



## Starch-carrageenan interactions in aqueous media: Role of each polysaccharide chemical and macromolecular characteristics



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### ABSTRACT

In this study, physico-chemical interactions between carrageenan chains and starch granules were investigated through methylene blue spectrophotometric method by considering the chemical and macromolecular characteristics of each polysaccharide. For that purpose, various proportions of  $\kappa$ -,  $\iota$ - or  $\lambda$ - carrageenan and different types of starches (native, chemically modified, “deproteinated” or not) were used. Blue dextran spectrophotometric method was also developed to evaluate the quantity of water absorbed by starch granules and hereby their swelling behavior allowing to determine the accurate amount of trapped carrageenan. It was demonstrated that the interactions between starch granules and carrageenan chains are not strongly impacted by starch chemical modifications. However, experiments with “deproteinated” starch showed that starch endogenous proteins can play a part in starch-carrageenan interactions. Three coexisting phenomena were found to occur when starch is pasted together with carrageenan. That consisted in: (i) partial penetration of carrageenan in starch granules, (ii) partial “exclusion” of carrageenan by starch granules and (iii) a predominant adsorption of carrageenan on starch granules due mainly to osmotic pressure effect. Moreover, the electrostatic interactions between starch endogenous proteins and carrageenan chains played a minor role. As expected, the interaction level appeared to be strongly depending from the carrageenan charge density: the lower the charge, the higher the interaction between starch and carrageenan, independently from starch chemical characteristics. Furthermore, it seemed that the rheological properties of the mixed systems are preferentially driven by the partial “exclusion” phenomenon as well as the role of starch granules as “filler”.

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### 1. Introduction

Starch - carrageenan combinations have been used in processed dairy products since about 1950 for a wide range of texturizing and sensorial properties as described elsewhere (BeMiller, 2011). However, due to the increasing demand of dairy materials, it is becoming important to optimize the use of both ingredients through rational designing of innovative and cost-effective dairy desserts. Indeed, as the aforementioned features mainly depend on the physico-chemical interactions that could be established between both biopolymers and other components, many industrial professionals wish to better understand the nature and type of these interactions.

Carrageenans are water soluble sulfated polysaccharides extracted from red seaweed (Campo, Kawano, Silva Jr., & Carvalho, 2009; Prajapati, Maheriya, Jani, & Solanki, 2014). Ideally, they are composed of a repeating unit of disaccharide consisting mainly of sulfate esters of galactose and 3,6-anhydrogalactose polysaccharides; these hexoses are alternately linked  $\alpha$ -1,3 and  $\beta$ -1,4 in the copolymer (Prajapati et al., 2014; Rochas, Rinaudo, & Vincendon, 1980). These natural polysaccharides exist in three main forms like kappa ( $\kappa$ -), iota ( $\iota$ -) or lambda ( $\lambda$ -), with  $\kappa$ - and  $\iota$ -carrageenan having the ability to form thermoreversible gels in the presence of gel-promoting cations (Prajapati et al., 2014; Rochas et al., 1980). Note that this classification into three types ( $\kappa$ -,  $\iota$ - or  $\lambda$ -carrageenan) was established according to the number (one, two or three) of sulfate groups per repeat unit of disaccharide, respectively. Gelation of both  $\kappa$ - and  $\iota$ -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

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zones formation by helices in a three-dimensional network upon cooling (Prajapati et al., 2014; Rochas et al., 1980). The  $\lambda$ -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, an abundant reserve of polysaccharide in higher plants, is 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. When starch granules are heated in excess water, they undergo a process called gelatinization (Achayuthakan & Suphantharika, 2008; Appelqvist & Debet, 1997; BeMiller, 2011; Singh, Kaur, & McCarthy, 2007; Singh, Singh, Kaur, Singh Sodhi, & Singh Gill, 2003). Above a characteristic temperature (gelatinization temperature), the granules swell irreversibly. Then, amylose leaches from the granules and some of the fragile swollen granules are disrupted. The resulting paste consists of a dispersed phase of swollen granules, granule ghosts and fragments within a continuous aqueous phase of dissolved starch polymer molecules (BeMiller, 2011; Singh et al., 2007; Singh et al., 2003). To limit amylose leaching and granule disruption, chemically modified starch can be used, but they do not always completely stop these phenomena (Desse et al., 2009). In fact, chemical modifications are performed to improve native starches tolerance to processing (heat, shear, and acidic) conditions (Kulicke, Eidam, Kath, Kix, & Kull, 1996). Another option is to use non-starch hydrocolloids such as carrageenan in combination with starch, for example to protect starch granules against shear during cooking, improve product texture/rheology (Kulicke et al., 1996), hold moisture, and protect against syneresis. Therefore, the modifications of product texture and rheology at the end of pasting as well as the porous nature of starch granules suggest the existence of particular interaction mechanisms.

