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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

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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).

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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

moisture content of less than 3% were fixed on the aluminum sample holder during which it was tried to keep the structural damage to a minimum. The samples were then sputtered with gold in a sputter coater (Polaron SC7640, UK). All samples were examined using a scanning electron microscope (Cambridge, UK) under high-vacuum conditions at an accelerating voltage of 20.0 kV and a working distance of 7.5–9.5 mm (i.e. the distance between the surface of the sample and the microscope lens).

2.2.6. Statistical analysis

Analysis of variance (ANOVA) of mechanical properties of samples was performed to determine significant differences between the means. Duncan factorial scheme was used to compare the means by Statistical Analysis System (SAS) software, version 9.3.1. All comparisons were made at $\alpha = 0.05$.

3. Results and discussion

3.1. Texture analysis

For gelation of carrageenan dispersions, a heating stage is required during which molecular conformation of carrageenan biopolymers is altered in a way to form a network and entrap water molecules and form a gel after cooling (Nunez-Santiago & Tecante, 2007). To achieve this, different heating regimes of 70 °C; 2 h (Mangione, Giacomazza, Bulone, Martorana, & San Biagio, 2003), 80 °C; 2 h (Thrimawithana, Young, Dunstan, & Alany, 2010), 70 °C; 30 min and 90 °C; 30 min (Moritaka, Takahashi, & Kubota, 2007) have been reported. However, in this paper without any heating stage during preparation, ultrasound processing or afterwards, a gel like structure was obtained. To compare the properties of the gels prepared by ultrasound waves with gels of conventional method (i.e. gels prepared by heating), the mechanical properties of the kappa carrageenan gels prepared by conventional heating regimes of 15–120 min at 80 °C are shown in Table 1.

The mechanical properties of US-KCl and KCl-US kappa carrageenan gels prepared with different sonication times are shown in Fig. 1. Up to 60 s of sonication the hardness of US-KCl and KCl-US kappa carrageenan gels increased and the hardness values were similar. Afterwards the hardness of KCl-US gels decreased however, and for US-KCl gels fluctuations in hardness was observed.

The hardness profiles of the gels indicate that if the salt is added after sonication of carrageenan dispersions, the mechanical properties were stronger than on adding KCl to carrageenan dispersions before ultrasound treatment. Moreover, TPA data demonstrate that in both US-KCl and KCl-US kappa carrageenan gels, after a certain time of sonication, ultrasound treatment had a negative effect on mechanical properties of the gels. This correlated well with SEM images (Fig. 2). All kappa carrageenan gels of US-KCl samples had greater values for hardness, compression energy, cohesiveness, chewiness and Young's modulus than the KCl-US samples (Table 2). Wang, Cheung, Leung, and Wu (2010) have shown that ultrasound irradiation can disrupt exopolysaccharide clusters and aggregates firstly by weakening the molecular forces and then loosening the networks formed by cross linking. Therefore, ultrasound processing can lead to full exposure and accessibility of the hydrophilic groups of polymers to water. These researchers reported ultrasonic treatment as an effective means for improving water solubility of high molecular weight exopolysaccharides.

As can be seen from Table 2, when a dispersion of 0.4% (w/v) kappa carrageenan in the presence of 0.12% (w/v) KCl was sonicated for 5 s and 10 s, the gel network was too weak to be measured by texture analyzer, whereas for the US-KCl sample with the same kappa carrageenan concentration, after ultrasound treatments of 5 s and 10 s gel structures measurable by texture analyzer were obtained.

3.2. Young's modulus

Young's modulus was calculated from equation:

$$E = \frac{F/A}{dH/H} \quad (2)$$

where F/A is the applied force per surface unit and dH/H is the uniaxial deformation. For the different sonication time and at different situation of presence or absence of potassium ion during ultrasound treatment, the Young's modulus showed changes similar to those observed for other mechanical properties (Table 2).

