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Rheology and synergy of κ-carrageenan/locust bean gum/konjac glucomannan gels

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ABSTRACT

The rheology and melting of mixed polysaccharide gels containing konjac glucomannan (KGM), locust bean gum (LBG) and κ-carrageenan (KC) were studied. Synergy-type peaks in the Young's modulus at optimal mixing ratios were found for both KC/LBG and KC/KGM binary gels at a fixed total polysaccharide content (1:5.5 for LBG:KC and 1:7 for KGM:KC). The Young's modulus peak for KC/KGM was higher than for KC/LBG gels. The same stoichiometric mixing ratios were found when either LBG or KGM was added to KC at a fixed KC concentration, where the Young's modulus increased up to additions at the stoichiometric ratio, but leveled off at higher LBG or KGM additions. Addition of KGM or LBG to the 2-component gels beyond the stoichiometric (optimal) mixing ratio at a fixed total polysaccharide content led to a decrease in the Young's modulus and an increase in the rupture strain and stress in extension, and both trends were stronger for KGM than for LBG.

Differential scanning calorimetry of the gels revealed the development of a second melting peak for the KC/KGM gels that increased with KGM addition up to higher KGM contents than the stoichiometric ratio. For the KC/LBG gels, only a slight broadening and shift to a higher temperature were observed. When the three polysaccharides were mixed, the DSC endotherms reflected only the main features of the interaction between KC and KGM, and the same was true for the fracture in extension. The different trends led to higher Young's moduli at intermediate KC concentrations when a 1:1 addition of LBG:KGM was used than when either only KGM or LBG was added at a fixed total polysaccharide concentration. This suggests that no special interactions arise when the three polysaccharides are mixed and the binding mechanisms are simply a sum of the bindings observed for KC/KGM and KC/LBG two-component gels.

1. Introduction

Addition of locust bean gum (LBG) or konjac glucomannan (KGM) to κ-carrageenan (KC) based gels is often employed in food applications to decrease syneresis and brittleness and increase the linear regime elastic moduli (Morris, 1990). Contradicting views of the nature of polysaccharide interaction have been brought forth, with reports of no evidence for change in the crystalline zones at high KC concentrations with added KGM (Cairns, Miles, & Morris, 1988) but reports of a development of a second DSC peak at lower KC concentrations with added KGM (Kohyama & Nishinari, 1997; Kohyama, Sano, & Nishinari, 1996; Williams, 2009; Williams, Clegg, Langdon, Nishinari, & Phillips, 1992; Williams, Clegg, Langdon, Nishinari, & Piculell, 1993) both found in the literature. The presence of associative interaction between KC and KGM was also inferred from NMR and ESR measurements (Piculell et al., 1994; Williams, 2009). Reports of similar but much weaker associative interaction have been given for KC–LBG systems (Williams et al., 1992; Williams & Langdon, 1996). Various investigations on the mechanical properties of mixed gels revealed increasing elastic moduli and/or fracture stress and strain for LBG (Chen, Liao, Boger, & Dunstan, 2001; Dea & Morrison, 1975; Dunstan et al., 2001; Goncalves, Gomes, Langdon, Viebke, & Williams, 1997; Lundin & Hermansson, 1998) or KGM (Kohyama, Iida, & Nishinari, 1993; Kohyama et al., 1996) added KC gels.

In the present study, we report on the mechanical and thermal properties of ternary gels containing KC, KGM and LBG. In an accompanying publication (Yang, Wang, Nakajima, Nishinari, & Brenner, 2013), we report on the effect of polysaccharide degradation on such gels containing sucrose and citric acid, i.e., a model of jelly desserts.

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2. Materials and methods

2.1. Gelling powders

The following gelling agent powders were a gift from San-Ei Gen FFI Co. (Osaka, Japan): Vistop D-2134 (KGM, batch lot 01227), Gel up J-4535 (KC, batch lot 40709001) and Vistop D-2050 (LBG, batch lot 012201). The sulphate group, cationic content and molecular weights of these gelling agents have been reported (Brenner, Achayuthakan, & Nishinari, 2013). For simplicity, we refer to each gelling agent by its polysaccharide species, i.e., we refer to LBG, KC and KGM powders. The total gelling powder content is henceforth referred to as the total polysaccharide content.