Although a great interest has been given to starch-carrageenan mixed systems in order to better understand the physico-chemical interactions between both polysaccharides, the type and nature of these interactions are still unclear. Additionally, the interaction mechanisms ("exclusion", adsorption on and/or penetration in the granules) are still a matter of debate. Different mechanisms are described in the literature. For example, some works claimed that starch-carrageenan mixed systems could lead to partial or total exclusion effect of swollen granules, which concentrate non-starch polysaccharides in the continuous water phase (Alloncle & Doublier, 1989; Tecante & Doublier, 1999, 2002). The authors pointed out the thermodynamic incompatibilities between starch and carrageenan to explain this exclusion phenomenon. On the other hand, confocal laser scanning microscopy (CLSM) observations have shown that carrageenan can either penetrate in (Savary, Handschin, Conde-Petit, Cayot, & Doublier, 2008) or adsorb on (Espinosa-Dzib, Ramirez-Gilly, & Tecante, 2012) starch granules. Both phenomena can even coexist without any exclusion mechanism. Recently, by using an indirect titration of carrageenan in starch-carrageenan mixed systems through flow measurements, Huc et al. (2014) hypothesized that depending on the carrageenan molecular weights and intrinsic viscosity, partial exclusion or trapping of carrageenans by swollen starch granules could take place. Contrarily to the claim that carrageenan can penetrate in swollen starch granules, Matignon, Barey, et al. (2014); Matignon, Moulin, et al. (2014) showed that there is no penetration of carrageenan into starch granules when both polysaccharides are pasted together. Through CLSM observations, the authors have also shown that when carrageenan appears to be penetrated into starch granules, it is in reality trapped inside the folded form of swollen granules. Based on this observation, the authors came to the conclusion that carrageenan can be both excluded and adsorbed on starch granules without any penetration of carrageenan chains into

starch granules. The level of adsorbed carrageenan on starch granules seemed to be promoted by low negatively charged carrageenan and by low molecular weight carrageenan (Matignon, Barey, 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 charged parts of endogenous starch proteins located on the surface of the granules (Matignon, Barey, et al., 2014; Matignon, Moulin, et al., 2014). However, these authors have worked with only one type of starch without considering the real impact of chemical characteristics of starch (presence or not of endogenous starch proteins, modified and non-modified starch) as well as the macromolecular features of each components. In addition, as most investigations were performed on the basis of qualitative observations (CLSM, for example), it appears important to consider this subject by using a quantitative analysis approach. Therefore, methylene blue spectrophotometric method developed elsewhere (Garnier et al., 2003; Michon, Konaté, Cuvelier, & Launay, 2002; Rohart, Jouan-Rimbaud Bouveresse, Rutledge, & Michon, 2015), coupled with complementary rheological evaluations could be original quantitative analysis approaches.

This study focuses on a better understanding the physico-chemical interactions between carrageenan and starch granules, taking into account the intrinsic characteristics of each ingredient. Various proportions of  $\kappa$ -,  $\iota$ - or  $\lambda$ - carrageenan and different types of starches (native, chemically modified, deproteinated or not) were then used. Following some existing approaches on spectrophotometric methods using methylene blue properties of absorption (Garnier et al., 2003; Michon et al., 2002; Rohart et al., 2015), we explored the possibility to quantify or characterize these interactions, in terms of the quantity of carrageenan trapped by starch granules. As starch granule swelling can strongly impact the evaluations of trapped carrageenan quantity, the exact swelling ratio of each starch sample was determined through another original spectrophotometric method using blue dextran as described elsewhere (BeMiller & Pratt, 1981; Tester & Morrison, 1989). As mentioned previously, rheological characterizations of starch-carrageenan mixed systems were performed to support the methylene blue spectrophotometry approach.

## 2. Materials and methods

### 2.1. Materials

Different starch and carrageenan samples of various chemical and macromolecular characteristics were provided by Cargill (Baupte, France; Vilvoorde, Belgium) for this study. The starch samples consisted of one native waxy maize starch and two chemically modified waxy maize starches (both stabilized and cross-linked) comprising acetylated distarch adipate and hydroxypropyl distarch phosphate. The waxy maize starches were composed of at least 99 wt% amylopectin; that allowed avoiding the presence of amylose in the continuous medium during starch granules pasting. All the starch samples contained a maximum of 0.4 wt% endogenous proteins. To highlight the potential role of the starch endogenous proteins in starch-carrageenan interactions, a part of the acetylated distarch adipate 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%. Besides the aforementioned four starch samples, three carrageenan samples composed naturally of a mix of kappa ( $\kappa$ ), iota ( $\iota$ ) and lambda ( $\lambda$ ) chains depending on the seaweed from which they were extracted, were also used. The chemical and the macromolecular features of each carrageenan sample are detailed in Table 1.

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