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Rheological characterisation of κ-carrageenan/locust bean gum mixtures

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Abstract

The rheological behaviour of the binary system of κ-carrageenan and locust bean gum (LBG) has been characterised using both compression and shear measurements. Slip effects caused by syneresis of the κ-carrageenan during dynamic shear measurements were eliminated through the use of pre-formed gels glued between parallel plates. The improved measurement system yielded very high G' values of the order 10,000–30,000 Pa for 1% κ-carrageenan gels in 0–0.2 M added KCl conditions. The introduction of LBG showed no synergistic peak in gel strength (G' and E) at any KCl concentration when the total polymer concentration was kept constant. Measurements of Young's modulus for the same gels yielded a Poisson's ratio of 0.5. Compression rupture stress and strain were also monitored to study the interaction between the two gums. A peak in rupture was observed at a κ-carrageenan/LBG ratio of ∼6:4. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Carrageenan; Locust bean gum; Young's modulus; Rheology

1. Introduction

Carrageenans are sulfated polysaccharides extracted from red seaweeds. Among them, κ-carrageenan is characterised by its repeating disaccharide units of 3-linked β-D-galactose 4-sulfate and 4-linked 3,6-anhydro-α-D-galactose. The solution of κ-carrageenan may form a gel upon cooling in the presence of specific cations such as potassium. The mechanism of gelation involves coil–helix transition of the κ-carrageenan molecules (Morris, Rees, & Robinson, 1980).

Locust bean gum (LBG) is a plant galactomannan containing (1 → 4)-β-D-mannopyranosyl backbone with attachment of (1 → 6)-α-D-galactose single units (Dey, 1978). LBG dissolves in hot water and forms a viscous solution which rheology is typical of that of macromolecular solutions (Doublier & Launay, 1981). The apparent gelation of LBG solution upon storage and its rheology had been systematically studied (Richardson & Norton, 1998; Richardson, Clark, Russell, Aymard, & Norton, 1999).

The binary system of κ-carrageenan and LBG has been studied extensively since LBG was found to be effective in improving certain properties of the gel network. Such 'synergistic' effects were first found when κ-carrageenan solution was diluted to a concentration too low to gel by itself, but formed a gel upon LBG addition (Dea & Morrison, 1975). It should be noted, however, the total polymer concentration was increased in that gelling system by the incorporation of the LBG.

The first model proposed for the binary system was a coupled network with unsubstituted mannan backbone binding to the carrageenan helix to form a number of junction zones (Dea, McKinnon, & Rees, 1972; Tako & Nakamura, 1986). Cairns, Miles, Morris, & Brownsey (1987) studied the X-ray fibre-diffraction patterns of the mixed polymer system and found no evidence of intermolecular interaction. However, they did find intermolecular binding between the synergistic xanthan and LBG system using the same method (Cairns, Miles, & Morris, 1986). They suggested that carrageenan forms a network that merely contains LBG.

It is generally accepted that by replacing part of the κ-carrageenan with LBG, the gel strength, indexed by the dynamic rigidity modulus (G') and compressive Young's modulus (E), increases with increasing LBG concentration and then decreases, creating a peak and the so-called 'synergistic' effect. However, several problems exist in this system that are difficult to explain in view of the existing results.

Firstly, the κ-carrageenan:LBG ratio at which the G' synergistic peak occurs and the degree of synergy varies widely. The percentage of LBG corresponding to maximum synergy in terms of G' was found to range from 8% (Arnaud, Choplin, & Lacrox, 1989) to 70% (Stading & Hermansson 1993) under different total polymer and KCl concentrations. Fernandes, Goncalves, and Doublier (1991)

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studied various samples of LBG and found the optimum κ-carrageenan/LBG ratio to be 4:1 in all types of LBG samples and KCl concentrations. The synergy, measured as G' using dynamic studies and Young's modulus (E) using compression techniques, also varies. The Young's modulus of the optimum mixture was found to be 1.3–2 times higher than that of carrageenan alone (Turquois, Rochas, & Taravel, 1992; Arnaud et al., 1989), compared with 1.3–10 folds when G' was taken as an index (Arnaud et al., 1989; Stading & Hermansson, 1993; Fernandes et al., 1991; Turquois et al., 1992).

