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Rheological behavior of starch/carrageenan/milk proteins mixed systems: Role of each biopolymer type and chemical characteristics

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ABSTRACT

In this study, rheological synergistic consequences of starch/carrageenan/milk proteins mixed systems were investigated by considering the role of each biopolymer type as well as their intrinsic characteristics. Through this study, we showed that starch endogenous proteins have no impact on the viscoelastic properties of starch/carrageenan mixed systems in presence or not of milk proteins. However, these properties were seen to be strongly dependent on the type of gelling carrageenans. Indeed, the ι-carrageenan-based systems led to lower viscoelastic properties compared to the κ-carrageenan-based systems, mainly due to the conformational ordering and the network characteristics of each gelling carrageenan-type. It was also demonstrated that whatever the type of gelling carrageenans, swollen starch granules filled in carrageenan gel network led to improved viscoelastic properties in comparison to pure carrageenan gels; the resulting filled composite gel strength becoming most pronounced in presence of milk proteins. This important reinforcement of the carrageenan gel networks in presence of both swollen starch granules and milk proteins appeared to be preferentially driven by the exclusion effect of swollen starch granules as well as their role as "filler". In addition, the dominant role of the exclusion phenomenon of swollen starch granules became limited upon increasing carrageenan concentration in the mixed system; this effect being slightly less pronounced in presence of milk proteins. Finally, in terms of structural organization, the ternary mixed system can be regarded as a filled composite gel in which carrageenan chains and casein micelles form a three-dimensional hybrid network filled and strengthened by swollen starch granules.

1. Introduction

Starch, carrageenan and milk proteins are three main components widely used in processed dairy products for a wide range of texturizing and sensorial properties as described elsewhere (BeMiller, 2011). Indeed, the nature and type of interactions that could be established between these components and others in the matrix are of direct importance for the quality of the aforementioned properties. Therefore, for rational designing of innovative and cost-effective dairy products, it is becoming important to better understand the texturizing consequences of such ternary assemblies considering the role of each biopolymer as well as their structural characteristics.

Carrageenans are water soluble sulfated polysaccharides extracted from red seaweed (Campo, Kawano, Silva Jr, & Carvalho, 2009; Prajapati, Maheriya, Jani, & Solanki, 2014). These natural polysaccharides exist in three main forms like kappa (κ-), iota (ι-) or lambda (λ-), with κ- and ι-carrageenan having the ability to form thermoreversible gels in the presence of gel-promoting cations (Prajapati et al., 2014; Rochas, Rinaudo, & Vincendon, 1980). Gelation of both κ- and ι-carrageenan is generally accepted to occur in a two main stage-processes: from coil (disordered state) to helix (ordered), followed by side-by-side aggregation and junction zones formation by helices in a three-dimensional network upon cooling (Prajapati et al., 2014; Rochas et al., 1980). The λ-carrageenan is unable to gel due to a high amount of sulfate groups and the absence of anhydro-bridges (Prajapati et al., 2014; Rochas et al., 1980). Besides carrageenans, starch is another polysaccharide mainly composed of two different glucosidic polymers: amylose and amylopectin. Both polymers are packed in more-or-less porous semi-crystalline granules which are very hydrophilic. In many applications, starch is often used in combination with non-starch hydrocolloids such as carrageenan, for example to protect starch

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granules against shear during cooking, improve product texture/rheology (Kulicke, Eidam, Kath, Kix, & Kull, 1996), hold moisture, and protect against syneresis.

Milk is a complex colloidal dispersion composed of about 3.6% proteins, of which 80% are in the form of caseins (α_{s1}, α_{s2}, β and κ) and the remaining 20% are whey proteins. If whey proteins can denature and aggregate at higher temperatures (>60 °C), caseins remain relatively stable at these conditions (Fox & Brodkorb, 2008). Caseins in milk have the particularity of self-associating into "micelles" (Fox et al., 2008). The p*I* of caseins is 4.6 (Fox et al., 2008). The κ-casein is mostly located on the periphery of the micelles and has a "positive patch" between residues 97 and 112 which still remains positively charged even at pH values above the p*I* (Fox et al., 2008).

