



Texture and rheological characterization of kappa and iota carrageenan in the presence of counter ions

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ABSTRACT

The effect of cation concentration and ion valency (0–0.2% (w/v) of KCl or CaCl₂·2H₂O) on the mechanical, micro-structural and rheological properties of aqueous kappa (κ) and iota (ι) carrageenan dispersions were investigated using a texture analyzer, cryo-SEM and an oscillatory rheometer, respectively. The probe penetration method demonstrated a decrease in “hardness” of carrageenan systems with increasing cation concentration, after exhibiting an initial maximum. The Young's modulus (*E*) of κ-carrageenan gels was determined using the uniaxial compression method. *E* was approximately 3 times the shear modulus recorded under the same experimental conditions; indicating the elimination of slip by the use of roughened parallel plates. The storage modulus of ι-carrageenan gels with Ca²⁺ demonstrated a similar trend to mechanical properties. However the syneresis observed in κ-carrageenan systems with storage, may have reduced the sensitivity of probe penetration method. Cryo-SEM observation of gels revealed a microstructure consistent with the observed mechanical properties.

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1. Introduction

Carrageenan is a widely used anionic polysaccharide extracted from marine red algae. Chemically, this polymer is a linear, sulphated galactan which is composed of alternating disaccharide repeating units of 3-linked β-D-galactopyranose (G units) and 4-linked α-D-galactopyranose (D units) or 4-linked 3, 6-anhydro-α-D-galactopyranose (DA units). Depending on the number and position of sulphate groups, three main carrageenans have been identified: iota (ι)-, kappa (κ)- and lambda (λ)-carrageenan (Van De Velde, 2008; Van De Velde, Peppelman, Rollema, & Tromp, 2001). Both κ- and ι-carrageenan dispersions undergo sol–gel transition upon cooling or the addition of counter ions such as Na⁺, K⁺ and Ca²⁺ (Belton, Chilvers, Morris, & Tanner, 1984; Michel, Mestdagh, & Axelos, 1997; Nunez-Santiago & Tecante, 2007). However, at a particular temperature the critical polymer concentration required for gelation is considerably lower in the presence of some alkali ions (Nijenhuis, 1996). Conversely, λ-carrageenan does not undergo gelation; presumably due to its high degree of sulphate substitution (Wang, Rademacher, Sedlmeyer, & Kulozik, 2005).

Many models have been proposed to describe the gelation process of polymers; yet that widely accepted for carrageenan is the “domain model”. Here, it is assumed that, in solution and at high temperature, carrageenans exist as random coils; and reduction in temperature induces the formation of double helices. This leads to the formation of small independent domains involving a limited number of chains via intermolecular association. However, when cations are incorporated, helices of different domains aggregate to enable long-range cross-linking which forms a cohesive network. This quaternary structure contributes to the mechanical and rheological properties of the resultant gels (Morris, Rees, & Robinson, 1980).

The role of various cations in promoting cross-link formation has been previously studied. It has been shown that calcium ions (Ca²⁺) favour the gelation of ι-carrageenan whereas potassium ions (K⁺) favour the gelation of κ-carrageenan (Morris & Chilvers, 1981; Tako & Nakamura, 1986; Tako, Nakamura, & Kohda, 1987). Calcium, being a divalent cation, is capable of forming intra-molecular bridges between the sulphate groups of adjacent anhydro-D-galactose and D-galactose residues of ι-carrageenan. Upon cooling, the quaternary structure forms due to intermolecular Ca²⁺ bridging. Conversely, K⁺ induces intermolecular association of κ-carrageenan by forming an ionic bond between K⁺ and sulphate group of D-galactose residues. This is followed by the formation of a secondary electrostatic bond between K⁺ and the anhydro-bridge oxygen atom of the adjacent galactose residue. Smaller univalent

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cations, such as Na^+ and Li^+ , are only able to bond ionically to the sulphate groups reducing their efficacy in controlling the flexibility of disaccharide units of carrageenan (Nijenhuis, 1996; Tako & Nakamura, 1986; Tako et al., 1987).

The effect of these cations on the physical properties of carrageenan gels has been investigated widely (Funami et al., 2007; Hermansson, Eriksson, & Jordansson, 1991; Hossain, Miyanaga, Maeda, & Nemoto, 2001; Ikeda & Nishinari, 2001; Macartain, Jacquier, & Dawson, 2003; Mangione et al., 2005; Nunez-Santiago & Tecante, 2007). Nonetheless, the assessment and comparison of the viscoelastic and mechanical properties of carrageenan gels at low polymer concentrations and a wide range of counter ions is scarce in the literature. Moreover, previous reports on the values of Young's modulus (E) are inconsistent or are not compared directly with shear modulus values obtained from rheological experiments.

The present study compares the mechanical and rheological properties of κ -carrageenan and ι -carrageenan dispersions in the presence of both potassium and calcium ions at low polymer concentration. A wide concentration range of the selected counter ions was studied to determine the optimum cation concentration for each system.

2. Materials and methods

2.1. Materials

Carrageenan, Genuvisco type \times 930-03 (κ) and type \times 931-03 (ι) were kindly gifted from CP Kelco (Lille Skensved, Denmark) and was used without further purification. κ -Carrageenan sample consisted of 5.1% (w/w) potassium, 1.6% (w/w) calcium and 0.87% (w/w) of sodium whereas the ι -carrageenan sample consisted of 5% (w/w) potassium, 0.031% (w/w) calcium and 4.8% (w/w) sodium (determined with ICP-OES). Potassium chloride (KCl) and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) were of analytical grade and purchased from Scharlau Chemie (Barcelona, Spain). Water purified by ion exchange (Millipore, Bedford, USA) to a resistance of $18.2 \text{ M}\Omega \text{ cm}$ at 25°C was used in the preparation of formulations and ion solutions.

