Food Hydrocolloids xxx (2016) 1–10

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Influence of gelation on ice recrystallization inhibition activity of κ-carrageenan in sucrose solution

Andreas Leiter*, Peter Emmer, Volker Gaukel

KIT (Karlsruhe Institute of Technology), Institute of Process Engineering in Life Sciences, Section I: Food Process Engineering, Kaiserstrasse 12, 76131 Karlsruhe, Germany

ARTICLE INFO

Article history:
Received 5 August 2016
Received in revised form
18 November 2016
Accepted 20 November 2016
Available online xxx

Keywords:
Aggregation
Gelation
Ion
κ-carrageenan
Ice recrystallization inhibition activity
Rheology

ABSTRACT

The objective of this study was to investigate the influence of gelation on the ice recrystallization inhibition (IRI) activity of κ-carrageenan. It is well known, that the addition of salt can promote gelation. Therefore, we used different cations (Na^+, Li^+, Ca^{2+}, K^+) and anions (Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}) in different concentrations to change the viscoelastic properties of a κ-carrageenan sucrose solution and compared the results with the IRI activity. Viscoelastic properties of the residual liquid at −12 °C and the degree of aggregation were characterized by oscillatory rheological measurements and compared with ice crystal sizes observed over a storage time of 96 h. Results show that the addition of 0.03 M Ca^{2+}, K^+, or Na^+ cations or 0.03 M Cl^- or SO_4^{2-} anions leads to a significant reduction of IRI activity compared to a pure κ-carrageenan sucrose solution. In addition, increasing the salt concentration decreases significantly the IRI activity with the exception of NaI showing no decreased IRI activity. Rheological experiments indicate that aggregation of κ-carrageenan molecules and thus the formation of a gel-like character is responsible for the decreased IRI activity. The addition of NaI prevents aggregation which is already known from the literature and therefore IRI activity retains.

1. Introduction

Recrystallization processes during frozen storage can affect the quality of food products. For example, recrystallization can lead to high drip loss during thawing and have a great impact on appearance and texture of frozen food (Pham & Mawson, 1997). Ice cream becomes coarse and unacceptable if ice crystals grow during storage and exceed a threshold detection size (Hartel, 1996, 2001). However, recrystallization processes can be influenced by storage temperature (Donhowe & Hartel, 1996) or formulation (Bahramparvar & Mazaheri Tehrani, 2011; Leiter & Gaukel, 2016; Miller-Livney & Hartel, 1997). Traditionally hydrocolloids are added to ice cream to inhibit recrystallization (Adapa, Schmidt, Jeon, Herald, & Flores, 2000; Bahramparvar & Mazaheri Tehrani, 2011) but despite a large amount of research work the exact recrystallization inhibition mechanism is still not understood in every detail. Although gelation is often discussed as one possible recrystallization inhibition mechanism, there is little research on the influence of gelation on ice recrystallization. Studies at constant storage temperature showed that the formation of a hydrogel is not a prerequisite for ice recrystallization inhibition (IRI) activity (Balcerzak, Febbraro, & Ben, 2013; Capicciotti et al., 2012). During storage under temperature fluctuations, Goff, Ferdinando, and Schorsch (1999) showed that the gelling stabilizer locust bean gum provides much stronger resistance to ice recrystallization than the non-gelling stabilizer guar gum. The authors suggested that during temperature fluctuation, ice melting and growth (melt-regrow mechanism) becomes more favorable within the pores of the gel network than water diffusion to larger crystals (melt-diffuse-grow). This results in a preservation of the initial ice crystal size distribution as long as the small crystals do not melt completely. However, Regand and Goff (2003) also demonstrated that some non-gelling stabilizers (e.g. xanthan) are more effective retarding recrystallization than gelling stabilizers (e.g. locust bean gum) at fluctuating temperatures and suggested that gelation is not the only IRI mechanism. Furthermore, gelation can reduce the ice crystal growth rate and can affect the morphology of growing ice crystals (Blond, 1988; Muhr & Blanshard, 1986). According to the review of Bahramparvar and Mazaheri Tehrani (2011), decreased molecular mobility of water molecules, (cryo-) gelation and phase separation due to the incompatibility of hydrocolloids with