3.3. Microstructure analysis

Considerable structural changes in SEM images of the carrageenan systems on applying ultrasound and increasing its time is observed (Fig. 2). For the control sample no coherent texture was observed as carrageenan granules are not soluble in cold water. Therefore the control sample does not form a gel. From Fig. 2 it is clear that by applying ultrasound, formation of a three dimensional structure is occurring with time. To form a gel using carrageenan granules solubilizing polymer molecules is a key step. Usually this is performed by heating (Whistler & BeMiller, 1997). In this research without heating and by using ultrasound waves the carrageenan granules became soluble. Indeed ultrasound waves acted the same role as heating step. Water solubility appears to increases with time until 5 min. Nonetheless, a further increase in ultrasonication time had a negative impact on the microstructure of the prepared gels. This was in line with texture data of the gels.

Adding salt after ultrasound process visibly increased the uniformity of gel network (Fig. 3). According to basic theories, in polyelectrolytes increasing concentration of counter-ions causes decreasing of electrostatic repulsations between polymer chains and coil dimensions. This means the intrinsic viscosity of the polymer decreases as counter-ion concentration increases (Snoeren, 1976; Vreeman, Snoeren, & Payens, 1980).

Although Núñez-Santiago, Tecante, Garnier, & Doublier, 2011 showed that in concentrations less than 4 mM of potassium ions (at 25 °C), there is a reverse relation between complex viscosity of the kappa carrageenan and concentration of potassium ion. While in concentrations more than 4 mM, this relation was direct. The concentration of potassium ion in the present study was 10 mM (0.12%, w/v of potassium chloride), so according to Núñez-Santiago et al. (2011) it can be concluded that total ionic concentration is located in vicinity of the sol–gel transition. Thus formation and

Table 1
Textural properties of kappa carrageenan gels prepared by conventional heating at 80 °C.

Conventional heating						
Time (min)	Hardness (g)	Compression energy (g mm)	Cohesiveness	Chewiness (g)	Gradient	Young's modulus (g/cm^2)
15	$48.5^{B} \pm 3.0$	$146.5^{B} \pm 13.0$	$0.6^{AB} \pm 0.0$	$26.5^{C} \pm 1.5$	$10.1^{B} \pm 0.3$	$1.6^{B} \pm 0.0$
30	$54.8^{A} \pm 4.5$	$176.6^{A} \pm 16.6$	$0.6^{B} \pm 0.0$	$30.8^{B} \pm 3.5$	$11.5^{A} \pm 0.8$	$1.8^{A} \pm 0.1$
120	$58.8^{A} \pm 3.1$	$176.7^{A} \pm 10.8$	$0.6^{A} \pm 0.0$	$34.3^{A} \pm 1.5$	$11.5^{A} \pm 0.9$	$1.8^{A} \pm 0.1$

Data are reported as mean ± stdev of six replicates. Mean values denoted in table by different letters (A–C) differ statistically significantly ($\alpha = 0.05$).