2.2. Preparation of the gels

The total polysaccharide (gelling powder) content was 1.2 wt%. We define two ratios to describe the composition of the mixtures, χ_{KC} and χ_{KGM}. The parameter χ_{KC} is the ratio of KC to the total polysaccharide content, i.e., $\chi_{KC} = C_{KC}/1.2\%$. The parameter χ_{KGM} expresses the fraction of KGM in the total added galacto- and glucomannan, i.e., $\chi_{KGM} = C_{KGM}/(C_{KGM} + C_{LBG})$. This parameter is of course not defined for $\chi_{KC} = 1$, and so in 3D representation of the data with the two independent variables χ_{KC} and χ_{KGM}, the dependent variable at $\chi_{KC} = 1$ is independent of χ_{KGM}. The KC powder contains, apart from counter-ions, also 14% of added KCl. The gel composition was chosen as either non-salt added, in which case the concentration of KCl decreases with decreasing χ_{KC}, or a constant added KCl concentration composition, where the concentration of added KCl was fixed to that of the highest KC concentration mixtures, i.e., $1.2\% \times 0.14 = 0.168$ wt%. This concentration was fixed by adding KCl at a concentration of $0.168\% \times (1 - \chi_{KC})$. The addition order was KCl (if added) followed by the polysaccharides, added under stirring at room temperature. The mixtures were further heated with stirring for 120 min at 40 °C and 30 min at 85 °C. The stirring was stopped for the last 25 min of the heating procedure to allow any trapped air to escape. Following heating, the hot solutions were poured into molds of different dimensions and then kept in a refrigerator (5 °C) for 16–20 h. Gels were equilibrated to room temperature (25 ± 2 °C) (about 60–120 min) before measurement.

2.3. Ring extension

Ring extension was performed on an XT.T2 Texture Analyser (Stable Micro Systems, Surrey, UK). Rings ($h = 11$ mm, outer Ø = 51 mm, inner Ø = 21 mm) were held with 2 metal bars (Ø = 8 mm). The lower bar was fixed and the upper bar was raised up to ring rupture (Kohyama et al., 1993). An engineering stress is obtained in this case by dividing the measured force with the initial cross section of the ring, 330 mm^2. An estimate of the average engineering strain that neglects strain due to body forces was suggested in the literature (Tschoegl, Rinde, & Smith, 1970). The body forces, i.e., gravity, cause vertical elongation of the hung ring. Here we propose a new expression for the total strain at the inner edge of the ring. We find this to be justified, because in all cases, regardless of the extent of elongation, the rings ruptured from the inside to the outer surface. This means that the critical strain for fracture was first reached on the inner surface (circumference) of the ring, where the elongation is at a maximum. At the limit of very large extensions, one half of the inner circumference of the ring is very well approximated from the distance between the centers of the bars, plus one half of the bar's circumference, 4π mm. Because the test starts at a separation of 13 mm between the bars' centers this distance is equal to $D + (4\pi + 13)$ mm, where D is the raising distance of the bar. Bearing in mind that the initial inner circumference of the ring is 21π mm, the elongation of the inner circumference of the ring ΔL may be approximated by $\Delta L/2 \approx D + (4\pi + 13 - 10.5\pi)$ mm $= D - 7.4$ mm. At small distances, this formula underestimates the elongation. For an estimate that minimizes this underestimate, we note that an initial deformation of a circle into an ellipse does not involve elongation, only bending (through a shear process). This process is complicated in the case of a ring because of the finite width, which means that for different positions on the annulus, a different elongation of the longer semi-axis at the expense of the shorter one takes place before the total circumference must be elongated. As an estimate of the extent of elongation-free deformation of the inner circumference, we find that the longer semi-axis may be extended 9.3 mm before the shorter semi-axis becomes 4 mm, i.e., the radius of the metal bar. While this is a poor estimate for the extent of the elongation-free initial deformation, especially seeing as the presence of shear must induce elongation at the earlier stages, the error in terms of the strain is small compared with the total strain. As a compromise for the large deformation estimate for the elongation ($\Delta L/2 \approx D - 7.4$ mm) and the estimate of the elongation-free initial deformation ($\Delta L/2 \approx D - 9.3$ mm), we decided to approximate the total elongation as $\Delta L/2 \approx D - 8.5$ mm. The error in the calculated strain should not exceed 0.03 at any elongation. We therefore write for the extensional strain ε