2.2. Sample preparation

Stock solutions of κ - and ι -carrageenan were prepared by dissolving the powder in an appropriate volume of water with continuous magnetic stirring at 80°C for 2 h. Polymer systems containing various concentrations of counter ions were then prepared by diluting the stock polymer solution with an appropriate amount of water and then adding the required volume of either KCl or $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ stock solution (2% (w/v)).

2.3. Construction of ternary phase diagrams

To study the effect of potassium and calcium on the phase behaviour of ι - and κ -carrageenan aqueous systems, partial ternary phase diagrams were constructed using Gibb's triangles. The apices of the triangle represent 100% by weight of one component, whereas the axis joining the apices corresponds to two component systems. The area within the triangle corresponds to all possible combinations of the three components under investigation.

Formulations were prepared as described above and were stored at room temperature (*ca.* 22°C) for 24 h. Formulations were then assessed visually by tilting the sample vials to an angle of 90° and were categorised as gels, gels with syneresis, partial gels and solutions. Gels with syneresis are systems with a water layer on the surface of a well formed gel. Partial gels are defined as systems comprising of gel clumps in solution.

2.4. Microstructure analysis

The microstructure of 0.4% (w/v) κ - and ι -carrageenan dispersions in the absence or presence of selected cations was examined using a cryogenic scanning electron microscope (Philips XL30S FEG, Netherlands). Samples were initially cured for 12 h at 4°C then loaded onto rivets and plunge frozen in liquid nitrogen slush (-200°C). These were then loaded into the cryo chamber (Gatan Alto 2500, England), fractured with a razor blade and sublimed at -80°C under vacuum for 30 min. Samples were sputter coated with gold (Polaron SC 7640 sputter coater, Quorum Technologies, England) for 2 min and then viewed at an accelerating voltage of 5 kV while being maintained at -180°C .

2.5. Texture profile analysis

Mechanical properties such as "hardness", "compressibility", "adhesiveness", "cohesiveness" and "elasticity" of the carrageenan systems were evaluated using a TA-XT plus texture analyzer (Stable Micro Systems, England). Samples were prepared and stored in hermetically sealed containers and maintained at ambient temperature (*ca.* 22°C) prior to analysis. At 24 h or 7 days of storage, an analytical probe (10 mm diameter) was compressed twice into the sample to a depth of 15 mm at a cross-head speed of 2 mm s^{-1} , allowing a relaxation period of 30 s between compression cycles. All measurements were done in triplicate. The data were statistically analysed by one-way ANOVA with Tukey's HSD post hoc test ($p < 0.01$ denoting significance) using SPSS version 16.0 for windows (SPSS Inc., Illinois, USA).

2.6. Young's modulus calculation

Young's modulus of binary systems comprising of κ -carrageenan (0.4% (w/v)) and KCl (0.12–0.2% (w/v)) was determined to compare compression measurements with dynamic measurements. Compression measurements on free standing gels were utilized to calculate the Young's modulus to avert bias due to buoyancy usually encountered with the probe penetration method.

Liquid samples at 80°C were poured into metal cylindrical moulds ($\text{Ø}20 \text{ mm} \times 20 \text{ mm}$). Moulds were over-filled by taping around the upper section. Samples were then stored at room temperature (*ca.* 22°C) for 3 h. The excess gel was trimmed off prior to analysis and the free-standing gel was placed at the centre of the texture analyzer (TA-XT2, Stable Micro Systems, England) testing platform. The gel was then compressed between parallel plates at a speed of 0.2 mm s^{-1} to a depth of 10 mm at room temperature (22°C). A strain of 5% was used to obtain the Young's modulus and all measurements were carried out in triplicate. The rupture stress and strain were also recorded as the gel fractured.

2.7. Rheological measurements

Dynamic viscoelastic properties of the carrageenan systems were performed with a controlled stress rheometer (AR-G2, TA Instruments, USA) equipped with a parallel plate (40 mm diameter) geometry. The upper plate was covered with sand paper (wet/dry P120) to minimize sample slip due to high amount of water present in the investigated gels and a solvent trap was used to prevent evaporation of water from the samples.

Carrageenan samples were placed on the peltier plate at 80°C and the gap was set to 1 mm. Temperature was decreased at a rate of 5°C min^{-1} and time sweeps were obtained at 22°C over 3 h in the linear viscoelastic region. The storage shear modulus, G' , and the loss shear modulus, G'' , were also measured over a

