different effect of the hydrocolloids on the hydration properties reflects different interactions between each hydrocolloid and the flour, and this in turn depends on the chemical structure of the hydrocolloids added.

3.2. Pasting properties

The RVA curves of different flour-hydrocolloid combinations are shown in figure 1. In figure 1b (native flour-hydrocolloid combinations) it can be seen that there was no change in the interaction between the flour and the hydrocolloid until a certain temperature was reached, and the viscosity of the combinations increased in a number of different ways. As hydrocolloids alone (without the presence of flour) showed no significant thickening power on the medium until their solutions were cooled, as observed in figure 1a, changes observed in the pasting properties of flours must be interpreted based on the different interactions that take place between the starch granules and the hydrocolloid. Both agars produced a fall in the onset temperature of gelatinization and an increase in peak viscosity (PV) and breakdown (BR); the increase in the latter two parameters was more marked in the case of *gelidium* agar than *gracilaria* agar. Shi and BeMiller (2002) and Liu and Eskin (1998) detected a decrease in the onset temperature of gelatinization, measured by RVA when studying the interaction between different starches and hydrocolloids, despite the fact that there were no changes in the gelatinization temperature measured by DSC; it could therefore be deduced that these hydrocolloids do not affect the availability of water required by the starch granules for the gelatinization process to occur. On the other hand, Christianson et al (1981) proposed that this fall in the temperature necessary to initiate the increase in viscosity was due to associations between solubilized/leached starch (primarily amylose) molecules and hydrocolloid molecules that developed before granule pasting, a finding supported by Eidam et al. (1995) and Shi and BeMiller (2002).

After reaching the PV, pastes presented a fall in their viscosity due to rupture of the starch granules, known as breakdown (BR); this was more pronounced in combinations of flour and agar than in preparations of flour alone or in combination with carrageenans. The higher PV and lower BR would support the hypothesis that agars enhance granule swelling, leading to much higher forces within the granules and further granule disintegration, permitting greater dissolution of the polymeric starch molecules.

In the case of carrageenans, an increase in the onset of viscosity was observed with the first increase in the gradient of the curve, but this increase was slow compared with the agar combinations. As in the case of agar, carrageenans also increased PV, but the time to reach that peak was longer; there were no marked differences between the two carrageenans studied. These findings do not coincide with results reported by Tye (1988), who detected a synergic effect between starch and ι-carrageenan but did not between starch and κ-carrageenan. Nonetheless, it should be stated that the composition of the κ-carrageenan used in our study included a potassium salt, which induces gelation (Tecante & Doublier, 1999). Those same authors also appreciated an increase in the PV after the incorporation of carrageenans; this was attributed to increased swelling of the starch granules in the presence of carrageenans. The increase in the time to peak viscosity in the samples with carrageenans could be due to the formation of hydrogen bonds between the carrageenans and the starch polymer molecules within swollen granules (Liu, Eskin & Cui, 2003), assuming the hydrocolloid molecules could penetrate into the granules, a phenomenon for which there is some evidence (Savary, Handschin, Conde-Petit, Cayot, & Doublier, 2008). The viscosity of carrageenan pastes in our study was higher than non-treated samples or the combinations with agars, both while the temperature was held at 95ºC and during the cooling stage. Those results could also be due to the interactions among proteins such as gluten and carrageenans, as several authors reported (Huebner & Wall , 1979; León et al, 2000). Meanwhile, Ribotta, Ausar, Beltramo and León (2005) demonstrated that carrageenan isoforms could form hydrophilic complexes with gluten proteins and the capacity of the complexation appeared to be related to the density of the anionic group in the hydrocolloid. Additionally, Wang, Zhao, Yang and Jiang (2006) reported that those electrostatic interactions could involve lysine and terminal NH_2 in gluten protein, thus not only starch granules could interact with hydrocolloids but also the protein fraction of wheat flours.