$$\varepsilon = \frac{D - \delta}{\pi R_i} \qquad (1)$$

where D is the distance of raising the bar and R_i is the initial inner radius of the ring (10.5 mm), while $\delta = 8.5$ mm minimizes the error at any elongation. The extensional strain-rate is given within our approximation by the speed of the raised bar divided with 10.5π mm. The test was started with a distance of 13 mm between bar centers, because the initial inner diameter is 21 mm and the bar diameter is 8 mm.

2.4. Complex Young's modulus

Values of the complex Young's modulus were obtained on a Rhelograph Gel (Toyo Seiki Seisakusho, Tokyo, Japan), as described by Nishinari, Horiuchi, Ishida, Ikeda, Date and Fukada (1980). The Rheolograph measures the longitudinal vibrations of the specimen at $F = 3$ Hz and amplitude = 100 μm (strain = 0.32%) and yields E' and E'' values (accuracy 0.1 kPa). For temperature dependence measurements, the sample was immersed in silicone oil and the temperature was changed in 5 °C steps. Readings were taken 15 min following equilibration at each temperature.

2.5. Extrusion test

The extrusion test was performed as previously described (Brenner, Hayakawa, et al., 2013). The liquid solutions were drawn into 10 ml syringes (Terumo syringe SS10SZ, Terumo Co., Tokyo, Japan), followed by removal of air-bubbles by tapping on the inverted syringe. The gels were cured in the same way as other molds. Calculation of sensory scores based on the extrusion forces was as reported elsewhere (Brenner, Hayakawa, et al., 2013).

2.6. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed on a Micro-DSC III (Setaram, Caluire, France). Samples (0.8 ml) were loaded into stainless steel cells, heated to 85 °C to erase the thermal history, and then cooled to 5 °C and reheated to 85 °C at 1 °C/min. Transition temperatures and enthalpies were determined using the built-in DSC software.

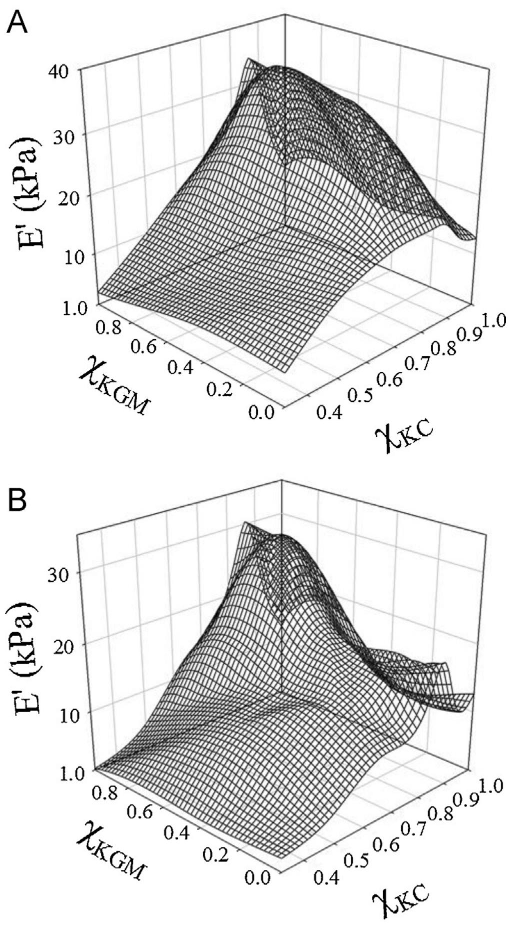

Fig. 1. Storage Young's modulus E' (T = 25 °C, F = 3 Hz) as a function of $\chi_{KC}$and χ_{KGM}. (A) Gels with fixed added fixed [K$^+$] = 22 mM and (B) gels with added [K$^+$] = 22 mM × χ_{KC}.