Secondly, no corresponding peak in the gel set temperature was found. In the carrageenan system, increasing gel strength can be achieved by increasing either the carrageenan or potassium ion concentration. In both cases, the gelling temperature increases accordingly (Rochas & Rinaudo, 1980, 1984). In this binary system, however, with the reported G' peak 3–10 times higher, gelling temperature showed no peak but actually *decreased* steadily as the LBG gradually increased in proportion (Stading & Hermansson, 1993; Fernandes et al., 1991). Gelling temperatures determined by conductivity measurements show the same trend (Dunstan, Salvatore, Jonsson, & Liao, 2000). Thus, at any given concentration and temperature when pure κ-carrageenan is not a gel, replacing a certain portion κ-carrageenan with LBG will not induce gelation.

Thirdly, the shear modulus (G) values reported are inconsistent with compressive Young's modulus (E) data. In theory, G and E are known to have the relationship:

$$G = E/2(1 + \nu) \qquad (1)$$

where ν is the Poisson's ratio, ranging from 0 to 0.5 for all known materials. As the flow content of a gel is small compared to G', G' can be taken as G approximately. Thus, the minimum value of G of any material, including the κ-carrageenan gels, should be at least one third of the Young's modulus theoretically. In fact, for a perfectly incompressive gel, the Poisson's ratio is found to be near 0.5, and the Young's modulus E and shear modulus G' of the gel should satisfy the relationship of $E \approx 3G'$.

However, taking a 1% κ-carrageenan gel in 0.1 M KCl for example, reported values of G' are often significantly less than theoretically expected (G' and E reported separately by different authors, e.g. Stading & Hermansson, 1993; Fernandes et al., 1991; Turquois et al., 1992).

The inconsistent results could be attributed to the syneresis of the κ-carrageenan gel, from which the released water creates slip when conducting dynamic measurements. A much higher G' (10^4 Pa for 1% gel in 0.1 M KCl) was reported when using a specially designed perforated concentric-cylinder geometry to avoid slip (Richardson & Goycoolea, 1994). The G' value recorded is more than 10 times higher than those of some other reports. Furthermore, G' values as high as 33,000 Pa were obtained when a 1.2% κ-carrageenan gel containing 0.2 M KCl was glued between two parallel plates (Winwood, Jones, & Mitchell, 1985). These results suggest that the G' of the κ-carrageenan system might be much larger than has been generally reported.

The role of the cation is also very important in the interaction of the κ-carrageenan/LBG system. No synergy was found in the Na- and Ca-forms of κ-carrageenan with LBG (Stading & Hermansson, 1993; Tako & Nakamura, 1986). In a recent study (Lundin & Hermansson, 1997), Na- and Ca-κ-carrageenan/LBG system was studied by fixing carrageenan concentration and increasing LBG progressively. Some enhancement was found in G' when LBG was added. Strictly speaking, this data could not be regarded as synergy since the total polymer concentration was increased. The lack of synergy in the Ca- and Na-forms of κ-carrageenan is further evidence for the unique nature of potassium ion in κ-carrageenan gelation.

The present study is aimed at measuring the rheology of the binary κ-carrageenan/LBG system under non-slip conditions by utilising two mechanical techniques: (1) glued parallel plates dynamic measurements; and (2) compression tests using a texture analyser. Determining the optimum ratio between the two gums and the exact extent of synergy, if any, is of prime interest in this study.

2. Materials and methods

2.1. Materials

Samples of κ-carrageenan (type III, lot 39h1211) from *Eucheuma cottonii* (presumably *Kappaphycus alvarezii*) and locust bean gum (lot 127H0527) were purchased form Sigma–Aldrich (St Louis, MO, USA). According to the labeling, the κ-carrageenan sample contains 6.7% K^+, 2.3% Ca^{2+} and 0.7% Na^+. The LBG sample was found to contain 0.32% K^+ and 0.08% Ca^{2+} by ICP method. κ-Carrageenan gels of pure potassium form show lower moduli than the mixed salt gels (Stanley, 1990). The presence of trace amounts of calcium having significant impacts on its rheology (Hermansson, Eriksson, & Jordansson, 1991). As κ-carrageenan is not exchanged to any single ion form in practical use, all samples in this study were used directly without further conversion to the pure ionic form. The mannose:galactose ratio of the LBG sample was determined to be 4.02:1 by the method involving hydrolysis in 2 M trifluoroacetic acid for 1 hr at 121°C, followed by reduction and acetylation, and the resulting alditol acetates separated and quantitated by gas chromatography, as described by Harris, Henry, Blakeney, and Stone (1984).