The curves of the agar combinations during these stages were very similar to the non-treated flour curves, though the viscosity was somewhat higher in the case of *gelidium* combinations. These final viscosity increases in the presence of carrageenans have been observed previously by Lai et al., (1999) and Huang, Kennedy, Li, Xu and Xie, (2007), who concluded that interactions between the hydrocolloid and the starch polymers (especially amylose) created bonds forming a network with crosslinking. Appleqvist and Debet (1997) stated that ι- and κ-carrageenan protected starch systems against shear stress, which would explain the decrease in BR. Another possible explanation of this decrease in BR in the carrageenan combinations would be the increase in the hydrocolloid concentration in the continuous phase as the starch granules absorb water and swell, simultaneously increasing the viscosity of the paste (BeMiller, 2011). In the case of carrageenans, retrogradation could be affected both by the increase in the effective concentration of starch molecules (primarily amylose) resulting from the immobilization of water by the hydrocolloid molecules (Yoshimura, Takata & Nishinari, 1988), and by the associative interactions between carrageenan and gluten.

As general conclusions, it may be considered that agars and carrageenans have different mechanisms of action on pasting properties. Agars would create bonds with solubilized/leached (primarily amylose) molecules, with a lower onset temperature of gelatinization, and no increase in amylose retrogradation in comparison with controls. Furthermore, the presence of agar would assist swelling of the granule, as indicated by the increase in PV and BR. The carrageenans, on the other hand, would not create bonds with solubilized/leached (primarily amylose) molecules, evidenced by the absence both of a decrease in the onset temperature of gelatinization and of final viscosity. Additionally, carrageenans would interact with gluten protein and would foster the water immobilization, resulting in an increase of the effective concentration of starch molecules (primarily amylose), which would favour retrogradation.

Figure 1c shows the results with extruded flour-hydrocolloid combinations. These flours showed a much greater cold thickening power than non-treated flours, but the viscosity of pastes decreased with increasing temperature and there was no significant increase in viscosity during the cooling stage. The incorporation of the different hydrocolloids increased the viscosity of flours without heating through distinct mechanisms. *Gelidium* and *gracilaria* agars increased the viscosity in a similar way, with *gelidium* having a greater effect. In the case of carrageenans, on the other hand, while κ-carrageenan produced a marked increase in the initial stage, followed by a sharp decline, ι-carrageenan produced a less intense increase in viscosity and its effect was delayed. This increase could be secondary to the concentration of hydrocolloid in the continuous phase as a result of the higher water absorption capacity of the extruded flour components without increasing the temperature (Martínez, Oliete & Gómez, 2013). Differences between the different hydrocolloids could be due to their capacity to form a network that immobilizes the water, increasing the viscosity of the continuous phase and the effective concentration of amylose (Savary et al., 2008); this could be particularly important in the case of κ-carrageenan in the presence of potassium ions (Therkelsen, 1993). Meanwhile, interactions among gluten proteins with carrageenan could be even higher in presence of extruded flours, since extrusion forces the unfolding and aggregation of proteins (Martínez, Calviño, Rosell & Gomez, 2014), which could boost additional electrostatic interactions. In the cooling stage, all hydrocolloids behave in a similar way, slightly increasing the viscosity of extruded flour pastes, showing the same trend as the majority of fluids as temperature decreases.

3.3. Steady shear rheological properties

The results of steady shear rheology are shown in table 1. For the range of shear rates used in this study, the power law model accurately described the flow behaviour of each paste. All the pastes showed n < 1, thus exhibiting shear-thinning behaviour.

The K values were higher in native flours than in extruded flours. . In the case of hydrocolloids, an increase in K was only observed with *gracilaria* agar and ι-carrageenan with non-treated flour, indicating a higher consistency. Techawipharat et al., (2008) also reported a higher K value in pastes with ι-carrageenan. Regarding the n value, there was no clear trend and we can only state that combinations of extruded flours with carrageenans showed higher values than the same flours with agar. Finally, we observed an increase in the thixotropic area in extruded flours when they were combined with agars, whereas carrageenans had the opposite effect, decreasing thixotropy both with extruded and with non-treated flours, although the differences were not significant in the case of extruded flours. In conclusion, depending on requirements, pastes made with combinations of extruded flours and agar could be a good option due to their greater thixotropy, which could be beneficial when making of sauces such as ketchup (Sahin & Ozdemir, 2004), whereas pastes made with combinations of carrageenans (particularly ι-carrageenan) and native or extruded flours could be suitable for their low thixotropy and high consistency. As it was commented earlier, (section 3.2), agar and carrageenans have different mechanisms of action. While carrageenans may interact with gluten proteins (Wang et al., 2005) and increase the amylose concentration in the continuous phase due to the immobilization of water molecules by the hydrocolloid (Yoshimura et al., 1988), agars may interact with solubilized/leached (primarily amylose) molecules and promote swelling of the granule, which could explain the different rheological behaviour among agars and carrageenans. In addition, the greater water holding capacity of the gelatinized starch of extruded flours (Martínez et al., 2013) could contribute to a fluidizing of pastes in the presence of stress.