3. Results and discussion

3.1. Linear rheology

Fig. 1 shows the storage Young's modulus of gels at 25 °C and f = 3 Hz. We note a peak of E' for KC–LBG binary gels at a ratio of 5.5:1 (KC:LBG), and for KC–KGM binary gels at a ratio of 7:1 (KC:KGM). This is true both for gels with a fixed added KCl concentration (Fig. 1A) and for gels where the KCl concentration decreases with decreasing χ_{KC} (Fig. 1B). As expected, when the concentration of added KCl was fixed (to 22 mM) E' was in general higher, as seen especially for lower concentrations of KC. We note that both the peak in E' for KC–KGM and also the decrease in E' when the concentration of KGM is further increased are more pronounced than for the binary KC–LBG gels. Separate measurements showed that when the concentration of KC was fixed instead of fixing the total polysaccharide content, further addition of KGM (beyond ≈ 0.14 eq. KC weight) or LBG (beyond ≈ 0.18 eq. KC weight) did not increase E', i.e., the elastic network is only strengthened up to the stoichiometric mixing ratio, see Fig. 2. Similar observations were made for addition of carob galactomannan to agarose (Turquois, Taravel, & Rochas, 1993) and to KC (Turquois, Rochas, & Taravel, 1992), and form one argument for the presence of heterotypic binding in these gels (Morris, 1995). As seen in the figure, beyond LBG concentrations of about 1/5.5 of the with decreasing KC concentration and beyond KGM concentrations of about 1/7 of the KC concentration, further addition of LBG or KGM does not increase E' further. The stoichiometric ratios KGM/KC and LBG/KC were thus about 7:1 and 5.5:1, respectively, as defined from the increase in E'. The fact that the stoichiometric ratio of LBG/KC is higher than that of KGM/KC gives us a clear hint as to why the decrease of E' is stronger with further addition of KGM beyond the stoichiometric ratio than for further addition of LBG beyond the stoichiometric ratio for the total fixed total polysaccharide concentration of 1.2%, see Fig. 1. This stronger concentration dependence of E' on the KC concentration could reflect either a higher degree of homogeneity of KC–KGM gels when compared with KC–LBG gels, or that the former gels are closer to the critical concentration for gel formation, C_g. The dependence of the elastic strength of the network on the polymer concentration is expected to be stronger close to the critical gel concentration than at higher concentrations within the framework of both cascade and percolation theories (Clark & Ross-Murphy, 1987; Stauffer & Aharony, 1992), and according to the former theory, the dependence is expected to be critical very close to C_g. If the stoichiometric ratio of LBG/KC is higher than for KGM/KC that means that KGM can form stronger but fewer bonds with KC. In such a case we expect the critical gelation concentration C_g to be lower for KC in the presence of excess LBG than in the presence of KGM. In the lack of a rigorous way to determine the critical gelation concentration at our disposal, we have reverted to estimating C_g by the inverted-tube method, that is, if a sample remained at the top of an inverted tube, it was deemed a gel. Inverted-tube tests at a constant added K$^+$ concentration of 12 mM confirmed that C_g of KC in the presence of KGM was higher than in the presence of LBG, with the former being ≈0.13% and the latter ≈0.10%. At the same K$^+$ concentration, C_g of KC alone was ≈0.23%.