2.2. Experimental methods

2.2.1. Sample preparation

Moisture contents of samples were determined by standard dry weight method and were compensated when

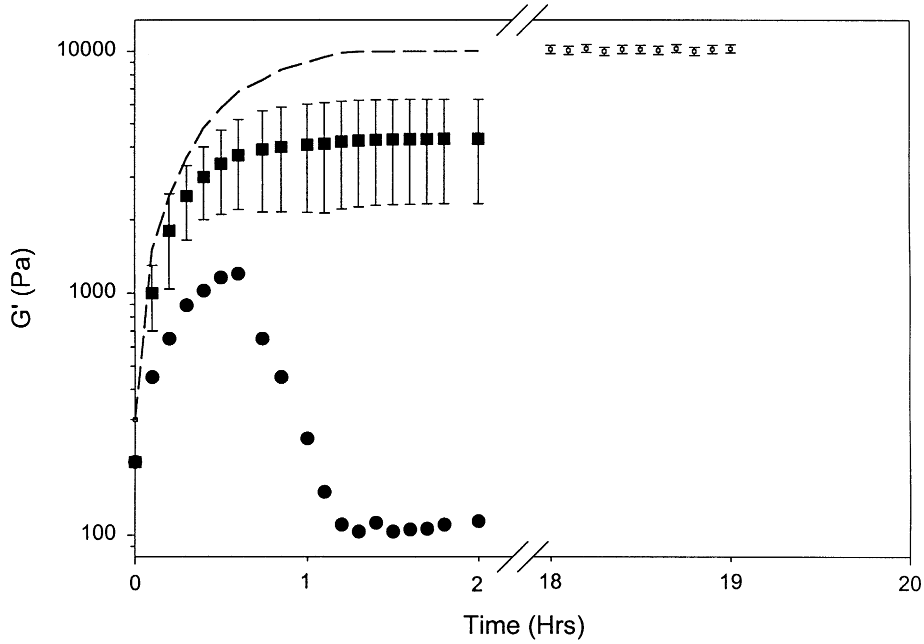

Fig. 1. Time sweeps for 1% κ-carrageenan gels in 0.01 M added KCl at 25°C, using three different methods. ■, nylon attached cone and plate method; ●, serrated cone and plate method; □, glued parallel plates method and the dashed line is a projected gel setting curve.

making solutions. Triple distilled water was used for the preparation of all sample solutions.

Stock solutions of 1% LBG were prepared by dispersing the LBG powder into KCl solutions of varying concentrations (0, 0.01, 0.05, 0.1, 0.2 M) with vigorously stirring at room temperature. The partially dissolved LBG solution were then brought up to 90°C in a water bath and stirred for 15 min to achieve complete hydration.

The 1% κ-carrageenan stock solutions were made by directly dispersing the powder into KCl solutions of desired concentrations (0, 0.01, 0.05, 0.1, 0.2 M) at 80°C and stirred for 30 min.

Mixtures of κ-carrageenan and LBG at a total polymer concentration of 1% with different κ-carrageenan/LBG ratios were made up by blending the appropriate volume of each stock solution. The mixtures were heated with stirring in an 80°C water bath for an additional 10 min before the rheological measurements were conducted.

2.2.2. Compression measurements

A texture analyser model TA-XT2 (Stable Micro Systems, England) was used for compression measurement purpose. Liquid samples at 70°C were poured into cylinder moulds (ϕ19 mm × 19 mm) sitting on glass plates. The upper section of the cylinder was taped around and the sample level was allowed to pass the cylinder's upper edge. A silicon oil layer was applied at the top to avoid evaporation of moisture. The sample was then stored at 25°C overnight before testing. The excess gel was trimmed off using a shaving blade just before testing. The free-standing gel cylinder was placed onto the texture analyser and compressed between parallel plates at a speed of 0.2 mm per second until rupture. Stress and strain were recorded accordingly.