* Corresponding author.
E-mail address: andreas.leiter@kit.edu (A. Leiter).

http://dx.doi.org/10.1016/j.foodhyd.2016.11.028
0268-005X/

proteins, are three potential mechanisms which can explain cryoprotective effects of hydrocolloids. In addition, a direct binding to the ice crystal surface is also discussed for some hydrocolloids (Gaukel, Leiter, & Spieβ, 2014; Sutton & Wilcox, 1998; Sutton, Cooke, & Russell, 1997; Sutton, Lips, & Piccirillo, 1996).

One such hydrocolloid is κ-carrageenan. It has strong IRI activity (Chun, Kim, & Min, 2012; Gaukel et al., 2014; Kamińska-Dwórznicka, Antczak, Samborska, & Lenart, 2015) and it has been suggested that this IRI activity stems from an interaction with ice crystal surface (Gaukel et al., 2014; Leiter, Ludwig, & Gaukel, 2017). κ-carrageenan is a linear, sulfated polysaccharide extracted from certain species of red seaweeds (Rhodophyceae) (McHugh, 2003). It is characterized by an alternating disaccharide unit of 1,3-linked β-D-galactose-4-sulfate and 1,4-linked 3,6-anhydro-α-D-galactose (Rochas & Rinaudo, 1984) and can form thermoreversible gels on cooling (Rinaudo, 2008). The polysaccharide is used as gelling, thickening, and stabilizing agent especially in food products but also in cosmetics and pharmaceutical formulations as excipient (Campo, Kawano, Silva, Dílson Braz da, & Carvalho, 2009; Rinaudo, 2008; van de Velde & De Ruiter, 2006). The gel formation of κ-carrageenan in aqueous solution depends on the chemical structure (Watase & Nishinari, 1987), molecular weight (Rochas, Rinaudo, & Landry, 1990), concentration of κ-carrageenan (Chen, Liao, & Dunstan, 2002), concentration and type of ions (Lai, Wong, & Lii, 2000; Morris & Chilvers, 1983; Morris, Rees, & Robinson, 1980; Rochas & Rinaudo, 1980), cooling rate (Iijima, Hatakeyama, Takahashi, & Hatakeyama, 2007; Moritaka, Takahashi, & Kubota, 2007) and temperature (Morris et al., 1980; Núñez-Santiago & Tecante, 2007). However, the molecular mechanisms of gelation are still not understood in detail. A widely accepted model of gelation is the “domain model” (Mangione, Giacomazza, Bulone, Martorana, & San Biagio, 2003; Morris et al., 1980). According to the “domain model”, κ-carrageenan molecules in solution exist as unstructured random coils above a certain temperature. A temperature reduction below this so called coil-helix transition temperature induces the formation of double helices. The intermolecular association between the double helices is confined to a formation of small independent domains involving a limited number of double helices. However, when cations are present, double helices of different domains aggregate to enable long-range cross-linking (Campo et al., 2009; Morris et al., 1980) which can lead to the formation of a gel (Mangione et al., 2003). This is due to a decrease of the charge density of the carrageenan helices with its negative sulfate groups oriented towards their external part shielding the electrostatic repulsion between helices (Piculell, 2006; Takemasa & Nishinari, 2004). In contrast certain anions like iodide bind specifically to the carrageenan helix resulting in an increase in the overall charge density along the helical chains and hence inhibiting helix aggregation (Grasdalen & Smidsroed, 1981; Pelletier, Viebke, Meadows, & Williams, 2001; Takemasa & Nishinari, 2004). An interhelical aggregation is usually evident from a thermal hysteresis between the transition temperatures from coil to helix and from helix to coil (Piculell, 2006). The coil-helix transition temperature depends, among others, on concentration and type of ions as well as the presence of sugars and polyols (Austen, Goodall, & Norton, 1988; Gekko, Mugishima, & Koga, 1987; Lai et al., 2000; Nishinari, Watase, Williams, & Phillips, 1990; Zhang, Piculell, & Nilsson, 1992). For example, Norton, Morris, and Rees (1984) showed that the coil-helix transition temperature follows the reversed Hofmeister series $SO_4^{2-} < Cl^- < Br^- \leq NO_3^- < I^-$ when salt concentration and cation type are held constant.