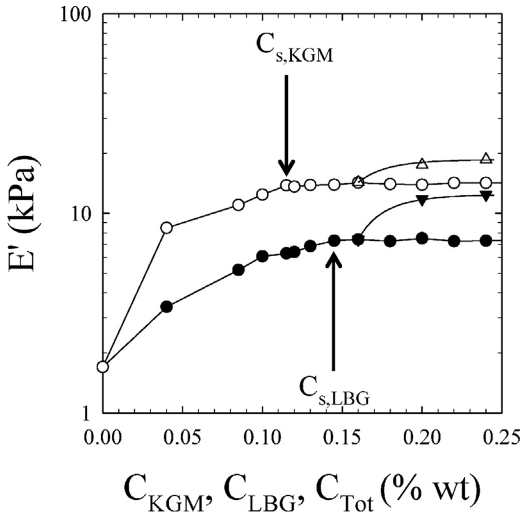

Fig. 2. Storage Young's modulus of 0.8% KC gels as a function of the added concentration of LBG (C_{LBG}; filled circles), added concentration of KGM (C_{KGM}; open circles), or $C_{Tot} = C_{LBG} + C_{KGM}$ (0.16% KGM + added LBG, open triangles; 0.16% LBG + added KGM, filled triangles). The concentration of added K$^+$ in all samples was fixed to 12 mM. The concentrations at which the formation of mixed elastic bonds is saturated are shown with arrows in the figure; these stoichiometric concentrations, $C_{s,LBG}$and $C_{s,KGM}$, are roughly equal to 1/5.5 and 1/7 of the KC concentration, respectively.

As can be seen from Fig. 2, once E' has leveled off at additions of LBG or KGM beyond their respective stoichiometric ratios at a fixed KC concentration, addition of the other polysaccharide (KGM to LBG-saturated gels or LBG to KGM-saturated gels) can increase E' further. The reasons for this further increase, however, are different, as should be clear from the discussion so far. Addition of KGM to a LBG-saturated gel leads to preferential formation of KGM-KC bonds at the expense of LBG–KC bonds, with the former bonds being stronger and thermodynamically more stable. The addition of LBG to a KGM-saturated gel, however, cannot lead to LBG replacing KGM molecules which are bonded with KC. Instead, it appears