The experiments can be divided into two stages: small strain and large strain. During the initial small strain stage, Young's modulus remained essentially unchanged below 10% strain and that was taken as the viscoelastic limit. A strain of 5% was then used to obtain the Young's modulus for every sample. Rupture stress and strain were recorded during the following large strain (40–80%) stage of the experiment when the gel fracture occurred.

2.2.3. Dynamic measurements

The glued parallel plates method developed by Navickis and Bagley (1983) for dealing with starch gels were adopted for dynamic measurements. Cyanoacrylate ester glue (Loctite superglue) was used in this study. Samples of 1% total polymer concentration at 70°C were poured into a 40 mm × 40 mm parallel glass plate mould with a gap of 3.00 mm. The samples were then stored at 25°C overnight before testing.

A Carri-Med CSL 100 rheometer was used during dynamic shear measurements. Upon testing, the gel piece was removed from the mould and glued between a pair of parallel plates 30 mm in diameter. The glue was carefully handled so that enough glue is applied but no excess oozing out from the edge to interfere with the measurement. Tests confirmed that the gel was glued tightly onto the parallel plates within seconds. The excess gel was trimmed off. A strain of 2% was used throughout the experiments, which is well within the linear viscoelastic region as shown by the

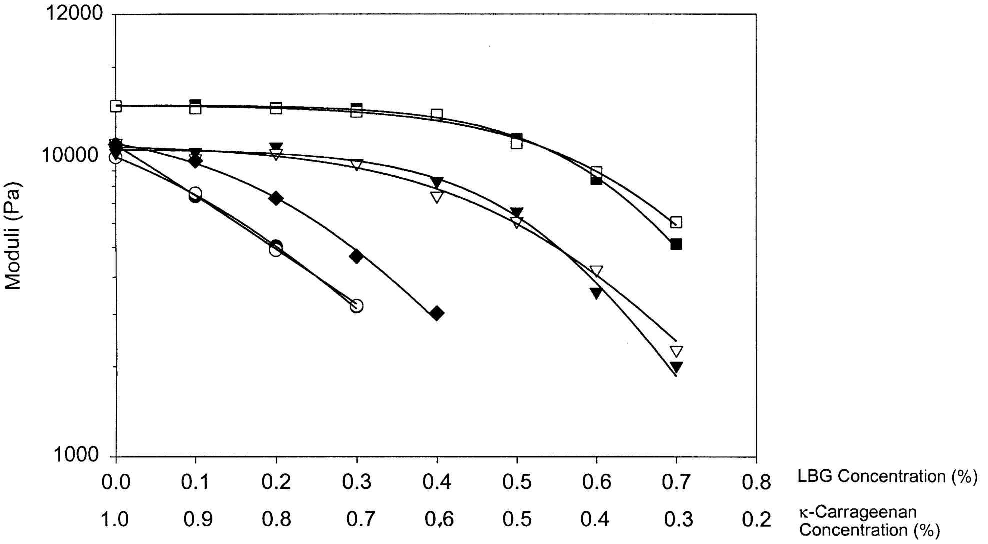

Fig. 2. G' and one-third of Young's modulus for κ-carrageenan and LBG mixtures in 0, 0.01 and 0.05 M added KCl. Total polymer concentration is kept at 1%, with the exception of κ-carrageenan alone in 0.01 M KCl, for which the κ-carrageenan concentration is the same as in the equivalent blend. ●, G', distilled water; ○, $1/3E$, distilled water; ▼, G', 0.01 M KCl solution; ▽, $1/3E$, 0.01 M KCl solution; ■, G', 0.05 M KCl solution; □, $1/3E$, 0.05 M KCl solution; ◆, G', κ-carrageenan alone in 0.01 M KCl solution.

constant G' values versus strain. Penetration of glue into the gel body was not observed after the completion of experiments. Comparative measurements were carried out on 15% gelatin gels that are free of syneresis, using both original cone and plate and the glued parallel plates geometries. Consistent results were achieved between the two measurements.

The glued parallel plates method and the compression testing require trimming and cutting of gels and are thus not applicable to weaker gels. Fortunately most gels dealt with in this study were quite rigid.

3. Results and discussion

Slip effects occur at the surface of testing geometry caused by syneresed water of κ-carrageenan gel has been a major problem when dealing with the rheology of κ-carrageenan bearing systems. A number of methods, including sanded parallel plates, serrated cone and plate, nylon attached cone and plate and the glued parallel plates were tried to avoid slip. Very different G' values were obtained using different methods. It was found that the better the reproducibility, the higher the G', suggesting that slip is the cause for low G' values. Reproducibility was thus taken as an index to evaluate the effectiveness of these methods.