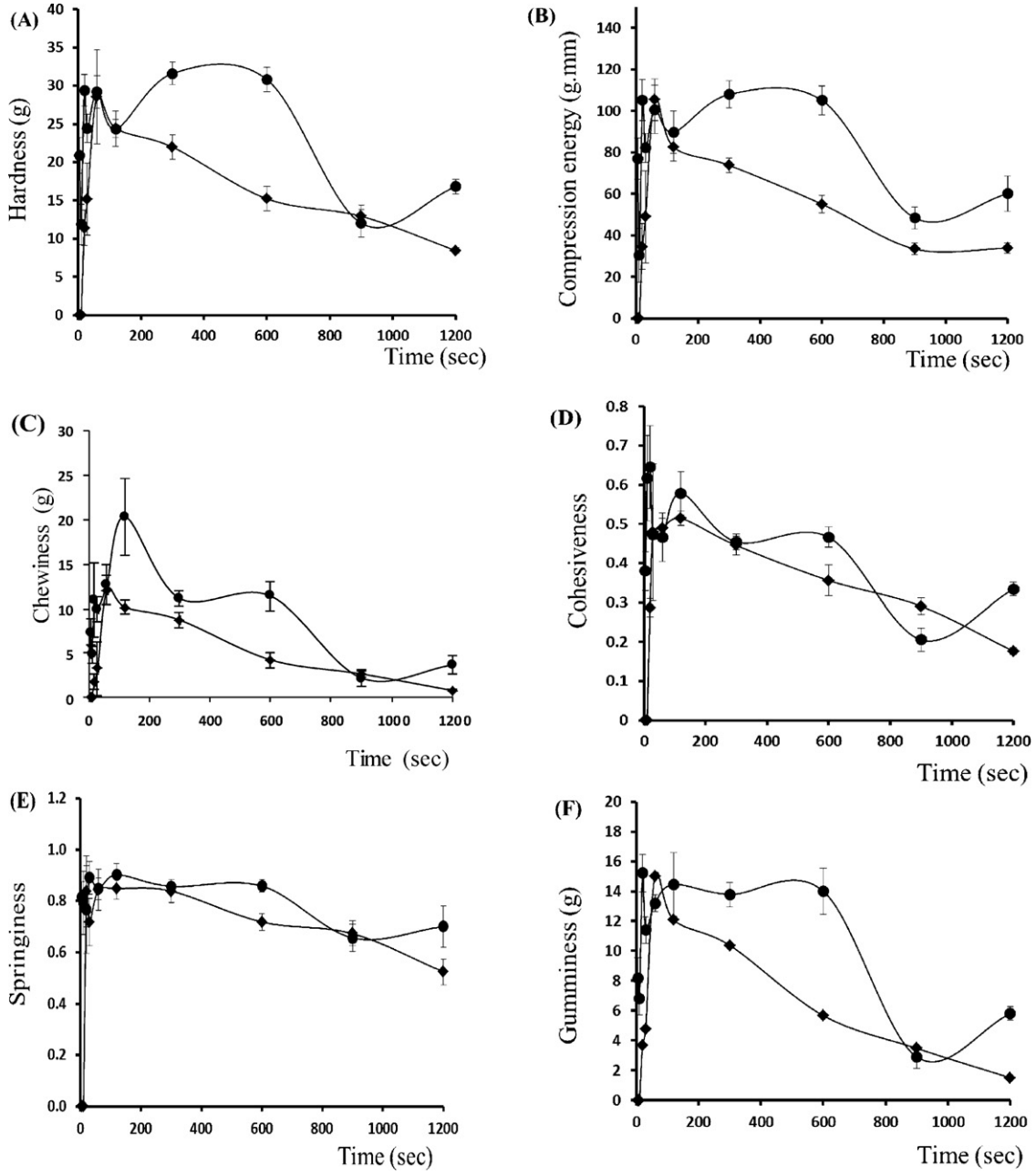

Fig. 1. Effect of ultrasonication time on the mechanical properties of KCl-US (♦) and US-KCl (●) samples. Mechanical properties presented are hardness (A), compression energy (B), chewiness (C), cohesiveness (D), springiness (E) and gumminess (F). Error bars represent stdev for six replicates.

Table 2
Values of hardness (g), compression energy (g mm), cohesiveness, chewiness and Young's modulus (g/cm^2) of US-KCl and KCl-US carrageenan gels at different sonication times.