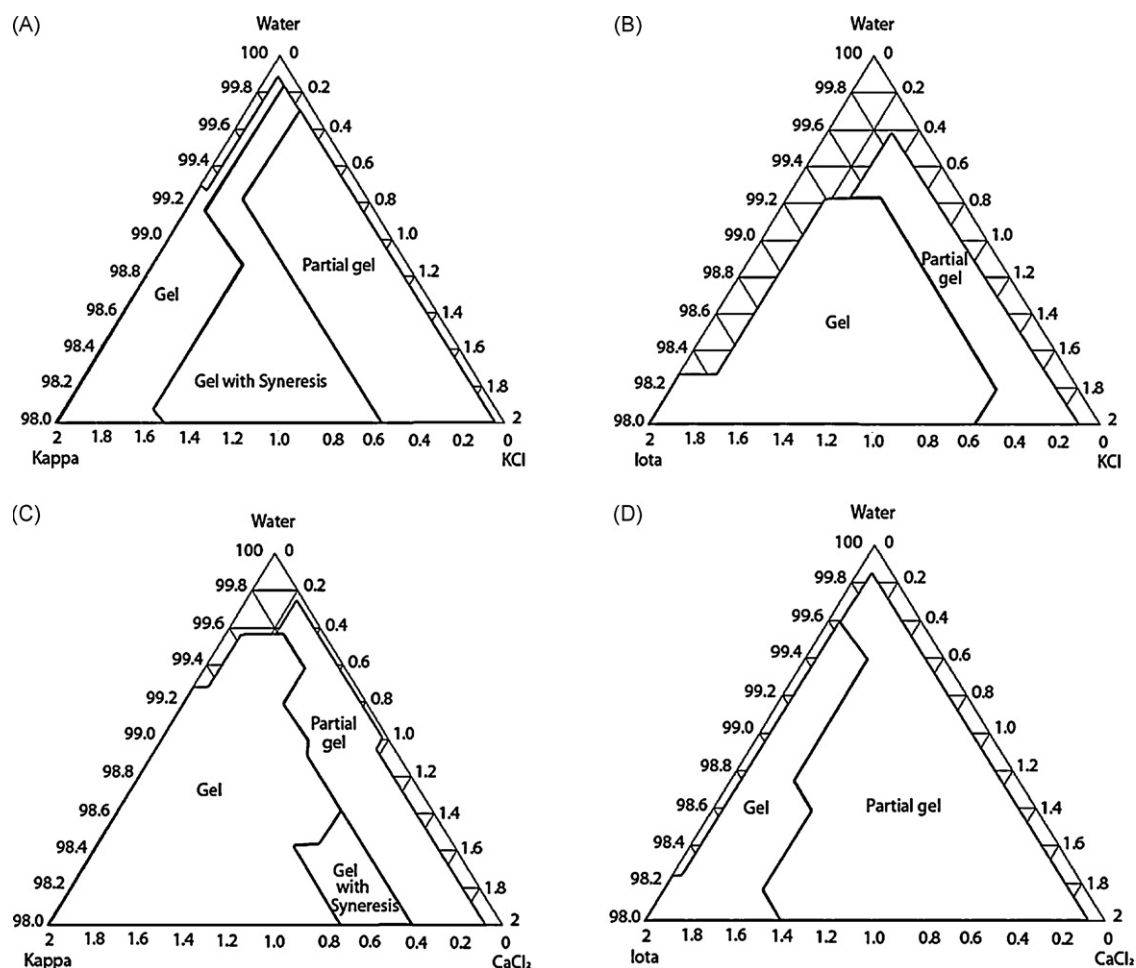


Fig. 1. Partial ternary phase diagrams of κ -carrageenan (A and C) and ι -carrageenan (B and D) aqueous dispersions in the presence of KCl or $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

frequency range of 0.1–10 Hz at 22 and 4 °C after 10 min of equilibration.

3. Results and discussion

3.1. Effect of cations on phase behaviour of κ - and ι -carrageenan systems

Gibbs phase triangles (Fig. 1) show substantial differences between κ - and ι -carrageenan in their response to KCl and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. As previously reported, κ -carrageenan responds promptly to K^+ and undergoes the coil to helix transition (Chen, Liao, & Dunstan, 2002; Hermansson, 1989; Tako & Nakamura, 1986). Conversely, ι -carrageenan displays this transition in the presence of low concentrations of Ca^{2+} (Hossain et al., 2001; Morris & Chilvers, 1981; Tako et al., 1987).

The minimum concentration of κ -carrageenan required to undergo a sol–gel phase change in the presence of cations at 22 °C was found to be about 0.2% (w/v). Conversely a minimum of 0.4% (w/v) polymer was required for the ι -carrageenan system to undergo the same phase change. Therefore a polymer concentration of 0.4% (w/v) was selected for the mechanical, microstructure and rheological characterization of these systems.

At relatively high counter ion concentrations, κ -carrageenan displayed syneresis; the polymer helices aggregate tightly and extrude water from the system. This behaviour was not observed with ι -carrageenan formulations. As counter ion concentration was further increased, both systems displayed partial gelling, demon-

strating insufficient polymer concentration to form a uniform gel matrix.

3.2. Microstructure analysis

Rapid freezing with liquid nitrogen employed in cryo-SEM reduces the ice crystal formation and preserves the spatial structure of these highly aqueous systems for further investigation. Moreover, sample distortion due to dehydration can be avoided in cryo-SEM (Echlin, 1992; Srimornsak, Thirawong, Cheewatanakornkool, Burapapadh, & Sae-Ngow, 2008).

Considerable differences in the SEM images of the two carrageenan systems were observed (Fig. 2). ι -Carrageenan dispersions in the absence of added cations, displayed no cross-linking; the polymers being arranged as pleats (Fig. 2A). Addition of Ca^{2+} induced the appearance of cross-linked structures, with the formation of rectangular pores (Fig. 2B and C). Nonetheless, a further increase in Ca^{2+} concentration had a negative impact on the microstructure of the ι -carrageenan system (Fig. 2D).