The sanded parallel plated method was first discarded because of problems in setting the right gap. Fig. 1 shows G' values for 1% κ-carrageenan gel in 0.01 M KCl using different methods. G' peaks were found during cooling when using a serrated cone and plate geometry and the shape of the curve is similar to those reported by Hermansson (1989) and Roesen (1992). Syneresed water could have caused the sharp drop of G', as the peak could be avoided when proper anti-slip method is applied (Richardson & Goycoolea, 1994). Temperature and time variation measurements using the serrated geometry are extremely irreproducible. Tiny drops of free water were observed on the testing geometry when the gel sample was removed. The nylon attached cone and plate method was designed in an attempt to absorb the syneresed water by the use of nylon. Reproducibility was improved significantly, with G' values falling within the range of $G'_{\text{aver}} \pm 50\%$. The G' peaks were not observed in these measurements. However, such reproducibility is still far from being regarded as satisfactory. As for the glued parallel plates method which requires overnight gel setting in moulds, the time sweep data of G' measurements began at 18 h after gel set and lasted for 1 h. The dashed curve indicates a possible gel strength evolution as for most gels. G' of the gels stayed almost unchanged at high values over the 1-h period of measurement. A reproducibility of $G'_{\text{aver}} \pm 5\%$ was achieved by the glued parallel plates method and this method was thus used throughout this study.

Dynamic experiments on samples at 1% total polymer concentration but with different κ-carrageenan/LBG ratio and different KCl addition were tested using the glued parallel plates method and were compared with the Young's modulus results obtained by compression experiments. The values of G' and one third of Young's modulus (E) of the binary blend samples in low potassium concentrations (0, 0.01, 0.05 M) are shown in Fig. 2. The line corresponding to G' of the κ-carrageenan alone in 0.01 M KCl solution is also shown for comparison. For pure κ-carrageenan samples and samples with LBG but no KCl addition, the

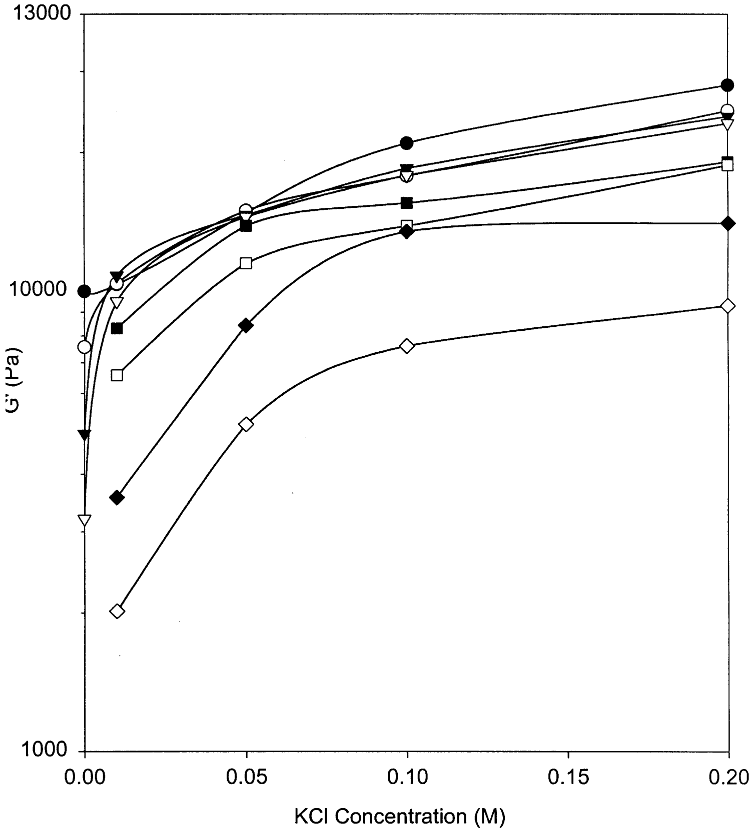

Fig. 3. G' as a function of added KCl concentration for different blending ratios of κ-carrageenan (C) and LBG (L), at a total polymer concentration of 1%. ●, $C : L = 10 : 0$; ○, $C : L = 9 : 1$; ▼, $C : L = 8 : 2$; ▽, $C : L = 7 : 3$; ■, $C : L = 6 : 4$; □, $C : L = 5 : 5$; ◆, $C : L = 4 : 6$; ◇, $C : L = 3 : 7$.

