Carbohydrate Polymers 95 (2013) 522–529

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Ultrasound assisted cold gelation of kappa carrageenan dispersions

Rezvan Azizi, Asgar Farahnaky*

Department of Food Science and Technology, School of Agriculture, Shiraz University, Shiraz, Iran

ARTICLE INFO

Article history:
Received 13 December 2012
Received in revised form 31 January 2013
Accepted 28 February 2013
Available online 13 March 2013

Keywords:
Cold gelation
Kappa carrageenan
Ultrasound
Texture profile analysis
Stress relaxation test

ABSTRACT

Usually to prepare a gel from kappa carrageenan, an aqueous dispersion of carrageenan powder is heated. This research presents evidence of cold gelation of carrageenan dispersions while no heat is needed. The occurrence of cold gelation is investigated in the absence or presence of potassium ions during ultrasound treatment by studying the mechanical and microstructural properties of the prepared gels using a texture analyzer and scanning electron microscopy, respectively. Carrageenan gels were obtained by applying power ultrasound. By increasing sonication time, gel hardness increased up to a certain level (in absence or presence of K^+ during ultrasound treatment) and further ultrasound application had a negative effect. Moreover, the mechanical properties of the gels in which K^+ ions were added before ultrasound were weaker than the samples when K^+ ions were added after sonication. Relaxation times of gels were calculated using the generalized Maxwell model with three elements.

1. Introduction

Carrageenan is a natural water soluble sulfated anionic polysaccharide extracted from marine red algae. Kappa-carrageenan backbone is based on repeating disaccharide units of (1-3)-D-galactose-4-sulphate and (1-4)-3,6-anhydro-D-galactose (Morris, Rees, & Robinson, 1980). The carrageenan fractions are distinguished by the number and position of sulfate groups and by the possible presence of 3–6 anhydrogalactose groups that promote helix formation, which is important for gelling (Sen & Erboz, 2010).

There are three main types of carrageenan: kappa, iota and lambda. These biopolymers are extensively used in the food industry, as a gelling, stabilizing and viscosity building agent (Van de Velde & De Ruiter, 2002). Kappa carrageenan has a two-step mechanism for gelation (Robinson, Morris, & Rees, 1980). At high temperatures, the biopolymer is present as random coils. Upon cooling, it undergoes a conformational transition, forming double helices (Hjerde, Smidsrod, & Christensen, 1999; Millane, Chandrasekaran, Dea, & Arnott, 1988), so the macromolecules interact forming a hard and brittle gel. Therefore, heating of the kappa carrageenan dispersion has been reported as a key step to form a gel.

Ultrasound is able to produce dispersions of carbohydrates due to its mixing power. It also can lead to depolymerization of macromolecules through intense mechanical and chemical effects associated with cavitation, a process which involves the formation, growth and violent collapse of small bubbles in liquids as a result of acoustic pressure fluctuation (Crum, 1995; Mason & Cordmas, 1996; Stephanis, Hatiris, & Mourmouras, 1997).

Application of high intensity ultrasound to modify biopolymers dates back to the 1930s, when natural polymers were subjected to sonication (Price, West, & Smith, 1994). Most of the recent works have focused on the ability of ultrasound to depolymerize polysaccharides such as dextran (Koda, Mori, Matsumoto, & Nomura, 1993), xanthan, guar gum and pectin (Tiwari, Muthukumarappan, Donnel, & Cullen, 2010), chitosan and starch (Czechowska-Biskup, Rokita, Lotfy, Piotr Ulanski, & Rosiak, 2005), carboxymethyl cellulose and polyvinyl alcohol (Mohod & Gogate, 2011) in which reduction in their functional properties, e.g., molecular weight, and viscosity have been reported.

Mohod and Gogate (2011) have established the role of different operating parameters such as time of ultrasonic treatment and depth of horn, as controlling factors for polymer degradation. Their results demonstrated that optimum immersion depth needs to be maintained for maximum effect. On the other hand, flow pattern of liquid in terms of direct circulation currents generated due to the acoustic streaming and reflection from the bottom of the reactor depends on the distance of horn tip immersed in the solution. The extent of mixing in the reactor also depends on the immersion depth of the horn as demonstrated by Nishida (2004). Since polymer degradation is controlled by physical effects of ultrasonic irradiation i.e. liquid circulation currents along with the local shear rates, any changes in flow pattern of liquid due to horn immersion depth will affect the final properties of polymers. However, new applications of ultrasound waves in hydrocolloid science is of great interest.

* Corresponding author. Tel.: +98 711 613 8229; fax: +98 711 6289017.
E-mail addresses: farahnak@shirazu.ac.ir, asgarfarahnaky@gmail.com (A. Farahnaky).

0144-8617/$ – see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.carbpol.2013.02.073

To the best of our knowledge, no published work is available in the literature on cold gelation of hydrocolloid dispersions using ultrasound waves. Therefore, as the first report, the main aim of this research is to investigate the ultrasound assisted cold gelation of kappa-carrageenan dispersions using a texture analyzer and scanning electron microscopy. Ultrasound assisted cold gelation is studied in the presence and absence of potassium ions during sonication.

