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

Mario M. Martínez*, Ana K. Macias, Mayara L. Belorio, Manuel Gómez

Food Technology Area, College of Agricultural Engineering, University of Valladolid, 34004 Palencia, Spain

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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 tan δ 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.

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,

* Corresponding author. Tel.: +34 (9) 79 108314; fax: +34 (9) 79 108302.
E-mail address: mario.martinez@iaf.uva.es (M.M. Martínez).

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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 (Lai, Huang, & Lii, 1999; Mohammed, Hember, Richardson, & Morris, 1998).

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, 69.09 μm 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, 99.37 μm 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 160 °C with a feed rate of 500 kg/h. The moisture content of this flour was 17% and the screw speed was 453 rpm. 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 100 mL of distilled water to 5 g (±0.1 g) of flour with 0.357 g (±0.001 g) of hydrocolloid and allowing it to hydrate for 16 h. Water holding capacity, defined

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 ($P \leq 0.05$).