Sonication time (s)	Hardness		Compression energy		Cohesiveness		Chewiness		Young's modulus	
	US-KCl	KCl-US	US-KCl	KCl-US	US-KCl	KCl-US	US-KCl	KCl-US	US-KCl	KCl-US
5	$21.0^{E} \pm 2.4$	$0.0^{J} \pm 0.0$	$76.8^{C} \pm 9.9$	$0.0^{G} \pm 0.0$	$0.4^{DE} \pm 0.0$	$0.0^{H} \pm 0.0$	$7.3^{E} \pm 1.5$	$0.0^{J} \pm 0.0$	$1.0^{BC} \pm 0.3$	$0.0^{I} \pm 0.0$
10	$11.9^{H} \pm 2.7$	$0.0^{J} \pm 0.0$	$30.4^{F} \pm 12.9$	$0.0^{G} \pm 0.0$	$0.6^{A} \pm 0.1$	$0.0^{H} \pm 0.0$	$4.8^{F} \pm 0.9$	$0.0^{J} \pm 0.0$	$0.5^{FG} \pm 0.1$	$0.0^{I} \pm 0.0$
20	$29.4^{AB} \pm 2.1$	$11.4^{H} \pm 2.3$	$105.1^{A} \pm 9.9$	$34.5^{F} \pm 11.0$	$0.6^{A} \pm 0.1$	$0.3^{F} \pm 0.0$	$10.9^{BCD} \pm 4.1$	$1.8^{HIJ} \pm 0.9$	$1.5^{A} \pm 0.4$	$0.6^{EF} \pm 0.1$
30	$24.4^{CD} \pm 1.9$	$15.1^{FG} \pm 4.7$	$82.1^{BC} \pm 7.0$	$48.9^{E} \pm 22.3$	$0.5^{C} \pm 0.0$	$0.5^{C} \pm 0.2$	$9.9^{CD} \pm 1.3$	$3.3^{FGH} \pm 3.2$	$0.7^{EF} \pm 0.1$	$0.5^{FG} \pm 0.1$
60	$29.2^{AB} \pm 2.1$	$28.5^{B} \pm 6.2$	$100.6^{A} \pm 11.6$	$105.3^{A} \pm 10.0$	$0.5^{C} \pm 0.1$	$0.5^{C} \pm 0.0$	$12.7^{B} \pm 2.3$	$12.1^{BC} \pm 1.7$	$0.8^{CDE} \pm 0.1$	$1.1^{B} \pm 0.2$
120	$24.3^{C} \pm 2.3$	$24.4^{CD} \pm 1.2$	$89.7^{B} \pm 10.2$	$82.5^{BC} \pm 7.0$	$0.6^{AB} \pm 0.1$	$0.5^{BC} \pm 0.0$	$20.3^{A} \pm 4.4$	$10.2^{CD} \pm 0.8$	$1.1^{B} \pm 0.1$	$0.7^{EF} \pm 0.1$
300	$31.6^{A} \pm 1.5$	$22.0^{DE} \pm 1.6$	$107.9^{A} \pm 6.6$	$73.7^{C} \pm 3.5$	$0.5^{C} \pm 0.0$	$0.4^{CD} \pm 0.0$	$11.1^{BC} \pm 0.9$	$8.7^{DE} \pm 0.8$	$1.0^{BC} \pm 0.3$	$0.6^{EF} \pm 0.3$
600	$30.8^{AB} \pm 1.6$	$15.2^{FG} \pm 1.6$	$105.0^{A} \pm 7.0$	$55.1^{DE} \pm 4.3$	$0.5^{C} \pm 0.0$	$0.4^{EF} \pm 0.0$	$11.4^{BC} \pm 1.6$	$4.2^{FG} \pm 0.9$	$0.8^{CDE} \pm 0.2$	$0.7^{EF} \pm 0.3$
900	$12.0^{H} \pm 1.8$	$12.9^{GH} \pm 1.5$	$48.4^{E} \pm 5.3$	$33.5^{F} \pm 2.8$	$0.2^{G} \pm 0.0$	$0.3^{F} \pm 0.0$	$2.2^{GHIJ} \pm 0.9$	$2.6^{FGHI} \pm 0.4$	$0.7^{EF} \pm 0.2$	$0.2^{HI} \pm 0.1$
1200	$16.8^{F} \pm 1.0$	$8.4^{I} \pm 0.4$	$60.1^{D} \pm 8.4$	$33.8^{F} \pm 2.4$	$0.3^{EF} \pm 0.0$	$0.2^{G} \pm 0.0$	$3.6^{FGH} \pm 1.0$	$0.8^{IJ} \pm 0.1$	$0.8^{DE} \pm 0.1$	$0.3^{GH} \pm 0.2$