gels were too weak to be tested when the κ-carrageenan concentration was lower than 0.7%. A sharp drop in gel strength was observed for samples with no KCl addition when the LBG content was increased. By contrast, when the potassium concentration was increased to 0.01 or 0.05 M, no significant drop in gel strength was observed until the LBG content reached ~30–40%. For the mixtures with no KCl addition, their background levels of potassium ions are accounted for by the endogenous ions of the biopolymers, with κ-carrageenan being the dominant source.

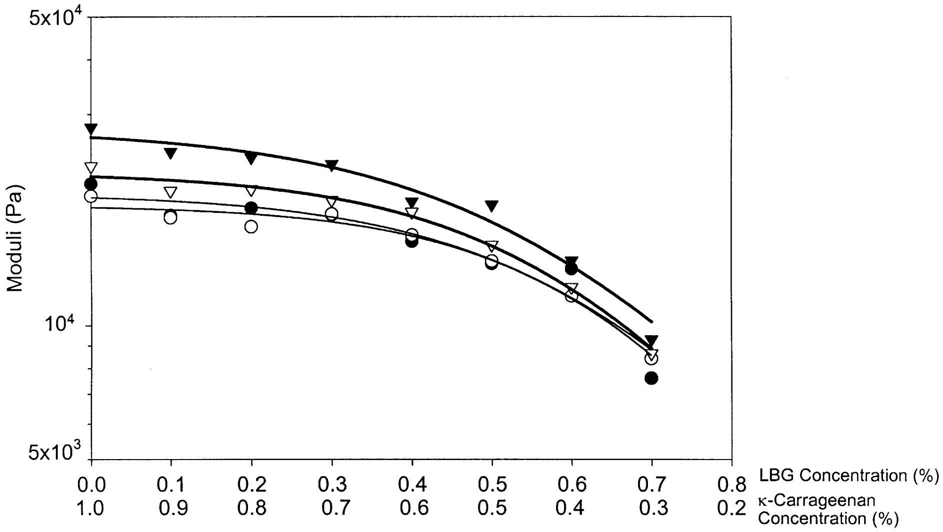

Fig. 4. G' and one-third of Young's modulus for κ-carrageenan and LBG mixtures in 0.1 and 0.2 M added KCl, at a total polymer concentration of 1%. ●, G', 0.1 M KCl solution; ○, 1/3E, 0.1 M KCl solution; ▼, G', 0.2 M KCl solution; ▽, 1/3E, 0.2 M KCl solution.

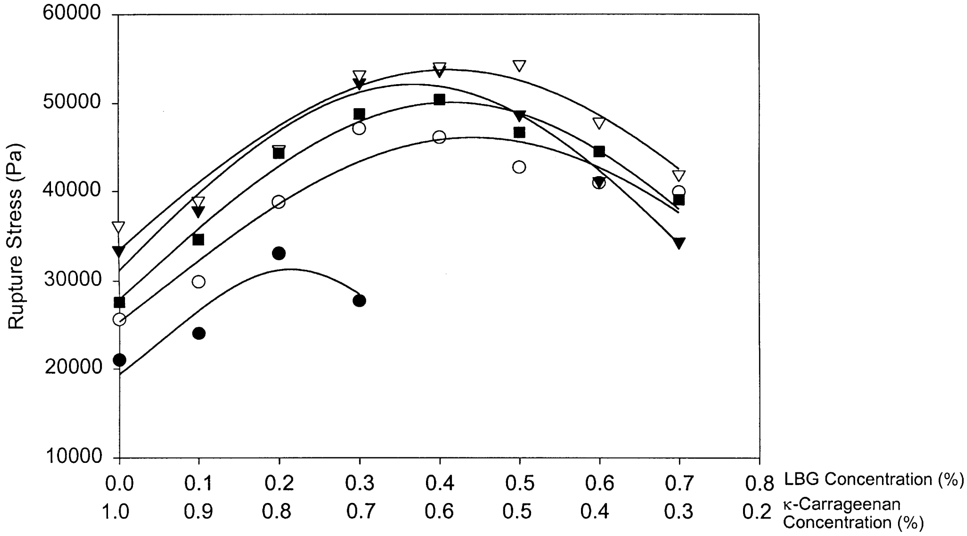

Fig. 5. Rupture stress of κ-carrageenan and LBG blends in different added KCl concentrations. ●, 0; ○, 0.01 M; ▼, 0.05 M; ▽, 0.1 M; ■, 0.2 M.