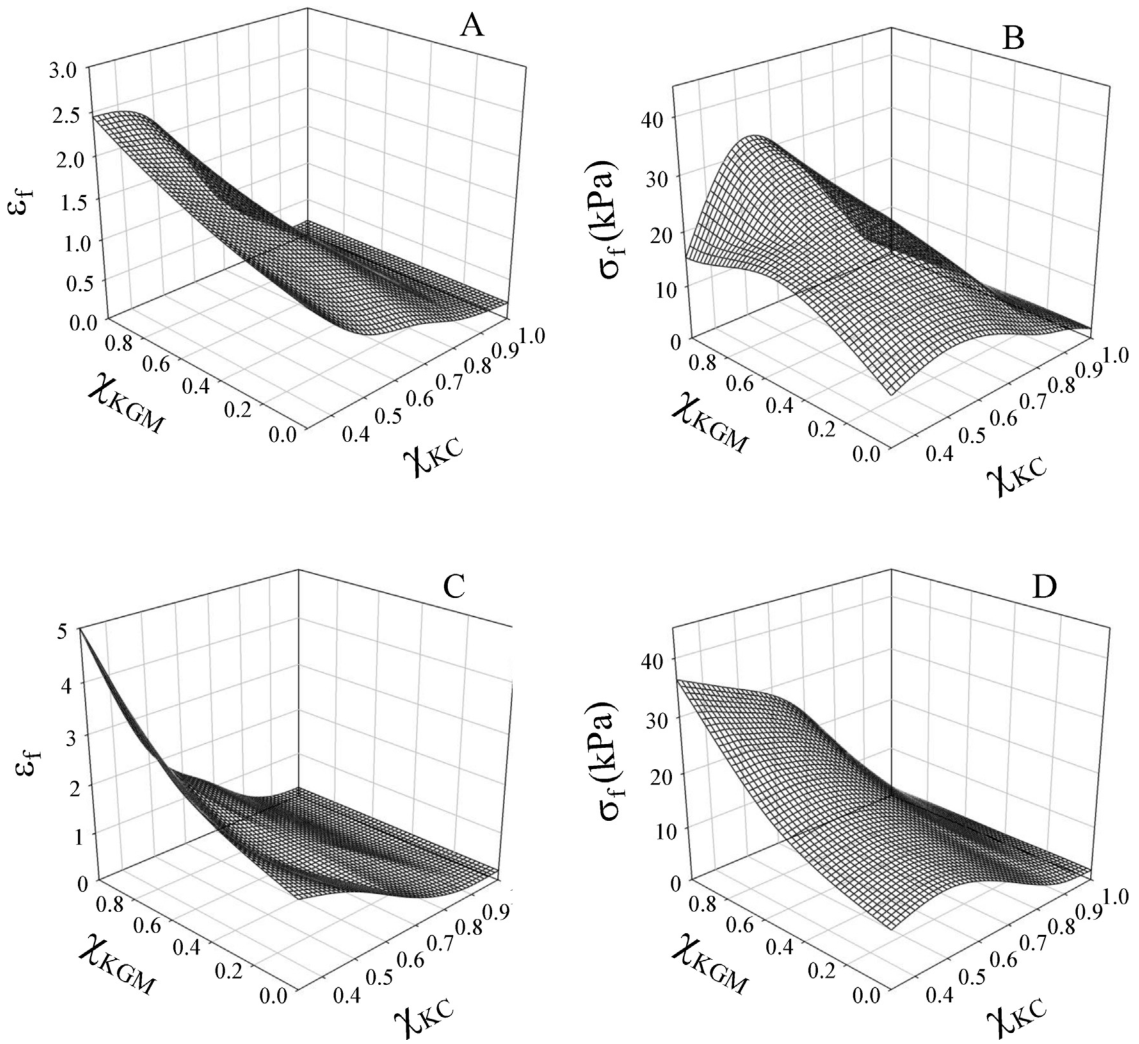

Fig. 3. Extensional fracture strain ε_f (A) and (C) and stress σ_f (B) and (D) at 25 °C as a function of $\chi_{KC}$and χ_{KGM}. Fig. 2A and B, gels with fixed added fixed $[K^+] = 22$ mM, Fig. 2C and D, gels with added $[K^+] = 22\ \text{mM} \times \chi_{KC}$.

that because KGM forms fewer (albeit stronger) bonds with the KC network, there are more sites to which LBG can bind, even after KGM has formed all the bonds available to it. This again reflects the higher stoichiometric ratio LBG/KC, $C_{s,LBG} \approx 1/5.5$, compared with $C_{s,KGM} \approx 1/7$, see Fig. 2.

An important point to note is that no specific new interactions when the 3 polysaccharide are mixed may be inferred from the results on the linear rheology. The general trends seem to simply reflect the sum of the KC–KGM and KC–LBG interactions. As a consequence, at χ_{KC} lower than about 0.7, that is, lower than the stoichiometric ratio with KGM (but not at very low χ_{KC} values), addition of 1:1 KGM and LBG leads to a higher E' than addition of only KGM or LBG at the same KC concentration. This is because the KGM interacts with KC to form stronger elastic bonds than LBG does, and once all the KGM that can bind to KC has done so, LBG can still interact with KC to form elastic bonds, on the merit of the its slightly higher stoichiometric ratio (1:5.5 for LBG:KC vs. 1:7 for KGM:KC).

3.2. Ring extension

Fig. 3 shows the extensional fracture strain ε_f and stress σ_f of the gels as a function of χ_{KGM} and χ_{KC}. As seen, at low additions of LBG or KGM, where a higher E' is found than for pure KC gels, there is already an increase in σ_f, but not in ε_f. The increase therefore corresponds to the higher E' values. Further addition of KGM or LBG leads to a strong increase in ε_f with a resulting strong increase of σ_f, and this trend is stronger for KGM than for LBG. Another point to note is that ε_f tends to be higher for the gels prepared with the lower KCl concentration, i.e., the gels where the KCl concentration decreases with decreasing KC concentration (Fig. 3C and D). This finding checks with the conclusions that salt strengthens the interactions between polyelectrolyte chains at the expense of the interactions of polyelectrolytes with neutral chains (Annable, Williams, & Nishinari, 1994).