3.4. Dynamic rheological properties

Table 2 shows the dynamic rheological values. In all cases higher values were found for G’ compared to G’’, which indicates that all pastes are elastic and develop distinct solid properties. Furthermore, it must be remembered that starch pastes, even when cooled, are in a metastable, non-equilibrium state (Biliaderis & Zawistowski, 1990) and, as a result, they will undergo further aggregation and partial crystallization during storage and thus become firmer pastes/gels. The addition of hydrocolloid to a starch paste or gel thus makes an already complex system even more complex.

All hydrocolloids except ι-carrageenan increased G' in non-treated flours whereas, in extruded flours, this effect was only observed in combinations with carrageenans. All hydrocolloids except κ-carrageenan increased G'' in the case of non-treated flours. In the case of extruded flours, with lower G'' than non-treated flours, only carrageenans achieved a significant increase in this value. A reduction in the tanδ value was observed both with native and with extruded flours when the flours were combined with carrageenans (this did not occur with agars) and this coincides with the increase observed in G' and G''. Therefore, carrageenans increased G' and G'' in extruded flours and decreased tanδ both in extruded and in non-treated flours. Lai and Lii (2003) have previously reported an increase in the elastic component of the sample (G') and a decrease in tanδ; they attributed this to a network formation after the addition of κ-carrageenan. In table 2, it can also be seen that carrageenans decreased the "a" value, both in non-treated and extruded flours, with the exception of ι-type in combination with non-treated flours, while agars did not modify this parameter. Regarding the "b" parameter, no clear effect was observed except for a decrease in this parameter in the case of non-treated flours combined with κ-carrageenans. The incorporation of hydrocolloids also reduced the "c" parameter in extruded flours, with the exception of *gelidium* agar. In non-treated flours, however, with lower "c" values, this effect was only observed with κ-carrageenan. Consequently, carrageenans, and particularly κ-carrageenan, provoked a decrease in the dependence of the modulus on frequency, which would produce pastes/gels with greater stability than flours without hydrocolloid or agar-flour combinations.

As has already been discussed, carrageenans besides not developing links with amylose, could increase its concentration (Yoshimura at al., 1988); this, together with the possible association with gluten proteins and the creation of crosslinking and entanglement of hydrocolloid molecules, would contribute to increase the stiffness and stability of samples against shear stress. In contrary, agars only increased elastic (G’) and viscous (G’’) modulus in non-treated flour pastes. As indicated in section 3.2, agars may develop interactions with solubilized/leached (primarily amylose) molecules, which could increase the viscosity and elasticity of pastes. Nonetheless, starch granules (Camire et al., 1990) and amylose chains (Mercier & Feillet, 1975) in flours that have undergone extrusion would fragment as a consequence of the high shear stress and temperatures, and linking between amylose molecules and agars would therefore be different, and the elastic and viscosity components of these pastes could be maintained.

3.5. Colour and textural properties of gels

The colour and texture results of the hydrocolloid-flour-water gels are shown in table 3. With respect to colour, all gels were darker (lower values of *L**) when elaborated with extruded flours, with the exception of gels obtained with *gelidium* agar. Gels made with carrageenans were lighter than agar gels when they were made with non-treated flours. However, the differences were smaller between the gels made with treated flours and no significant trend was observed, though the *gracilaria* gels were darker and the ι-carrageenan gels lighter. Regarding the *a** parameter, the values were lower in carrageenan gels with non-treated flours than in the agar gels with these flours; the gels obtained with extruded flours showed no significant differences. Nor were there any significant differences in the *a** values between the carrageenan gels made with extruded flours and with non-treated flour, but significantly higher *a** values were obtained when agar gel were combined with non-treated flours. Flour type had a greater effect on the *b** parameter, with higher values being observed with non-treated flour gels. Of the hydrocolloids, ι-carrageenan gels achieved the highest values, but in the case of gels of hydrocolloids with non-treated flour, significant differences were only observed with *gelidium* agar. Extruded flours showed a darker colour due to Maillard reactions that occur during the extrusion process (Camire et al. 1990), which could have an influence on the colour of gels obtained. In addition, the greater proportion of damaged and gelatinized starch in extruded flours (Martínez et al., 2013) would favour the accumulation of solutes in the continuous phase, decreasing the luminosity of samples. In general, differences between the distinct hydrocolloids were small, with the exception of the lighter colours (high L^*) of the gels elaborated with carrageenans and non-treated flours. Thus, although it seems that the flour colour dominates the final colour of gels, the different molecular structures of the hydrocolloids and their interactions with flour components could also have an influence on the colour of pastes/gels.