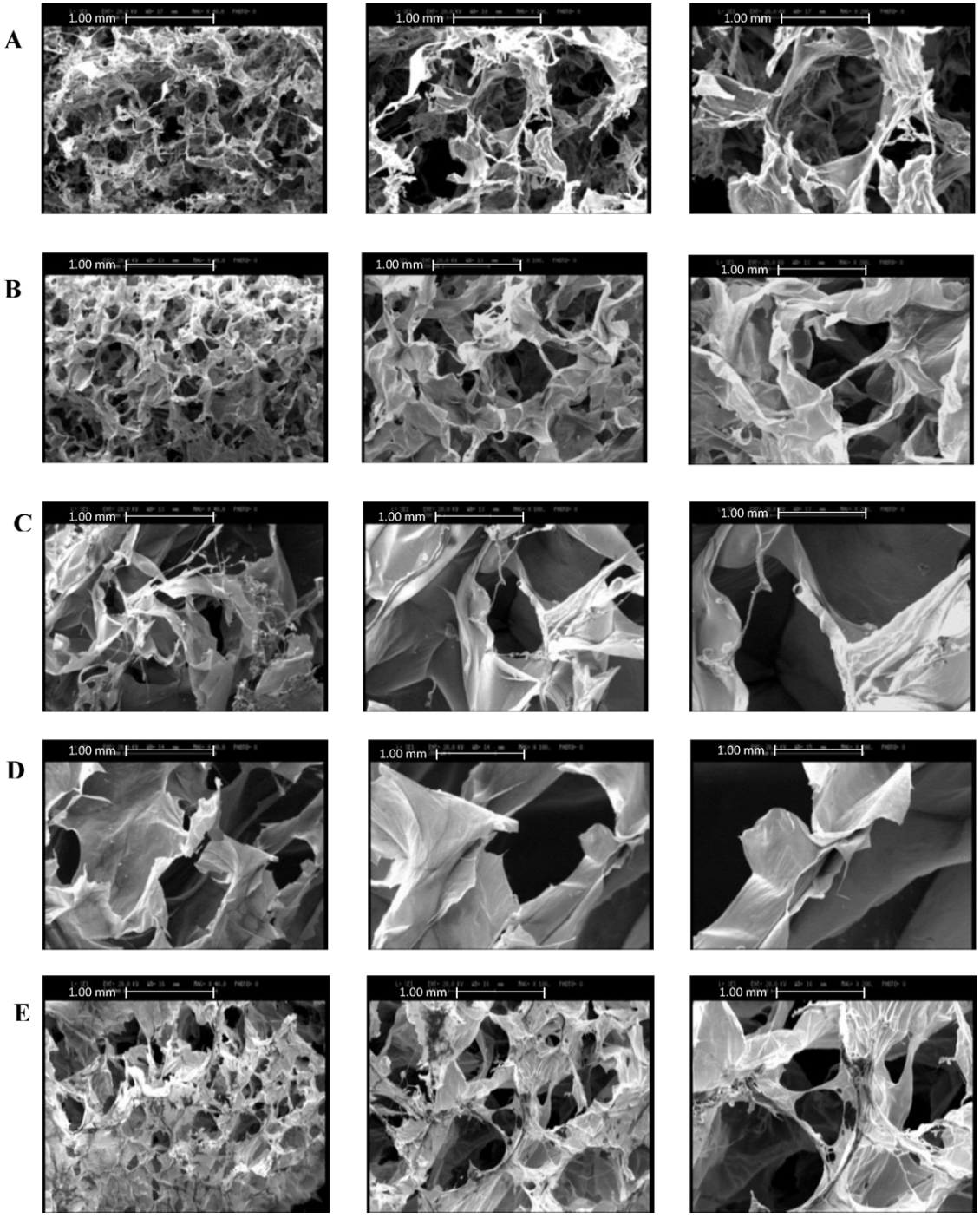

Fig. 2. Scanning electron micrographs of cold set kappa carrageenan dispersions (0.4%, w/v) prepared by ultrasound, in the presence of KCl (0.12%, w/v) during ultrasound process; times for ultrasonication are: 0 represented as control (A), 10 s (B), 1 min (C), 5 min (D), 15 min (E), respectively. Magnification of images in each row are 40, 100 and 200, from left to right respectively.

possibility of developing aggregation of helical chains is promoted, increasing the number of junction zones driving the chains to network formation. According to Grasdalen and Smidsroed (1981) and Belton, Morris, & Tanner (1986) potassium ions bind to the kappa carrageenan helices and thus reduce repulsion by decreasing the effective charge of individual helices. This allows extensive associations of helices into large "superstrands" (Hermansson, 1989; Ikeda, Morris & Nishinari, 2001).

