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Rheology and microstructure of mixed κ-carrageenan – galactomannan gels

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ABSTRACT

Mixed gels of the K-κ-carrageenan and locust bean gum were studied at a total concentration of 1%. The storage modulus, G', showed a synergistic effect for gels formed in the presence of ≤0.1M KCl. At higher KCl-concentrations addition of locust bean gum caused a decrease in G'.

INTRODUCTION

κ-carrageenan is a sulphated polysaccharide from red marine algae which forms a gel on cooling. Galactomannans, including locust bean gum, do not form gels on their own, but they enhance the gel strength when mixed with κ-carrageenan[1-3]. A mixture may even form a gel under conditions when pure κ-carrageenan does not gel[1]. Both polysaccharides are approved as food additives and form clear gels at low concentrations.

The gelation process of κ-carrageenan starts with a coil-helix transition followed by aggregation and network formation and depends on the counter-ion present[4]. Hermansson *et al.* have showed that the microstructure of the network changed very much with the potassium concentration. Around 0.2 M KCl the network consisted of a mixture of coarse, rigid superstrands and fine strands. The superstrands were at least formed by dimers of double helices and gave a brittle network of rigid rods. The fine strands supported the brittle superstrands resulting in a gel with high G' and low phase angle, δ. At lower potassium concentration, ~0.1 M KCl, there were almost no fine strands resulting in a brittle network with lower G'. At low potassium concentration, ≤10 mM KCl, there was no network of superstrands but only a few of them dispersed in a network of fine strands.

Locust bean gum is extracted from the seeds of carob trees and consists of a mannose backbone with some substituted units at the 6 position of galactose. The mannose to galactose ratio, M/G, ranges from 3-5 for locust bean gum. A high M/G ratio gives stronger mixed gels with higher G' [3].

Several models have been proposed to explain the synergistic effect between κ-carrageenan and locust bean gum, e.g. that the network consists of a coupled network with specific junction zones[2,5-6]. Another model has proposed a continuous κ-carrageenan network containing a galactomannan solution[7].

This paper will present the rheological behaviour of mixed gels formed at potassium concentrations from 8–0.2 M KCl. Only the pure potassium form of κ-carrageenan is used and the synergistic effect will be discussed in terms of the gel structure. A more detailed description of the mixed gels is given in reference 8 where also other ionic forms are studied. The microstructure of the mixed gels has been studied by electron microscopy and the results will be published separately[9].

MATERIAL AND METHODS

Materials

κ-carrageenan and locust bean gum were purchased from Sigma Chemicals (St Lois, MO, USA).

The pure potassium form was prepared by ion exchange of a hot 1% carrageenan solution in a column at 85°C with a commercial ion exchange resin (AG 50W-X8, BioRad) and freeze-dried.

The locust bean gum was prepared by first dissolving the powder in distilled water at 20°C. The dispersion was then centrifuged to remove unsolved powder. The locust bean gum in the supernatant was precipitated by addition of ethanol and the precipitate was freeze-dried. The ratio of mannose to galactose (M/G) was estimated by gas chromatography to be 3.

Preparation of mixed samples

The two polysaccharides were mixed separately, stirred, heated 1h at 90°C and mixed hot to give a total concentration of 1% w/w. The composition of the samples will here be denoted κ-carrageenan/locust bean gum. The mixed solutions were stirred for another 10 minutes and then transferred to the preheated cup of the Rheometer.

Dynamic viscoelastic measurements

A Bohlin VOR Rheometer was used (Bohlin Rheology, Lund, Sweden) and the measuring geometry was a serrated, couette type cup and bob measuring system (DIN 53 019). A thin layer of paraffin oil was applied on the surface of the sample to avoid evaporation.

Since biopolymer gels are strain-sensitive during the gelation, the strain was kept low, 4×10^{-4}, so as not to disturb the gelation[10]. This was well within the linear region. The frequency was 1 Hz.

The temperature was decreased linearly from 90°C to 20°C at 1.5°C/min. The sample was then kept at 20°C for 1 h. The presented values of G' and δ are the ones recorded after 1 h at 20°C.

RESULTS AND DISCUSSION

Strong synergistic effects occurred at KCl-concentrations up to 100 mM as shown by G' in Fig. 1. At 8 mM KCl G' had a maximum for a composition of 80/20 and G' was fairly low. Synergy also occurred at higher KCl-concentrations. Figure 1 shows a synergistic maximum for a composition of 50/50 in 50mM KCl and for 35/65 in 100mM KCl. At 200 mM KCl no synergy was found and G' decreased almost linearly when κ-carrageenan was replaced by locust bean gum.

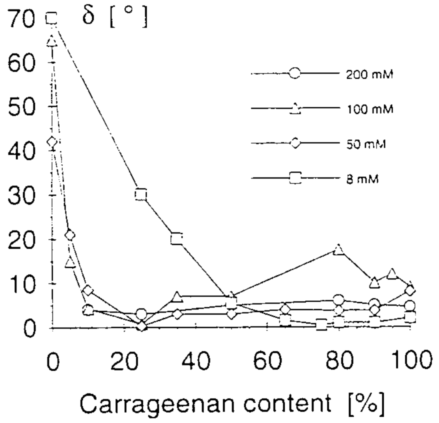

Figure 1. Storage modulus of the mixed gels as a function of composition. The legends show the KCl-concentration.