Gels containing κ-carrageenan were harder, whether using extruded flours or native flours. In the case of extruded flours gels, no differences in hardness were observed with the other hydrocolloids, but in the case of non-treated flours, the ι-carrageenan gels were softer, followed by *gelidium* agar gels. Regarding the breaking strain, the native flour-carrageenan combination gels together with the native control sample presented higher values, but no clear trend was observed in the combinations with extruded flours. Lafargue, Lourdin and Doublier (2007) showed how the addition of κ-carrageenan (with potassium) produced an increase in the hardness of modified pea starch gel. In contrast, Eidam et al. (1995) reported greater gel strength after the incorporation of ι-carrageenan than if κ-carrageenan was used, contrary to the findings of the present study. However, those authors used pure κ-carrageenan without potassium ions, which increase the gelling power of carrageenan (Therkelsen, 1993) and would explain the greater hardness of the κ-carrageenan gels used in our study.

Despite the fact that seaweed agars, particularly *gracilaria* agar, showed a greater gelling power than carrageenans when used alone in water (figure 1a), the hardness of their gels in combination with flour was lower than observed with κ-carrageenan-flour gels. Therefore, the nature of the interaction between the hydrocolloid and the flour starch is a key factor in the hardness of flour-hydrocolloid-water gels. Lai et al., (1999) and Huang et al., (2007) concluded that hydrocolloid-starch (particularly amylose) interactions resulted in the formation of a network and/or crosslinking, which could explain gel hardness. Nonetheless, considering the hypothesis that carrageenans do not interact with solubilized/leached starch molecules, the greater hardness of these gels may also be due to the associations among carrageenans and gluten proteins (Wang et al., 2005) and the increase in the concentration of amylose in the continuous phase resulting from water immobilization by the hydrocolloid (Yoshimura et al., 1988).

4 Conclusions

Native and extruded wheat flour-hydrocolloid pastes/gels exhibit different properties depending on the type of hydrocolloid. Results suggested that agars and carrageenans have different mechanisms of action on pasting properties. Agars could create bonds with solubilized/leached (primarily amylose) molecules, with a lower onset temperature of gelatinization, and no increase in amylose retrogradation in comparison with controls. Furthermore, the presence of agar could assist swelling of the granule, as indicated by the increase in PV and BR. The carrageenans, on the other hand, could create associations with gluten proteins and could not create bonds with solubilized/leached (primarily amylose) molecules, evidenced by the absence both of a decrease in the onset temperature of gelatinization and of final viscosity. In the case of extruded flours, marked differences are also observed in flour viscosity without heating after the incorporation of distinct hydrocolloids. Furthermore, results showed that carrageenans, besides producing stiffer and more stable pastes, gave rise to harder and clearer gels compared to those made with agar, both for their combination with extruded and native wheat flours, thus carrageenans could be suitable for product stability. Meanwhile, pastes made with combinations of extruded flours and agar could be a good option due to their greater thixotropy, which could be beneficial when making of sauces.

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Figure Captions

Figure 1. Pasting properties of hydrocolloids without flour (hydrocolloids alone), native wheat flour with hydrocolloids and extruded wheat flour with hydrocolloids. Flours without hydrocolloids (black line), κ-carrageenan (continuous dark red line), ι-carrageenan (discontinuous dark red line), *gelidium* agar (continuous blue line), *gracilaria* agar (discontinuous blue line). Temperature profile (dotted red line).

Table 1: Individual effects of flour-hydrocolloid combinations on hydration and steady flow properties.