In the absence of added K^+ , κ -carrageenan displayed some regular order (cross-linking) (Fig. 2E). This was further enhanced by the addition of K^+ (Fig. 2F and G). Moreover, increasing K^+ concentration to 0.12% (w/v) visibly increased the density of cross-links (Fig. 2G). The polymer arrangement of κ -carrageenan systems resembled a honeycomb structure; which may contribute to the known high tensile properties of these systems. Again, the addition of 0.4% (w/v) K^+ disrupted the cross-linking of κ -carrageenan (Fig. 2H). This negative impact may be attributed to saturation

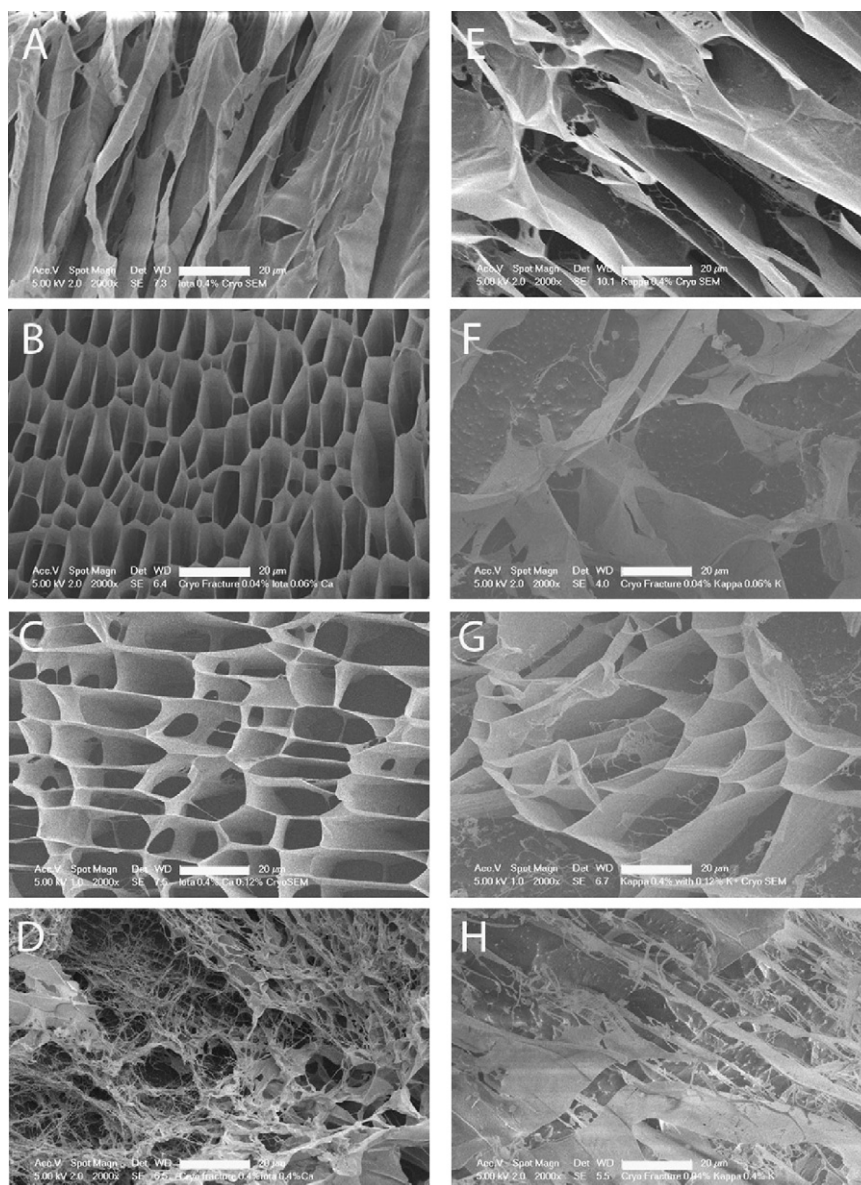


Fig. 2. Cryo-SEM images of ι -carrageenan dispersions (0.4%, w/v) in the absence of added cations (A), and in the presence of 0.06%, w/v (B), 0.12%, w/v (C) and 0.4%, w/v (D) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and κ -carrageenan dispersions (0.4%, w/v) in the absence of added cations (E) and in the presence of 0.06%, w/v (F), 0.12%, w/v (G) and 0.4%, w/v (H) of KCl (scale bars = 20 μm).

of cross-linking zones, and aggregation of polymer groups which would disrupt the cohesive quaternary structure of the systems.

3.3. Texture profile analysis

Texture profile analysis (TPA) is a simple and rapid analytical technique that has been used extensively in the food industry. It is also used to some extent, in the pharmaceutical industry to characterize semi-solid formulations. The mechanical properties “hardness”, “cohesiveness”, “compressibility”, “adhesiveness” and “elasticity” of the carrageenan systems were derived from the force vs. time plots as described by Jones et al (Jones, Woolfson, Djokic, & Coulter, 1996; Jones, Woolfson, & Brown, 1997). The mechanical properties of κ - and ι -carrageenan systems in the presence of various concentrations of selected cations are shown below (Fig. 3).

The hardness profiles demonstrate the rapid cross-linking effect of K^+ on κ -carrageenan when compared to Ca^{2+} . Moreover, the concentration of KCl required to initiate intermolecular bridging was 0.04% (w/v), whereas about 0.12% (w/v) of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was

required. However, the maximum hardness of κ -carrageenan gels was comparable in both cation systems.