It seems likely that sonication causes partial disruption of kappa carrageenan superstrands, allowing helix–helix associations within strands to be replaced by new associations between strands, to give a continuous network. Formation of weaker gels when KCl was added before sonication, rather than after, can then be explained by the higher concentrations of potassium ions generating superstrands that are larger, more stable, and more difficult to disrupt.

By comparing textural properties of carrageenan gels prepared by heating method (Table 1) and ultrasound waves (Table 2), it can be concluded that ultrasound, when applied to unheated dispersions of kappa carrageenan, is able to induce gel structures comparable to those obtained by cooling hot solutions. The maximum values of hardness, compression energy and Young's modulus

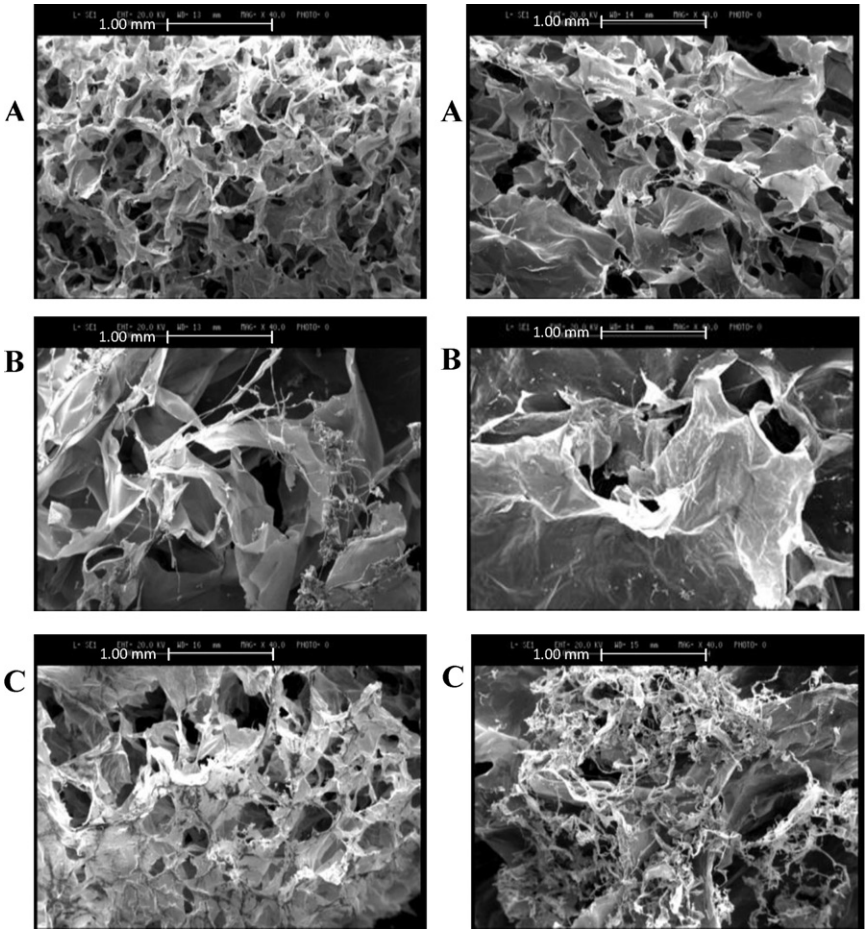

Fig. 3. Scanning electron micrographs of KCl-US (A, B, C) and US-KCl (A′, B′ and C′) samples after ultrasonication respectively for 10 s, 1 min and 15 min. Magnification of images is 40.

of the gels prepared by ultrasound were somewhat lower than those obtained by the conventional method, but the differences were relatively small, i.e., less than a factor of 2 for all three indices of gel strength.

3.4. Stress relaxation test

Since the first of the three terms of Maxwell model had a major contribution (90%) to the total modulus (Baragale, Irudayaraj, & Marquis, 1994), the value of relaxation time (τ_1), decay modulus (E_i) and equilibrium modulus (E_e) of the first term was used for analysis of results. In this work the variables were ultrasonication time and presence or absence of K^+ ions during ultrasound processing. The stress relaxation curves (Fig. 4) show the decay behavior of specimens with increasing experimental time irrespective of absence or presence of potassium ions during ultrasonication. In Table 3 E_e, τ_1 and E_i values are presented. An increase in E_e, E_i and τ_1 were observed with increasing ultrasonication time from 5 s to 5 min; after that, increasing sonication time had negative effects on residual modulus (E_e) and initial compressive stress (E_i). Moreover, it is clear from Fig. 4 and Table 3 that there are significant differences between gels of US-KCl and KCl-US samples. The values of (E_e), (E_i) and (τ_1) were greater when salt was added after ultrasound treatment. Initial compressive stress (E_i) represented the resistance of the sample toward compression prior to relaxation, so the higher E_e and E_i values revealed that the