	WHC (g/g)	Swelling (mL/g)	WBC (g/g)	K (Pa.s^n)	n	Thixotropic area
Native flour	5.95a	115.00a	0.73a	60.10b	0.326ab	0.27b
NFgelidium	13.36a	136.22a	1.32c	54.26b	0.456cde	0.17ab
NFgracilaria	10.69a	145.45a	1.10b	85.98c	0.332abc	0.02a
NFι-carrageenan	68.74c	811.11e	4.98ef	93.55c	0.314ab	0.05a
NF κ-carrageenan	32.42b	310.00b	1.94d	51.35b	0.434bcde	0.00a
Extruded flour	37.34b	480.00c	4.93ef	4.42a	0.420abcd	0.26b
EFgelidium	42.22b	410.00bc	4.94ef	12.26a	0.405abc	0.66c
EFgracilaria	42.87b	435.72c	4.98ef	21.63a	0.306a	0.82c
EFι-carrageenan	64.74c	600.00d	5.03f	3.07a	0.555e	0.15ab
EF κ-carrageenan	56.66c	491.35cd	4.89e	5.20a	0.537de	0.16ab

Flour type: extruded flour (EF), native flour (NF).

WHC, water holding capacity; WBC, water binding capacity; K, consistency coefficient; n, flow behaviour index.

Values followed by different letters within each column indicate significant differences (*P≤0.05*).

Table 2: Individual effects of flour-hydrocolloid combinations on oscillatory tests.

	G’ (Pa)	a	G’’ (Pa)	b	tanδ	c
Native flour	171.9a	0.172bc	47.2b	0.295bc	0.274ab	0.127bc
NFgelidium	556.1d	0.118ab	105.9cd	0.252ab	0.196ab	0.130bc
NFgracilaria	740.6e	0.108ab	125.9de	0.234ab	0.171a	0.122bc
NFι-carrageenan	342bcd	0.176bc	89.3c	0.251ab	0.279ab	0.079b
NF κ-carrageenan	1128.5	0.070a	48.4b	0.089a	0.13a	0.015a
Extruded flour	25.7a	0.201c	9.2a	0.454cd	0.423cd	0.236e
EFgelidium	38.3a	0.250c	17.3a	0.483d	0.519d	0.217de
EFgracilaria	81.7a	0.216c	30.5ab	0.396bcd	0.382bc	0.173cd
EFι-carrageenan	452.2c	0.100ab	111.8cd	0.366bcd	0.102a	0.160c
EF κ-carrageenan	260abc	0.114ab	48.4b	0.288bc	0.192ab	0.164cd

Flour type: extruded flour (EF), native flour (NF).

G’, storage modulus at 1Hz; G’’, loss modulus at 1Hz; tanδ, loss factor; a, dependence of G’ on frequency; b, dependence of G’’ on frequency; c dependence of tanδ on frequency.