In addition, calcium induced κ -carrageenan gels required longer time to stabilize with the maximum mechanical properties attained after 24 h of equilibration. This may be due to the inability of Ca^{2+} to form the proposed bonding with the anhydrous oxygen group and the sulphate groups of the adjacent disaccharide units, which reduces intermolecular association. However, at higher Ca^{2+} concentrations, charge neutralization may lead to intermolecular association at a slower rate. Alternatively, the long stabilization time may reflect longer diffusion times caused by the cross-linking of adjacent polymer molecules.

ι -Carrageenan did not respond to KCl in the range tested, but was able to form soft gels in the presence of divalent cation, Ca^{2+} . Maximum ι -carrageenan gel strength was observed at 0.1% (w/v) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and was ca. 0.3 \times lower than the maximum hardness of κ -carrageenan gels. This high tensile strength of κ -carrageenan gels can be attributed to the microstructure of these systems (Fig. 2) as typical honeycomb structures possess high ductility and are able

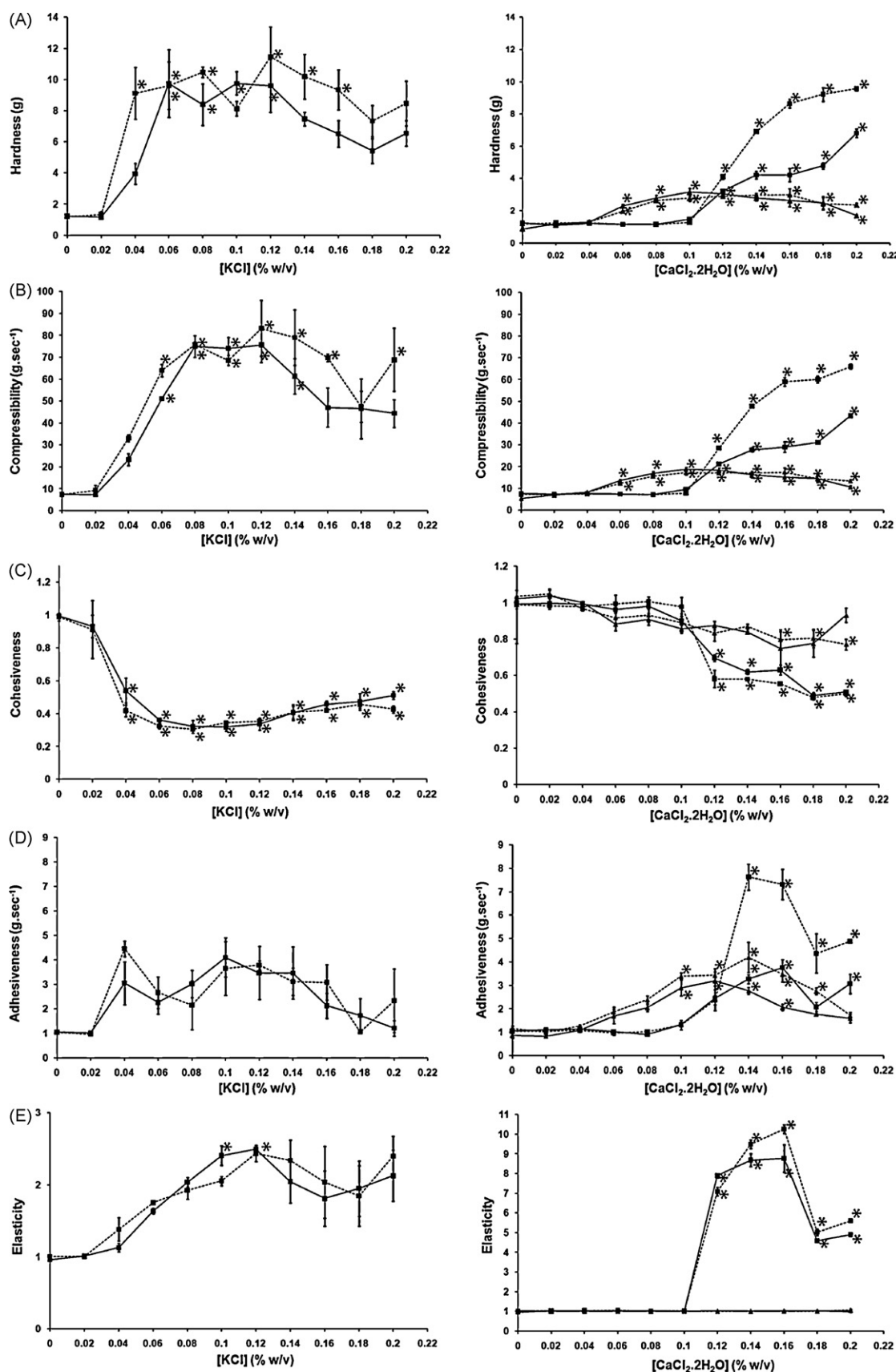


Fig. 3. Effect of cations on the mechanical properties of 0.4% (w/v) κ -carrageenan (■) and ι -carrageenan (▲) dispersions at 24 h (solid) or 7 days of storage (dashed) at various KCl or $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ concentrations. Mechanical properties presented are "Hardness" (A), "Compressibility" (B), "Cohesiveness" (C), "Adhesiveness" (D) and "Elasticity" (E). Error bars represent SEM ($n=3$) and *denotes significant changes from baseline ($P<0.01$; ANOVA with Tukey's HSD post hoc test).