1.1. Theoretical considerations: stress relaxation test

Stress relaxation test is one of the most important evaluation tools used for determining rheological properties of food gels, that are related to the properties of cross-linkings in gel networks (Ziegler & Rizvi, 1989). Relaxation data are interpreted by fitting equations derived from discrete Maxwell models (Mohsenin, 1970; Sherman, 1970). Mechanical models consisting of n Maxwell elements and a free spring in parallel, each element consisting of one spring (representing the elastic component) and one dashpot (representing viscous fluid) are often used to explain rheological properties of hydrogels (Mitchell, 1980; Steffe, 1992). Preliminary modeling results showed that the simplest model able to accurately fit the experimental data was the generalized Maxwell model with $n = 3$ represented by the following equation:

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

where $E(t)$ is the modulus decay curve determined from experiments, t is the experimental decay time (s), τ (s) is the relaxation time of the i-th Maxwell element, E_i is 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.

The relaxation times are the ratio between the viscosity of the dashpot and the elastic modulus of the spring for each Maxwell unit (Cespi et al., 2007). The decay modulus of the Maxwell model (E_i) represents the elastic components, and thus provides a measure of the elasticity of the material (Khazaei & Mann, 2005). The equilibrium stress (E_e) is positively related to the strength of the gels and, thus, to the degree of crosslinking in the polymer network, so the magnitude of E_e can be taken as a measure of the "stiffness" of the materials i.e. hydrogels (Campus et al., 2010; Tang, Tung, & Zeng, 1998).

2. Materials and methods

2.1. Materials

Kappa carrageenan powder was kindly supplied by Behin Azma (Shiraz, Iran) and used without further purification. All other chemicals were of analytical grade unless otherwise mentioned.

2.2. Methods

2.2.1. Preparation of kappa carrageenan solutions and gels

Kappa carrageenan solutions at 0.4% (w/v) were prepared by dispersing the powder in deionized water or in 0.12% (w/v) KCl solution depending on the treatment with continuous magnetic stirring at 25 °C for 15 min. To examine the importance of the presence of KCl during ultrasound processing, two sets of experiments were compared. For set 1, 0.4% (w/v) carrageenan was dispersed in an aqueous solution of KCl (0.12%, w/v) then ultrasound was applied; these samples are called KCl-US. For another set of samples, 0.4% (w/v) carrageenan was dispersed in distilled water, ultrasound was applied and then KCl was added (0.12%, w/v); these samples are called US-KCl.

For conventional heating process, a stock solution of kappa carrageenan was prepared by dissolving the powder in an aqueous solution of KCl (0.12%, w/v) with continuous magnetic stirring at 80 °C for 15 min, 30 min or 120 min. Liquid samples were then poured into cylindrical glass sample holders (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. All experiments were performed in three replicates.

2.2.2. High intensity ultrasound treatment

Prepared solutions were ultrasonicated for different times (5 s, 10 s, 20 s, 30 s, 1 min, 2 min, 5 min, 10 min, 15 min and 20 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%. A high grade titanium tip (TT13, diameter 13 mm) was used to sonicate 100 ml of sample in a 120 ml cylindrical jacketed glass reactor of height and diameter of 85 mm and 65 mm, respectively. Distilled water mixed with ethylene glycol with a constant temperature of 15 °C was circulated in the jacketed vessel for temperature control. The depth of the horn is an important factor in polymer degradation, and in this work we chose 2 cm as the constant horn depth for all treatments.

2.2.3. Texture profile analysis

Textural properties of prepared gels were studied using a texture analyzer (Texture Analyzer, TA Plus, Stable Microsystems, Surrey, England) with a load cell of 30 kg, by performing texture profile analysis (TPA). TPA involves a double compression force test using a cylindrical probe having dimensions greater than of the sample dimensions. The samples were compressed to 25% of their original heights by two consecutive compressions using a cylindrical probe of 100 mm diameter. The crosshead speed was maintained at 0.25 mm/s. The waiting time between the two-cycles of the TPA test was 10 s. The texture profile parameters derived were hardness, defined as maximum force of the first compression peak, compression energy as the area under force versus time until maximum force, springiness as a ratio of the time recorded between the start of the second area and the second probe reversal to the time recorded between the start of the first area and the first probe reversal, and cohesiveness as the ratio between the area under the second peak and the area under the first peak (Bourne, 1968). Gumminess was determined by multiplying hardness and cohesiveness. Chewiness was derived from gumminess and springiness and was obtained by multiplying these two. All parameters were calculated from the compression force versus time curves using the software Texture Exponent Lite developed and supplied by the manufacturer.

All textural measurements were performed at room temperature (22 ± 2 °C) on six replicates for each sample.

2.2.4. Stress relaxation test

Stress relaxation tests were performed using a texture analyzer (Texture Analyzer, TA Plus, Stable Microsystems, Surrey, England). Cylindrical gel sections (20 mm diameter × 5 mm high) were compressed to 25% of their original height using a stress relaxation test. Force values were collected over a period of 120 s. All experiments were conducted at 22 ± 2 °C on three replicates for each sample.

2.2.5. Scanning electron microscopy

The prepared gels were frozen completely in a freezer set at −20 °C before being transferred to a freeze dryer (Dena Vacuum, Iran). The pressure during freeze drying was maintained at 7×10^{-2} mbar or below. The freeze dried porous samples with