The phase angle changed with composition in 8mM KCl as shown in Fig. 2. When κ-carrageenan was replaced by locust bean gum in higher concentrations of KCl, δ did not change in either 50, 100 or 200 mM KCl but remained the same as for pure κ-carrageenan, down to as low a κ-carrageenan content as 5/95.

Fig. 3 shows how the gelation temperature T_g depends on composition. T_g was defined as the temperature at the cross-over of G' and G", i.e. when δ=45°. At low KCl-concentration T_g increased with increasing κ-carrageenan content. At higher KCl-concentrations, 50-200 mM KCl, δ was independent of composition and remained essentially the same as for pure κ-carrageenan down to a very low κ-carrageenan content.

The dependence of the composition of the storage modulus, the phase angle and the

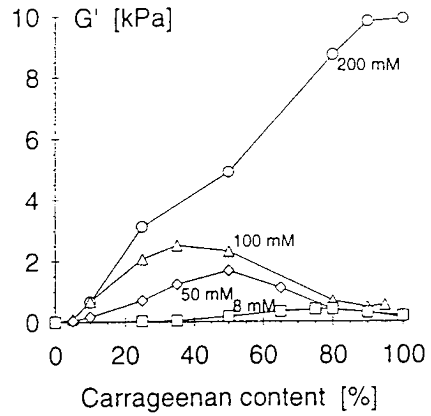

Figure 2. Phase angle of the mixed gels as a function of composition. The legends show the KCl-concentration.

gelation temperature together show that κ-carrageenan was the dominant network component in medium and high KCl-concentrations, 50-200 mM KCl. Both T_g and δ were almost independent of composition and had the same value as for pure κ-carrageenan gels. If the structure had been a coupled network with molecular interactions between the two components, T_g would have changed with composition.

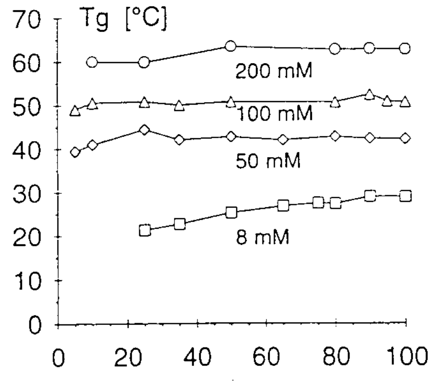

Figure 3. Gelation temperature of the mixed gels as a function of composition. The legends show the KCl-concentration.

The pure K-κ-carrageenan gels in 100 mM KCl were fragile due to the network of rigid superstrands. When locust bean gum was added, it probably stabilised the κ-carrageenan network, which can explain the synergistic effect at 100 mM KCl.

At low KCl-concentrations, 8 mM KCl, the κ-carrageenan was not at all so dominant as at medium and high KCl-concentrations, and locust bean gum contributed more to the structure. This is shown by the gelation temperature, T_g, and the phase angle, δ, which both varied with composition.

REFERENCES

1. Dea, I. C. M. & Morrison, A. (1975). "Chemistry and interactions of seed galactomannans". *Adv. Carbohydr. Chem. Biochem.*, **31**, 241-312.

2. Rochas, C., Travel, F. R. & Turquois, T. (1990). "N.m.r. studies of synergistic kappa-carrageenan–carob galactomannan gels". *Int. J. Biol. Macromol.*, **12**, 353-358.

3. Fernandes P. B., Gonçalves, M. P. & Doublier, J. L. (1991). "A rheological characterization of kappa-carrageenan/galactomannan mixed gels: a comparison of locust bean gum samples". *Carbohydr. Polym.*, **16**, 253-274.

4. Hermansson, A-M., Eriksson, E. & Jordansson, E. (1991). "Effects of potassium, sodium and calcium on the microstructure and rheological behaviour of kappa-carrageenan gels". *Carbohydr. Polym.*, **16**, 297-320.

5. Tako, M. & Nakamura, S. (1986). "Synergistic interaction between kappa-carrageenan in aqueous media". *Agric. Biol. Chem.*, **11**, 2817-2822.

6. Turquois, T., Rochas, C. & Travel, F. R. (1992). "Rheological studies of synergistic kappa-carrageenan–carob galactomannan gels". *Carbohydr. Polym.*, **17**, 263-268.

7. Cairns, P., Miles, M. J., Morris, V. J. & Brownsey G. J. (1987). "X-ray fibre-diffraction studies of synergistic, binary polysaccharide gels". *Carbohydr. Res.*, **160**, 411-423.

8. Stading, M. and Hermansson, A-M. (1993) "Rheological behaviour of mixed gels of κ-carrageenan–locust bean gum". *Carbohyd. Polym.*, **22**, 49–56.

9. Lundin, L. and Hermansson, A-M. "Influence of locust bean gum on the microstructure of κ-carrageenan". Submitted to Carbohydrate Polymers.

10. Stading, M., Hermansson, A.-M. (1990). "Viscoelastic behaviour of β-lactoglobulin gel structures". *Food Hydrocoll.*, **4**, 121-135.