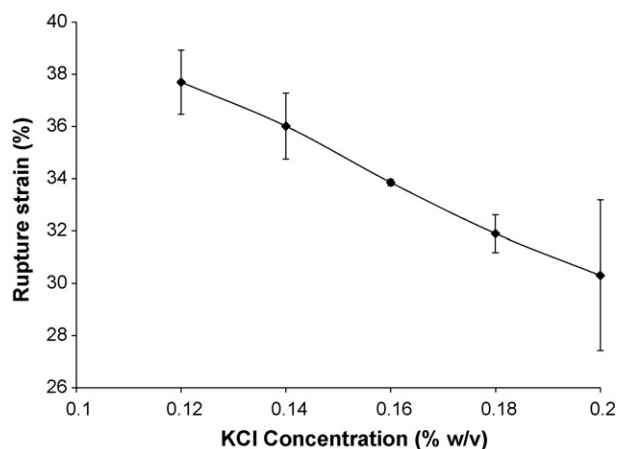


Fig. 4. Effect of KCl concentration on the rupture strain of κ -carrageenan gels. Error bars represent standard deviation from the mean ($n=3$).

to reduce local stresses by transferring forces (Wang, Qiu, & Zhang, 2007).

Nonetheless, ι -Carrageenan gels were more “cohesive” and “elastic” than κ -carrageenan systems, which exhibited increasing brittleness with increasing KCl concentration (Fig. 4). The brittle nature of κ -carrageenan is likely to be due to the syneresis of these gels which removes water from the gel structure. The difference in

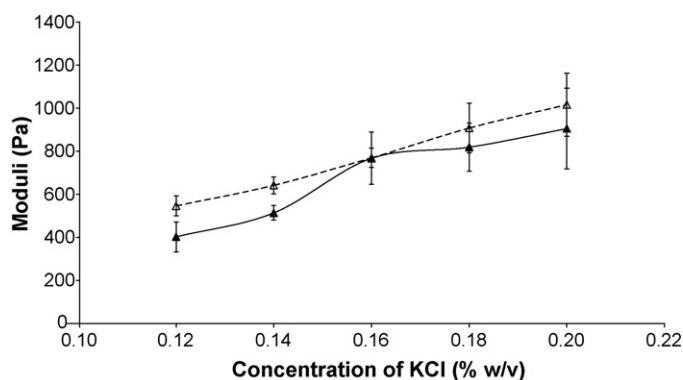


Fig. 5. Shear modulus (G') (\blacktriangle ; $n=2$) and one-third of Young's modulus ($1/3E$) (\triangle ; $n=3$) of κ -carrageenan (0.4%, w/v) gels in the presence of various concentrations of KCl. Error bars represent standard deviation from the mean.

observed microstructure may also be attributed to the variation in elasticity of these gels, where an increase in cross-linking leads to reduced flexibility of polymer chains.

TPA data demonstrates a general reduction in mechanical properties of carrageenan dispersions with increasing cation concentration, after exhibiting an initial maximum. This correlates well with the findings of MacArtain et al. (2003), who demonstrated a reduction in gel strength with an increase in calcium to carrageenan