Table 3
Element Maxwell model parameters for US-KCl and KCl-US gels prepared by ultrasound at 20 °C.

Ultrasonication time (s)	US-KCl				KCl-US			
	E_i	τ_1	E_e	R^2	E_i	τ_1	E_e	R^2
5	1.7^{CD}	1.8^{H}	0.2^{KJ}	0.9	0.0^{G}	0.0^{H}	0.0^{K}	–
10	1.7^{CD}	19.5^{EF}	0.3^{IJ}	0.9	0.0^{G}	0.0^{H}	0.0^{K}	–
20	2.1^{B}	25.5^{BC}	2.0^{CD}	1.0	0.8^{F}	17.4^{F}	0.5^{HI}	0.8
30	2.1^{B}	21.2^{DE}	2.1^{C}	1.0	1.2^{E}	11.8^{G}	0.6^{GH}	0.8
60	2.0^{B}	27.7^{AB}	3.4^{A}	1.0	1.4^{DE}	20.3^{DE}	1.4^{F}	0.9
300	2.6^{A}	27.2^{AB}	2.7^{B}	1.0	1.7^{C}	28.9^{A}	1.8^{DE}	1.0
600	2.5^{A}	27.9^{AB}	1.6^{E}	1.0	1.7^{CD}	23.1^{CD}	0.3^{IJ}	1.0
900	1.6^{CD}	24.7^{BC}	0.7^{G}	0.9	1.4^{DE}	23.4^{CD}	0.3^{J}	0.9
1200	2.0^{B}	21.1^{DE}	0.1^{KJ}	1.0	1.2^{E}	9.7^{G}	0.0^{K}	0.9

Data are reported as means of three replicates. Values with different superscripts differ significantly at $\alpha < 0.05$.