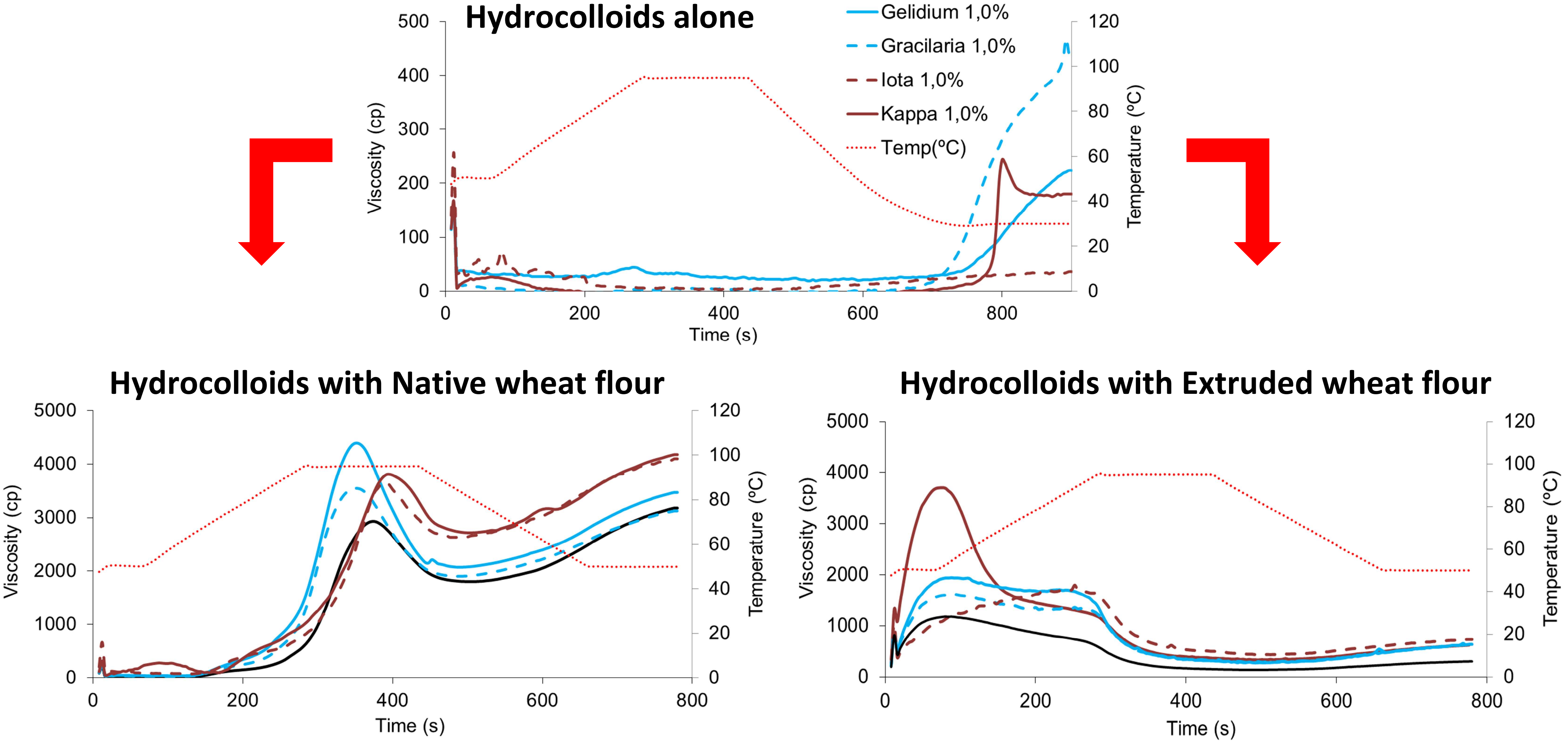
Values followed by different letters within each column indicate significant differences (*P≤0.05*).

Table 3: Individual effects of flour-hydrocolloid gels on colour and textural properties.

	*L**	*a**	*b**	Hardness (N)	Breaking Strain(mm)
NF Control	70.75f	-0.44de	7.56f	2.18ab	4.97c
NFgelidium	64.95ab	-0.49de	5.19d	7.19c	1.64a
NFgracilaria	65.54bc	-0.40e	5.79de	11.18d	1.93ab
NFι-carrageenan	71.02f	-0.68cd	6.13e	2.88ab	4.82c
NF κ-carrageenan	70.00e	-0.93abc	5.68de	18.19e	3.75bc
EH Control	66.18cd	-0.86abc	2.53c	1.66a	4.29bc
EHgelidium	65.56bc	-1.08a	1.49b	2.76ab	4.91c
EHgracilaria	64.34a	-0.99ab	1.07ab	4.03b	4.31bc
EHι-carrageenan	66.68d	-0.82bc	3.27c	2.ab	4.92c
EH κ-carrageenan	65.38b	-1.01ab	0.65a	22.73f	3.20b

Flour type: extruded flour (EF), native flour (NF).

Values followed by different letters within each column indicate significant differences (*P≤0.05)*


Hydrocolloids alone
Gelidium 1,0%
Gracilaria 1,0%
Iota 1,0%
Kappa 1,0%
Temp(ºC)
Viscosity (cp)
500
400
300
200
100
0
Temperature (ºC)
120
100
80
60
40
20
0
0
200
400
600
800
Time (s)
Hydrocolloids with Native wheat flour
Viscosity (cp)
5000
4000
3000
2000
1000
0
Temperature (ºC)
120
100
80
60
40
20
0
0
200
400
600
800
Time (s)
Hydrocolloids with Extruded wheat flour
Viscosity (cp)
5000
4000
3000
2000
1000
0
Temperature (ºC)
120
100
80
60
40
20
0
0
200
400
600
800
Time (s)

Highlights

Native and extruded wheat flour-hydrocolloid pastes/gels were studied

The addition of hydrocolloids to extruded flours significantly increased cold viscosity

Agar pastes showed greater consistency and higher thixotropy

Carrageenan pastes exhibited greater stiffness and stability

Carrageenan gels exhibited greater hardness than agar gels