Calculations reveal that there is very little free salt in the κ-carrageenan sample and the contribution of ions from LBG is negligible. The supplier's composition data suggest that 54% of the κ-carrageenan is in K^+ form, with 36 and 10% for Na^+ and Ca^{2+} forms, respectively.

The dramatic change affected by the addition of KCl is clearly shown in Fig. 3. With 0.01 M added KCl, the G' of the pure κ-carrageenan only increased marginally, while those of all the other binary mixtures increased sharply. In the 0.01 M KCl samples, there is enough K^+ for association with every sulfate ester group, compared to a maximum possibility of only 69% in samples with no KCl addition. The difference between the two KCl conditions indicates that LBG will be more effective when more κ-carrageenan is in the potassium form than in the calcium or sodium form. Between potassium concentrations 0.01–0.2 M, the G' increase pattern of pure κ-carrageenan samples and binary mixture samples with high proportion of κ-carrageenan are quite similar, indicating that when the κ-carrageenan is predominantly in the potassium form, the role of LBG is similar, regardless of the excess potassium available.

The value of G' (~10,000 Pa, Figs. 2 and 3) of 1% κ-carrageenan in 0.01 M added KCl is very high compared to several hundred or even less than 100 Pa reported by other researchers (e.g. Stading & Hermansson, 1993; Fernandes et al., 1991).

In gels with 0.01–0.1 M added KCl, the Young's modulus index (E) shows the same trend as G'. Furthermore, the curve based on one-third of E almost superimposes with G' (Figs. 2 and 4). The value of E is in the same order of magnitude with the work from Turquois et al. (1992), who observed a degree of synergy of 30% when the κ-carrageenan/LBG ratio

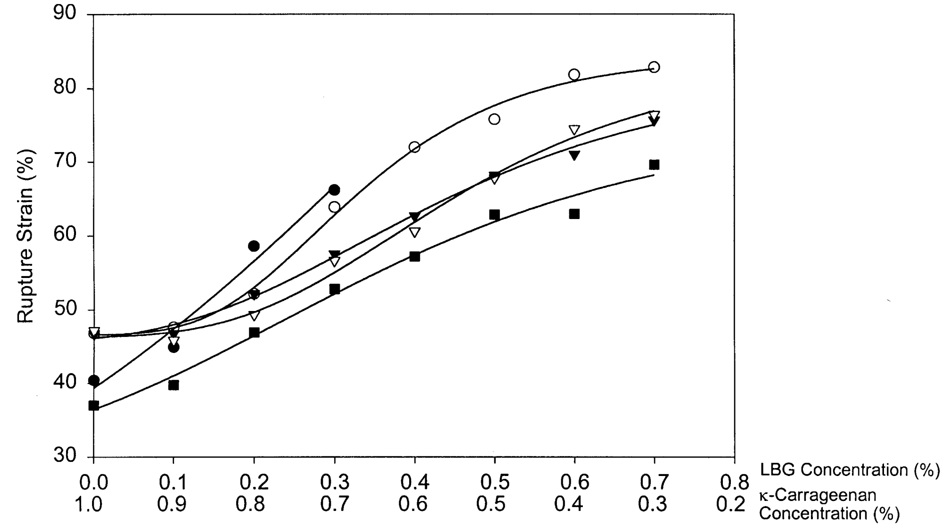

Fig. 6. Rupture strain of κ-carrageenan and LBG blends in different added KCl concentrations. ●, 0; ○, 0.01 M;, ▼, 0.05 M; ▽ 0.1 M; ■, 0.2 M.

was 65:35. However, no synergistic peaks are found in the current study. In fact, the results suggest that in the binary system with a 1% total polymer concentration, LBG can replace κ-carrageenan up to 30–40% without causing significant changes to the gel strength when the potassium concentration is high enough.