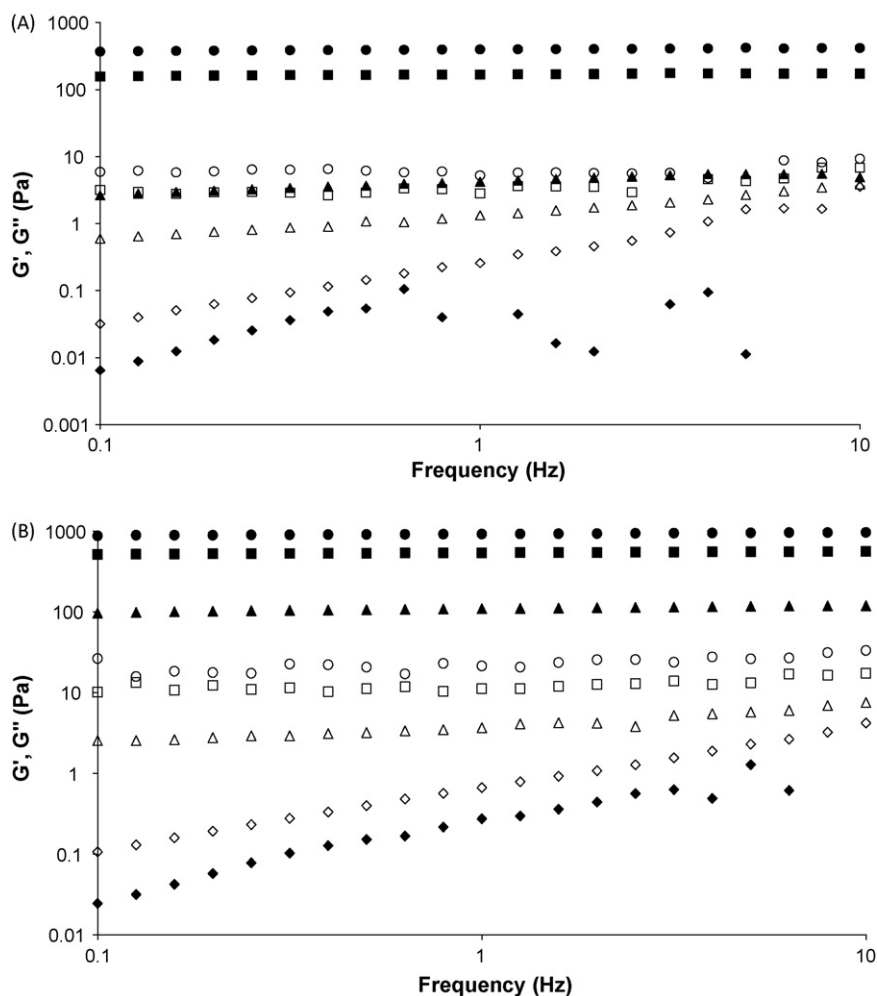


Fig. 6. Frequency dependence of G' (filled) and G'' (open) of κ -carrageenan dispersions (0.4%, w/v) in the absence (\diamond) and presence of added KCl at 22 °C (A) and 4 °C (B). Concentrations of KCl are 0.06% (\triangle), 0.12% (\square) and 0.2% (\circ) (w/v) ($n=3$).

ratio (MacArtain et al., 2003). Michel et al. (1997) also investigated the effect of Ca^{2+} , Cu^{2+} , Na^+ and K^+ on the shear moduli of κ - and ι -carrageenan and demonstrated a threshold for the amount of salt incorporated. The authors concluded that beyond this threshold, neither the cation concentration nor the type of cation had any effect on shear moduli (Michel et al., 1997). In the present study we have demonstrated a reduction in mechanical properties of the carrageenan systems under investigation when the cation threshold is exceeded.

3.4. Rheological measurements

Syneresis of κ -carrageenan gels has been cited frequently as a limiting factor in measuring the dynamic moduli of these systems, as the water removed from κ -carrageenan systems leads to slip effects. Slipping of testing geometry can result in erroneous measurements and demonstrate considerably lower storage moduli (G') to the actual (Richardson & Goycoolea, 1994). Therefore serrated geometry, sanded parallel plates, perforated concentric cylinders or glued parallel plates have been used to overcome this issue (Chen, Liao, Boger, & Dunstan, 2001; Norziah, Foo, & Karim, 2006; Richardson & Goycoolea, 1994). As shown by Chen et al. (2001) and Richardson and Goycoolea (1994), the glued parallel plate and the perforated cylinder methods, respectively, give considerably larger values of G' for aqueous gels compared to the other methods. However, the glued parallel plate method cannot be used successfully for weak gel measurements, such as the systems under investigation.

In order to minimize the effect of slip, a roughened geometry was utilized in this study. The slip effect was evaluated by comparing the Young's modulus (E) data derived from the uniaxial compression to the shear moduli (G') values obtained from the dynamic rheology measurements (Fig. 5). Initially time sweeps at 22°C (room temperature) were performed in the linear viscoelastic region (LVR) to determine the period of testing and equilibration of the κ -carrageenan systems was reached within 3 h. As syneresis of these systems was observed with extended storage, the moduli (E and G') were evaluated at 3 h of equilibration at 22°C .

Theoretically the G' of any material should satisfy the relationship of $E \approx 3G'$, derived from Eq. (1):

$$E = 2G'(1 + \nu) \quad (1)$$

where ν is the Poisson's ratio, ranging from 0 to 0.5 for all known materials. For a perfectly incompressible gel, the Poisson's ratio is found to be near 0.5 (Menard, 1999).

G' of κ -carrageenan systems were comparable to one-third E of the gels obtained from the compression measurements at room temperature (22°C) (Fig. 5). This confirmed the validity of rheological measurements in the present study. Compression measurements were also performed on larger samples ($\varnothing 40\text{ mm}$); however the E values calculated were not comparable to the G' in this instance. It was noted that these samples took longer to stabilize as the $E:G'$ ratio was well below 2.5 for most gels at 3 h of equilibration. Therefore the sample volume plays an important role in satisfying the above relationship. Furthermore it was not possible to compare the moduli of κ -carrageenan at lower K^+ concentra-