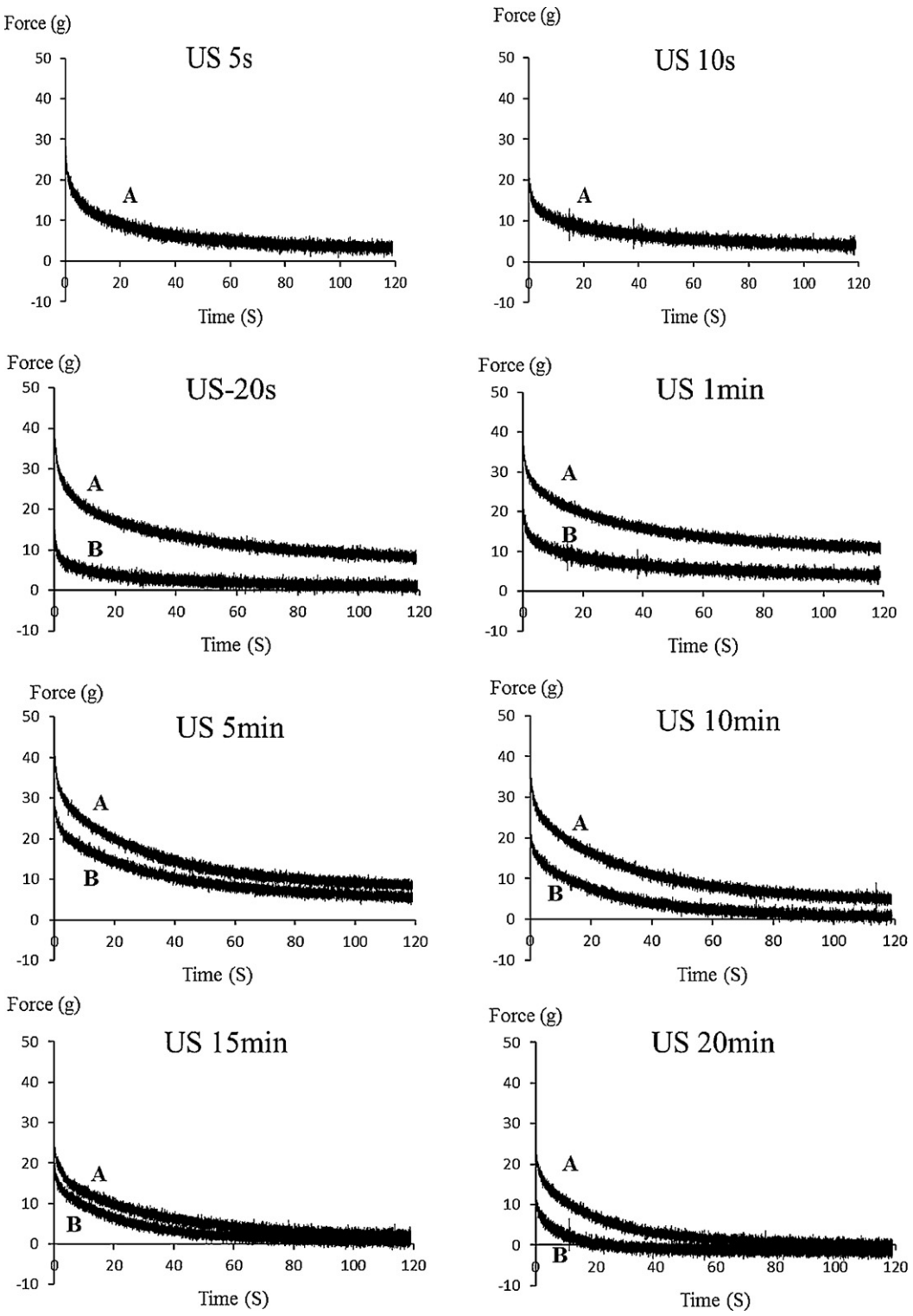

Fig. 4. Stress relaxation curves of kappa carrageenan gels at different time of ultrasonicaion. In each curve (A) US-KCl sample and (B) KCl-US sample.

sample has a more solid-like texture, hence the force required for compression increased (Bhattacharya, 2010). The results presented in Table 3 demonstrate that when the salt is added after sonication the ultrasonicated samples for 1, 5 and 10 min had the most rigid and elastic gels with greatest values of E_e, E_i and τ_1. The results for τ_1 values are in accordance with Herrero, Heia, and Careche (2004) and Campus et al. (2010) who demonstrated that higher values of τ_1 show that the sample is firmer and more elastic.

As can be seen from Table 3 the highest values of E_e (3.439 g and 2.732 g) were obtained for US-KCl treatment after 1 and 5 min of ultrasonication, respectively and they are significantly higher than that of KCl-US. In this work higher stress relaxation rates were obtained when the gel samples were weaker in terms of textural properties. Tang et al. (1998) reported similar results and stated that relaxation rate is positively related to the pore sizes in the gel matrix as evidenced by SEM images.

4. Conclusion

In this research power ultrasound processing was used for gelation of kappa carrageenan dispersions without using heat, successfully. It seems that ultrasound waves can cause disruption of carrageenan macromolecules, allowing helix to helix associations within strands to be replaced by new associations between strands, resulting in formation of a continuous network. This seems similar to opening up helix to helix carrageenan superstrands by heating. When heating is used carrageenan gel is formed after cooling, but when ultrasound is applied to cold carrageenan dispersions the gel is formed instantaneously. Gel hardness increased with ultrasound processing up to 10 min, but longer ultrasound times weakened the gel structure and this could be related to the degradation of polymers caused by ultrasound cavitation and its resulting high shear forces. Hardness data and relaxation parameters were consistent among the samples. To the best of our knowledge this is the first report on ultrasound cold gelation of dispersions of any gelling biopolymer. More research is required to investigate the effects of different ultrasound conditions (i.e. power and amplitude) and reveal the mechanism of ultrasound assisted cold gelation of kappa carrageenan. We hope to report more on this interesting issue with our continuing research.

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