Recently, by using multiple staining and confocal laser scanning microscopy, Matignon, Moulin, et al., 2014 showed that when starch, carrageenan and milk proteins are mixed together in aqueous media, carrageenan/milk proteins interactions are formed preferentially with no observable interactions between starch and milk proteins (especially casein micelles). Moreover, a competition between carrageenan/casein micelles and carrageenan/endogenous starch-associated proteins interactions was pointed out (Matignon, Moulin, et al., 2014). According to the authors, the adsorption of carrageenan on starch granules can be due to electrostatic interactions between negatively charged carrageenan chains and positively charge parts of endogenous starch-associated proteins located on the surface of the granules (Matignon, Barey, et al., 2014; Matignon, Moulin, et al., 2014). Similarly, numerous studies reported that carrageenan associates with casein micelles through an electrostatic interaction between its negatively charged sulfate groups and a positively charged region of κ-casein (Bourriot, Garnier, & Doublier, 1999; Bourriot, Garnier, Doublier, & Phillips, 2000; Garnier et al., 2003; Langendorff et al., 1999; Langendorff, Cuvelier, Launay, & Parker, 1997; Langendorff et al., 2000). On the other hand, Sun, Liang, Yu, Tan, and Cui (2016) have demonstrated that the interactions of starches and casein micelles included electrostatic adhesion, steric stabilization and hydrogen bond. More recently, by using a quantitative method based on methylene blue spectrophotometry, Lascombes et al. (2017) demonstrated that the implication of starch endogenous proteins in starch/carrageenan interactions would be minor. The adsorption of carrageenan chains on starch granules was identified to be mainly due to osmotic pressure effect (Lascombes et al., 2017). Additionally, they also make evidence of partial penetration of carrageenan in starch granules and partial "exclusion" of carrageenan by starch granules; that concentrates carrageenan in the continuous water phase. All these observations raised a question about how the above physico-chemical phenomena could affect the texturizing properties of starch/carrageenan/milk proteins assemblies. Moreover, although a great interest has been given to the interactions between binary mixtures of each biopolymer as well as their influence on the rheological properties of the resulting mixed systems (Alloncle & Doublier, 1991; BeMiller, 2011; Chaudemanche & Budtova, 2008; Noisuwan, Bronlund, Wilkinson, & Hemar, 2008; Ptaszek et al., 2009; Savary, Handschin, Conde-Petit, Cayot, & Doublier, 2008), little is known on the rheological consequences of ternary starch/carrageenan/milk proteins mixtures that implied above interactions.

The objective of the work reported in this paper is to investigate the rheological synergistic consequences of starch/carrageenan/milk proteins mixed systems, considering the role of each biopolymer as well as their intrinsic characteristics. Various proportions of κ- or ι-carrageenan and two chemically modified starches were then used. Skimmed milk (milk proteins-based solvent) and permeate (non-proteins-based solvent) were also chosen to be as close as possible to commercial dairy products like the approaches developed elsewhere (Considine et al., 2011; Verbeken, Bael, Thas, & Dewettinck, 2006; Verbeken, Thas, & Dewettinck, 2004).

2. Materials and methods

2.1. Materials

Both stabilized and cross-linked waxy maize starch (acetylated distarch adipate) and gelling carrageenans were provided by Cargill (Vilvoorde, Belgium; Baupte, France) for this study. The starch was composed of at least 99% of amylopectin (i.e. less than 1% amylose) and of a maximum of 0.4 wt% endogenous proteins. To highlight the potential role of the starch endogenous proteins in the mixed system behavior, a part of this starch sample was enzymatically treated with a protease to eliminate as much as possible its proteins. The final residual endogenous protein content of this protease treated starch was seen to be ~0.04 wt%.

The gelling carrageenans used were comprised of two different carrageenan samples composed naturally of a mix of kappa (-κ) and iota (-ι) and lambda (-λ) chains depending on the seaweed from which they were extracted.

Besides the above ingredients, reconstituted skimmed milk and permeate were used as milk proteins-based solvent and non-proteins-based solvent, respectively. The skimmed milk and permeate in powdered form were kindly provided by Isigny-Ste-Mère (Isigny, France) and Arla Foods Ingredients (Denmark), respectively. Permeate (obtained from skimmed milk), was used to remain as close as possible to the ionic environment of the skimmed milk without changing the composition of the continuous phase. This strategy ensures that, by comparing the behavior of the mixed systems formulated in skimmed milk or in permeate, one can only access the impact of milk proteins (casein micelles).

The chemical and the macromolecular features of each carrageenan sample are detailed in Table 1.

2.2. Sample preparation and polysaccharide mixtures

Starch-carrageenan mixed systems were prepared in variable proportions in reconstituted skimmed milk (milk-proteins-based solvent) or in permeate (non-proteins-based solvent). Both solvents were reconstituted by dissolving skimmed milk or permeate powder, respectively at 10% w/w or 10.4% w/w (required standard concentrations allowing equivalent ionic strength), in ultrapure water (18.2 MΩ.cm resistivity) under stirring for 4 h at room temperature, following the recipes communicated by the powder manufacturers. Carrageenan concentration in the mixtures was varied from 0.02% w/w to 0.50% w/w, while maintaining fixed starch concentration at 2% w/w. Both polysaccharide concentrations were chosen in the typical ranges of neutral dairy dessert creams. For sample preparation, starch and carrageenan powders were weighed in a suitable final proportion, thoroughly mixed and slowly dispersed in the defined dispersing medium (skimmed milk or permeate) under magnetic stirring (500 rpm). Stirring was maintained for 30 min at room temperature to ensure carrageenan dissolution and complete hydration of starch granules. Then, the sample still under stirring at 500 rpm was heated to 80 °C (for ~ 30 min), and held at this temperature for supplemental 3 min. The same sample preparation methods were rigorously used to prepare each carrageenan (-κ or -ι) solutions (0.02–0.5% w/w) and starch suspensions (2% w/w) in the corresponding solvents (skimmed milk or permeate).

To ensure the non-disruption of starch granules during pasting and a relatively good swelling state, particle size determinations were performed before and after the applied thermo-mechanical treatment by using an optical microscope (Nikon Eclipse Ni,