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Using power ultrasound for cold gelation of kappa-carrageenan in presence of sodium ions

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ABSTRACT

Usually a heating stage is required to solubilize kappa carrageenan dispersions for gel formation on cooling. This work reports cold gelation of kappa carrageenan in the presence of sodium ions using power ultrasound without using any heating stage. Carrageenan gels were prepared using ultrasound in the presence or absence of NaCl and their textural properties were compared with the gels prepared with conventional heating method. Mechanical properties of the gels strongly increased with ultrasonication time up to a certain level, and further sonication reduced mechanical characteristics. Addition of Na^+ ions after ultrasonication was more effective in increasing textural hardness than when Na^+ is present during ultrasonication. Microscopic images demonstrated that increasing ultrasonication time up to a certain level leads to coherent gel networks and further ultrasound has a negative impact on the gel network. Solubility and intrinsic viscosity results are also presented. Moreover, Maxwell model with three elements was used to analyze stress relaxation data.
Industrial relevance: So far, all documented reports have indicated that to induce gelation of kappa carrageenan dispersions a preheating step is required followed by cooling. In the present work, using power ultrasound a new method for cold gelation of carrageenan dispersions is introduced. Using ultrasound, food and non-food processors can use kappa carrageenan as a viscosifying and gelling agent without using heating.

1. Introduction

Kappa carrageenan is one of most important gel forming polysaccharides extracted from marine red algae. Three interaction modes; hydration and solubilization, gelation and protein binding, have been reported for kappa carrageenan in food systems (Fisher, 2009). It has a primary structure based on repeating linear chains of galactant units. This disaccharide repeating unit is a dimer of galactose and anhydrogalactose linked by a beta-1,4-glycosidic linkage. These dimers are then linked together by alpha-1,3-glycosidic linkages. This polysaccharide contains one sulfate group per disaccharide unit at carbon 2 of the 1,3 linked galactose unit (BeMiller & Whistler, 1996; Whistler & BeMiller, 1997). For secondary structure the chair conformation was proposed to minimize steric repulsations caused by axial components (Therkelsen, 1993). Thermoreversible gelation of kappa carrageenan involves a conformational transition. At high temperatures, the biopolymer is present as random coils and upon cooling, it forms double helices which may be followed by the aggregation of the ordered molecules to form an infinite network (Hjerde, Smidsrod, & Christensen, 1999; Millane, Chandrasekaran, Arnott, & Dea, 1988). The water solubility of biopolymers is dependent on their secondary (helical and double helical chains) and tertiary structures (inter- and intra-molecular chain associations), and the lengths of the main and branch chains (Rochas, Rinaudo, & Landry, 1990; Wang, Cheung, Leung, & Wu, 2010).

In the presence of Na^+ ions, kappa carrageenan is found in the coil state at room temperature (Slootmaekers et al., 1988). However in the presence of K^+, depending on salt concentration and temperature coil or helix states can be possible (Rochas & Rinaudo, 1980; Takemasa, Chiba, & Date, 2002). More recently it was suggested that Na^+ ions, at high salt concentrations and low temperatures can induce a conformational transition in kappa carrageenan (Meunier, Nicolai, & Durand, 2000; Norton, Goodall, Morris, & Rees, 1983).

It has been found that irradiation (use of ionizing radiation) and sonication (use of ultrasound waves) are two alternative polysaccharide degradation methods (Ulanski, Wojtasz-Pajak, Rosiak, & Von Sonntag, 2000). Effect of ultrasound on polymer solubility should be attributed to alteration of secondary and tertiary structural properties in water (Rochas et al., 1990; Wang et al., 2010). A main advantage of ultrasonic treatment over other radiation methods of degradation is that ultrasound treatment is a simpler, safer and more convenient means for depolymerization of the large polysaccharide molecules. Moreover, large-scale ultrasonic vessels and reactors are available for industry application (Mason & Lorimer, 2002). Also ultrasonic treatment has been shown as an effective means for controlled degradation of bioactive polysaccharides without induced drastic changes in the primary chemical structures (Wang et al., 2010). The ultrasonic degradation of polymers is of great interest, and degradation of

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several polymers such as dextran (Koda, Mori, Matsumoto, & Nomura, 1993), high-methoxyl pectin (Seshardi, Weiss, Hulbert, & Mount, 2003), starch and chitosan (Czechowska-Biskup, Rokita, Lotfy, PiotrUlanski, & Rosiak, 2005), agarose and carrageenan (Lii, Chen, Yeh, & Lai, 1999) has been studied.

Mohod and Gogate (2011) have investigated the effect of ultrasound on degradation of carboxymethyl cellulose and polyvinyl alcohol as two kinds of water soluble polymers. They have suggested that ultrasound can yield polymer degradation as indicated by a significant reduction in the intrinsic viscosity or the molecular weight. Also they have suggested that the viscosity of the polymer solutions decreased with an increase in the time of ultrasonic irradiation and approached a limiting value.

So far, all documented reports have indicated that to induce gelation of kappa carrageenan dispersions a preheating step is required followed by cooling. In the present work, using a Texture Analyzer and scanning electron microscopy, ultrasound-assisted cold gelation of kappa carrageenan dispersions in the presence of Na^+ ions without using any heating steps has been investigated and studied.