The G' values of a pure κ-carrageenan gel in 0.2 M KCl reached as high as 28,000 Pa (Fig. 4). This results is in agreement with that reported by Winwood et al. (1985). In 0.2 M added KCl, however, more significant discrepancies between G' and E were observed, especially when G' is greater than 20,000 Pa. We speculate this result could be related to larger errors during compression experiments. Again, the Young's modulus and G' show the same trend with no synergistic peak observed from the mixtures.

The rupture stress and strain data as a function of κ-carrageenan/LBG ratio and KCl concentration are shown in Figs. 5 and 6, respectively. In contrast to the shapes of curves of G' and E with varying κ-carrageenan/LBG ratios, the rupture stress and rupture strain show a degree of synergy in various potassium ion environments. The increase in rupture stress and strain with the incorporation of LBG indicates that the gel becomes harder to fracture. The rupture stress gradually increases with potassium concentration up to 0.1 M, and then decreases upon further addition up to 0.2M (Fig. 5). While having the highest G' and E, the samples in 0.2 M KCl become very brittle, as shown by having the lowest rupture strain in Fig. 6. At all potassium concentrations, the rupture strain increased with the LBG content.

The present study has observed a different rheology profile for the κ-carrageenan/LBG binary gelling system compared to that previously reported. Potentially misleading results are obtained when slip is not properly eliminated. It is speculated that under slip conditions, replacing a portion of κ-carrageenan with LBG may slow the syneresis process and thus reducing slip to yield higher G' readings. The observed higher G' values may then be interpreted as a 'synergistic effect' at intermediate LBG ratios. A perfect sinusoidal phase curve does not necessarily indicate that slip has been eliminated, as it could be obtained with a geometry to which no anti-slip measures were applied.

The Young's modulus data, obtained by compression experiments that are apparently free from slip problems, are also quite different from those reported by many other researchers. For κ-carrageenan/LBG blends, Arnaud et al. (1989) and Turquois et al. (1992) found synergistic peaks of 1.3 and 2 times those of the pure κ-carrageenan, respectively when doing Young's modulus measurements. However, the current results are in agreement with the work of Duran, Fiszman and Costell (1985) and Cairns, Morris and Brownsey (1986), who also found no peak when measuring the Young's modulus as a function of κ-carrageenan/LBG ratio. A possible reason for the variation could be the different molecular weights of the κ-carrageenan samples used. κ-Carrageenan molecular weight below a critical value could result in lower modulus (Rochas, Rinaudo, & Landry, 1990). Furthermore, non-gelling low molecular weight κ-carrageenan can form a gel with added LBG (Dea et al., 1972), and the rheology profile of LBG blended with κ-carrageenans of a spectrum of molecular weight could vary widely. This could be an interesting point for further studies.

The much higher measured values of G' when slip was eliminated satisfied the Poisson's relationship between E and G' obtained in this work. The gel strength also showed the same trend as the gel set temperature of slight decrease with increased LBG content. Both values show a plateau followed by a rapid decrease. Although the synergistic peak was absent from G' and E measurements, the results from this study do not dismiss the effect of LBG on the binary system. As shown in Fig. 2, the G' values for pure κ-carrageenan are far lower than those of the mixtures, and the addition of LBG can significantly increase gel strength of the binary gel, although it is not as effective as the addition of the same amount of κ-carrageenan.

4. Conclusion

Much higher shear moduli were obtained when slip was eliminated in the κ-carrageenan/LBG gel system than has been reported previously. Increasing potassium salt concentration increases the κ-carrageenan gel rigidity (G') while decreasing its rupture strain. LBG interacts with κ-carrageenan in the potassium form more effectively than in calcium or sodium form. At a total polymer concentration of 1%, the κ-carrageenan/LBG gel has the highest rupture stress when 30–40% of the polymer is LBG.

Under the specified experimental conditions, especially with a κ-carrageenan sample containing 2.3% Ca^{2+}, no synergistic peaks in terms of gel rigidity were found among the κ-carrageenan/LBG gelling systems using both shear and compression techniques. In contrast to clear evidence of synergy from rupture stress and strain results, we suggest that the word 'synergy' be replaced with 'interaction' when 'gel rigidity' is specified as the index for the κ-carrageenan and LBG binary system.

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