In a previous study (Leiter et al., 2017) we showed that the presence of sodium and potassium cations leads to a decreased IRI activity of κ-carrageenan. We assumed that the reduced IRI activity is related to a pronounced gelation of κ-carrageenan which is contrary to the depicted cryoprotective effect of gelation as proposed by Bahramparvar and Mazaheri Tehrani (2011). But assuming that the IRI activity of κ-carrageenan is based on an interaction of κ-carrageenan molecules with the ice crystal surface (Gaukel et al., 2014), a gelation would lead to a reduced interaction of κ-carrageenan molecules with the ice crystal surface. In the gel the mobility of κ-carrageenan molecules is reduced. Furthermore, due to the fixation in the gel less κ-carrageenan molecules are freely available for an interaction with the ice crystal surface.

The objective of this study was to prove this theory. Therefore, we investigated the influence of gelation on the IRI activity of κ-carrageenan. The viscoelastic properties of a κ-carrageenan sucrose solution were modified by changing the concentration and type of different cations and anions. The properties were characterized by oscillatory rheological measurements (frequency and temperature sweeps). Afterwards results were compared with results of recrystallization experiments to see if there is a relationship between gelation and IRI activity of κ-carrageenan.

2. Materials and methods

2.1. Material

κ-carrageenan was used as an unstandardized extract from the red seaweed Eucheuma Cottonii produced by gel-press method in the Philippines. It was provided by Eurogum A/S (Herlev, Denmark) and was used in this study without further purification. Salt and sulfate content of the unstandardized sample is presented in Table 1.

Because composition of natural κ-carrageenan may differ from batch to batch (van de Velde, Knutsen, Usov, Rollema, & Cerezo, 2002), κ-carrageenan from the same production batch was used for all experiments. The used sucrose was common household sugar bought in a supermarket. Sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), sodium sulfate (Na_2SO_4), potassium chloride (KCl), lithium chloride (LiCl), and calcium chloride dihydrate ($CaCl_2 \cdot 2\ H_2O$) were purchased from Carl Roth (Karlsruhe, Germany). Sodium nitrate ($NaNO_3$) was purchased from Merck KGaA (Darmstadt, Germany).

2.2. Sample preparation

Aggregation and recrystallization inhibition activity was studied in a 49% (w/w) sucrose solution which was used as a simplified food model system based on ice cream. The solution was prepared with demineralized water and κ-carrageenan with a concentration of 1 mg mL^{-1}. To get this final concentration in the sample solution, 20 mg of κ-carrageenan were added to a 20 mL flask and filled up with the previously prepared 49% (w/w) sucrose solution. In order to investigate the influence of cations (Na^+, Li^+, Ca^{2+}, K^+) and anions (Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}), the appropriate amount of salt (final concentration 0.0003 M, 0.03 M or 0.1 M) was mixed with the κ-carrageenan powder before adding the sucrose solution. The counterion for all cations was Cl^- and for all anions Na^+. For

Table 1
Salt and sulfate content of the used κ-carrageenan extract.

Ion type	Mass fraction [%]
K^+	7.29
Na^+	0.80
Cl^-	0.83
Ca^{2+}	0.13
Mg^+	0.06
SO_4^{2-}	19,55

Please cite this article in press as: Leiter, A., et al., Influence of gelation on ice recrystallization inhibition activity of κ-carrageenan in sucrose solution, *Food Hydrocolloids* (2016), http://dx.doi.org/10.1016/j.foodhyd.2016.11.028