1.1. Theoretical consideration: stress relaxation test

The stress relaxation test is widely used for determining viscoelastic properties of food products. A generalized Maxwell model is frequently used to interpret stress relaxation data (Campus et al., 2010; Jain, Pathare, & Manikantan, 2007; Ziegler & Rizvi, 1989). In this study the experimental data were fitted to the Maxwell model with n = 3, represented by Eq. (1):

$$E(t) = E_{e+}\sum_{i=1}^{n} E_i \exp\left(\frac{-t}{\tau}\right) \quad (1)$$

where E(t) is the modulus decaying parameter determined from experiments, t is the experimental decay time (seconds), τ (seconds) is the relaxation time of the i-th Maxwell element, E_i is the decay modulus in each term, and E_e is the equilibrium or residual modulus at the fully decayed state (N), that is, when all relaxable stress is fully relaxed. For liquid foods, which are polymers without permanent cross-linking, $E_e = 0$. For solid foods, polymers with permanent cross-links, E_e is a non-zero constant (Mitchell, 1980).

2. Material and methods

2.1. Gel preparation

Kappa carrageenan powder was purchased from Behin Azma (Shiraz, Iran), and used without further purification. Depending on the treatment, 0.4% kappa carrageenan dispersions were prepared by dispersing the powder in deionized water or in 0.12% w/v of NaCl solution with continuous magnetic stirring at 25 °C for 15 min. To investigate the effect of ultrasonication on textural and microstructural properties of carrageenan dispersions in the absence or presence of NaCl salt, two sets of samples were prepared.

For set one called NaCl-US, firstly 0.12 g NaCl was dissolved in distilled water (100 ml) and then 0.4 g kappa carrageenan was dispersed with continuous magnetic stirring at 25 °C for 15 min. Ultrasound treatment was performed as explained in the next section. For set two,0.4 g carrageenan was dispersed in distilled water (100 ml) with continuous magnetic stirring at 25 °C for 15 min, ultrasound was applied and then NaCl added (0.12 g), this sample is named US-NaCl. To obtain the testing gel, the prepared homogeneous mixture was poured in cylindrical molds (5 mm in height and 20 mm in diameter) and covered with a glass plate to avoid any moisture loss. The sample holders containing the samples were then kept in a cold room set at 5 °C for 16 h before textural and mechanical properties of the gels were measured.

For comparing the properties of gels prepared by ultrasound with the gels of conventional heating method, another set of samples was prepared by dissolving the same carrageenan concentration as ultrasound samples, in an aqueous solution of NaCl (0.12% w/v) with continuous magnetic stirring at 80 °C for 15 min, 30 min or 120 min. Cylindrical shape gels were then prepared using the same molds and conditions as ultrasound gels.

2.2. High intensity ultrasound treatment

The prepared carrageenan dispersions were transferred to ultrasonic vessel (120 ml cylindrical jacketed glass reactor of height and diameter of 85 mm and 65 mm, respectively) and ultrasonicated for different times (5 s, 10 s, 30 s, 1 min, 2 min, 5 min, 10 min) using an ultrasonic processor (HD3200, Bandelin, Germany) operating at a frequency of 20 kHz, constant power of 100 W and an amplitude of 100%. Distilled water mixed with ethylene glycol with a constant temperature of 15 °C was circulated in the jacketed vessel for temperature controlling.

A high grade titanium tip (TT13, diameter 13 mm) was used to sonicate 100 ml of sample. Depth of ultrasound horn is one of the important factors affecting polymer degradation (Mohod & Gogate, 2011) and the extent of mixing in the reactor is also dependent on the immersion depth of the horn (Nishida, 2004). Therefore, in this work the constant horn depth of 2 cm was used for all treatments.

2.3. Instrumental texture profile analysis (TPA)

A Texture Analyzer (Texture Analyzer, TA Plus, Stable Micro Systems, Surrey, England),with a load cell of 30 kg, by performing texture profile analysis (TPA), was used to obtain the force–time curves of the carrageenan gels. The samples were compressed twice using a cylindrical probe (100 mm in diameter) at a pretest speed of 5, test speed of 0.25 and posttest speed of 5 mm/s and a trigger force of 3 g. The deformation level was 25% of original sample height and interval time of 10 s. All textural measurements were performed at room temperature (22 ± 2 °C) on six replicates for each sample.

2.4. Stress relaxation test

Stress relaxation characteristics of the cylindrical gel samples (20 mm diameter × 5 mm high) were determined by subjecting the samples to a compressive engineering strain of 25% employing a cross head speed of 0.25 mm/s using the Texture Analyzer (Texture Analyzer, TA Plus, Stable Microsystems, Surrey, England). After completing compression stage, force values were collected over 120 s of relaxation period. All measurements were conducted at 22 ± 2 °C on three replicates.

2.5. Determination of solubility

Solubility of the control and ultrasonicated samples was determined using a method previously used for starch solubility (Mukerjea, Slocum, & Robyt, 2007). 0.5 ml of each sample was poured into a micro centrifuge tube and after that 0.5 ml of distilled water was added. The mixture in each tube was shaked vigorously using a shaker at room temperature for 15 min, followed by centrifugation (Centrifuge model SW14R, Froilabo, France) at 10,000 rpm for 20 min. The undissolved residues were separated from supernatant and the supernatant was dried in an oven (ASUZU, Japan) at 90 °C for 24 h. From the weights of initial sample and the supernatant the solubility of each sample was calculated.