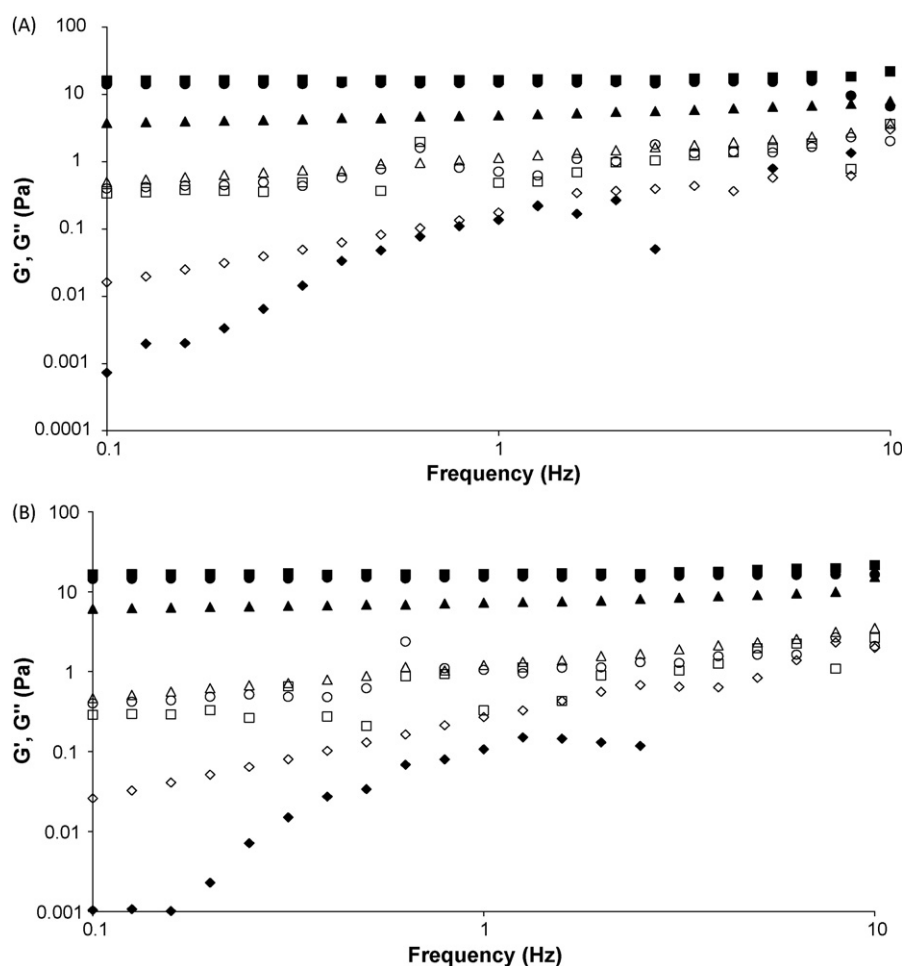


Fig. 7. Frequency dependence of G' (filled) and G'' (open) of ι -carrageenan dispersions (0.4%, w/v) in the absence (\diamond) and presence of added $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at 22°C (A) and 4°C (B). Concentrations of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ are 0.06% (Δ), 0.12% (\square) and 0.2% (\circ) (w/v) ($n=3$).

tions and the ι -carrageenan systems, as these are too weak for large deformation measurements (not stand alone gels). Attempts were also made to determine the shear moduli using the penetration method outlined by Gregson, Hill, Mitchell, and Smewing (1999). However this was unsuccessful; probably due to variables such as gel height, diameter, probe width and buoyancy (Gregson et al., 1999).

Fig. 6a and b shows the effect of K^+ concentration on the storage (G') and loss (G'') moduli of κ -carrageenan at 22 °C and 4 °C, respectively. The viscoelastic properties of these systems were dependent on both cation concentration and the temperature. Addition of K^+ ions induced cross-link formation as reflected by the relatively high G' compared to G'' (low $\tan \delta$) over the frequency range tested (Ferry, 1980). However, the limiting effect of K^+ , observed in TPA was not apparent in these rheological measurements. Nevertheless a rapid increase in G' was not observed at KCl concentrations above 0.12% (w/v), whereas a 40-fold increase in G' was observed as the K^+ concentration was increased from 0.06% (w/v) to 0.12% (w/v). The apparent reduction in κ -carrageenan gel hardness that was observed beyond 0.12% (w/v) K^+ in TPA could be due to syneresis of these gels observed with extended storage, which is likely to reduce the sensitivity of the penetration method.

The rheological measurements of ι -carrageenan systems (Fig. 7) show the soft nature of these systems compared to the κ -carrageenan systems. Nonetheless, cross-link formation was observed in ι -carrageenan systems with added Ca^{2+} (low $\tan \delta$). The temperature only had an effect on the ι -carrageenan systems with lower Ca^{2+} concentration, confirming the maximum packing or cross-linking density at 0.12% (w/v) of Ca^{2+} . Moreover, a limiting effect of Ca^{2+} beyond 0.12% (w/v) was observed with a slight reduction in G' as the cation concentration was increased from 0.12% (w/v) to 0.2% (w/v) at both 22 °C and 4 °C. This trend is similar to what was observed with TPA measurements, where a reduction in gel hardness, compressibility as well as adhesiveness was observed as the Ca^{2+} concentration was increased from 0.12% to 0.2% (w/v).

4. Conclusion

The present study details the effect of wide concentration range of selected cations on mechanical, microstructure and rheological properties of aqueous κ - and ι -carrageenan dispersions. Comparable results were obtained from the texture profile analyzer and the rheometer. However, the sensitivity of probe penetration method in detecting mechanical properties of the κ -carrageenan systems was reduced due to the syneresis observed in these gels with storage/equilibration. The Young's modulus of κ -carrageenan gels (calculated using the uniaxial compression method) was approximately 3-folds the shear moduli recorded at 3 h of equilibration. This confirmed the elimination of slip with the use of sanded parallel plate method for systems under investigation. The rheological measurements demonstrated a temperature dependence of κ -carrageenan gels in the presence of added KCl (0–0.2% (w/v)). Conversely, at concentrations above 0.12% (w/v) of $CaCl_2 \cdot 2H_2O$, ι -carrageenan did not display temperature dependence. Increasing the counter ion concentration beyond a threshold also had a negative impact on microstructure and mechanical properties of the investigated carrageenan systems.

The present study reinforces the significance of selected counter ion concentration on the physical properties of carrageenan systems. Consequently, fine-tuning of carrageenan to cation ratio can be used to formulate a semi-solid system with requisite physical characteristics at a given temperature. In the future these systems will be investigated as drug delivery platforms, where variation in counter ion concentration is likely to modify the rate of release of entrapped particles.

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