We have noted so far that a small amount of either KGM or LBG can form elastic bonds with KC that lead to higher E' values than those of pure KC gels, and that the excess of either KGM or LBG increases strongly the fracture strain and stress. Macromolecules inserted in suspensions or gels can increase the stress during deformation if they cannot relax. However, without specific interaction, such filler macromolecules should not affect the fracture strain of the elastic network. We therefore conclude that the excess KGM or LBG reinforces existing elastic bonds and increases the fracture strain, and is not simply present as a non-interacting filler. To consolidate this point, we measured the fracture strain and stress dependence on the strain rate. The results are shown in Fig. 4. The very weak dependence of both σ_f and ε_f on the strain rate confirms

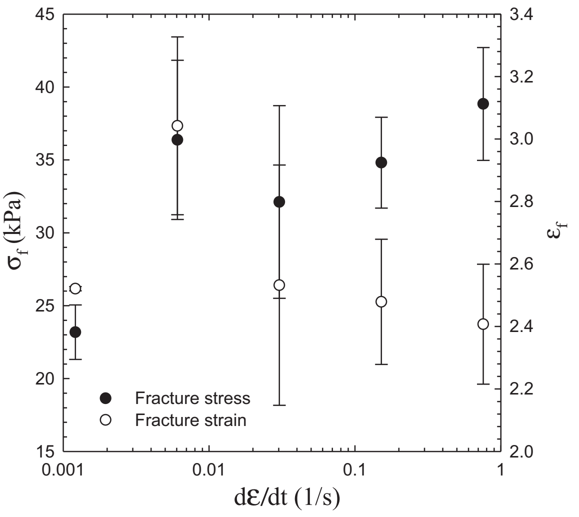

Fig. 4. Extensional fracture strain ε_f (open circles) and stress σ_f (filled circles) at 25 °C as a function of extensional strain rate. The gel contains 0.4% KC and 0.8% KGM (added [K$^+$] = 7 mM, χ_{KC} = 0.33, χ_{KGM} = 1). Error-bars indicate one standard deviation.

that the increase in ε_f due to excess gluco- or galactomannans is due to a colloidal process, and not just the relaxation of single polymer chains, which would lead to a much stronger dependence on the strain rate.

A molecular view that reconciles the failure to confirm different crystalline patterns in crystalline fibers of galacto- or glucomannan added KC (Cairns et al., 1988) with the rheological and DSC evidence supporting heterotypic binding has been proposed in galacto- and glucomannan added KC and agarose mixtures (Morris, 1995). According to this view, the galacto- or glucomannan can interact with crystallites formed of KC (or agarose) chains. The interaction may take place at random sites, so that the diffraction pattern is not affected. From our findings, we may put forth the following molecular picture. KC forms a partly crystalline gel during cooling from the hot solution. KGM and LBG may bind and connect zones of crystalline-packed double KC helices. In this way, KGM and LBG can form new elastic bonds, yielding a stronger elastic 3D network. Once all the elastic binding possible has taken place, excess KGM or LBG may bind only to the KGM or LBG chains connecting the crystalline zones, and thus do not form new connections in the 3D elastic network. Instead, these excess chains can dissipate stress and strongly increase the fracture strain of the gels. Seeing as LBG can interact with the KC crystallites at slightly higher ratios compared with KGM, there are slightly more sites compatible for LBG binding, and when KGM has already interacted elastically to the possible extent, LBG may still form new elastic bonds.

3.3. Differential scanning calorimetry

The differential scanning calorimetry (DSC) endotherms of KC solutions with different KGM contents is shown in Fig. 5A. The ratio

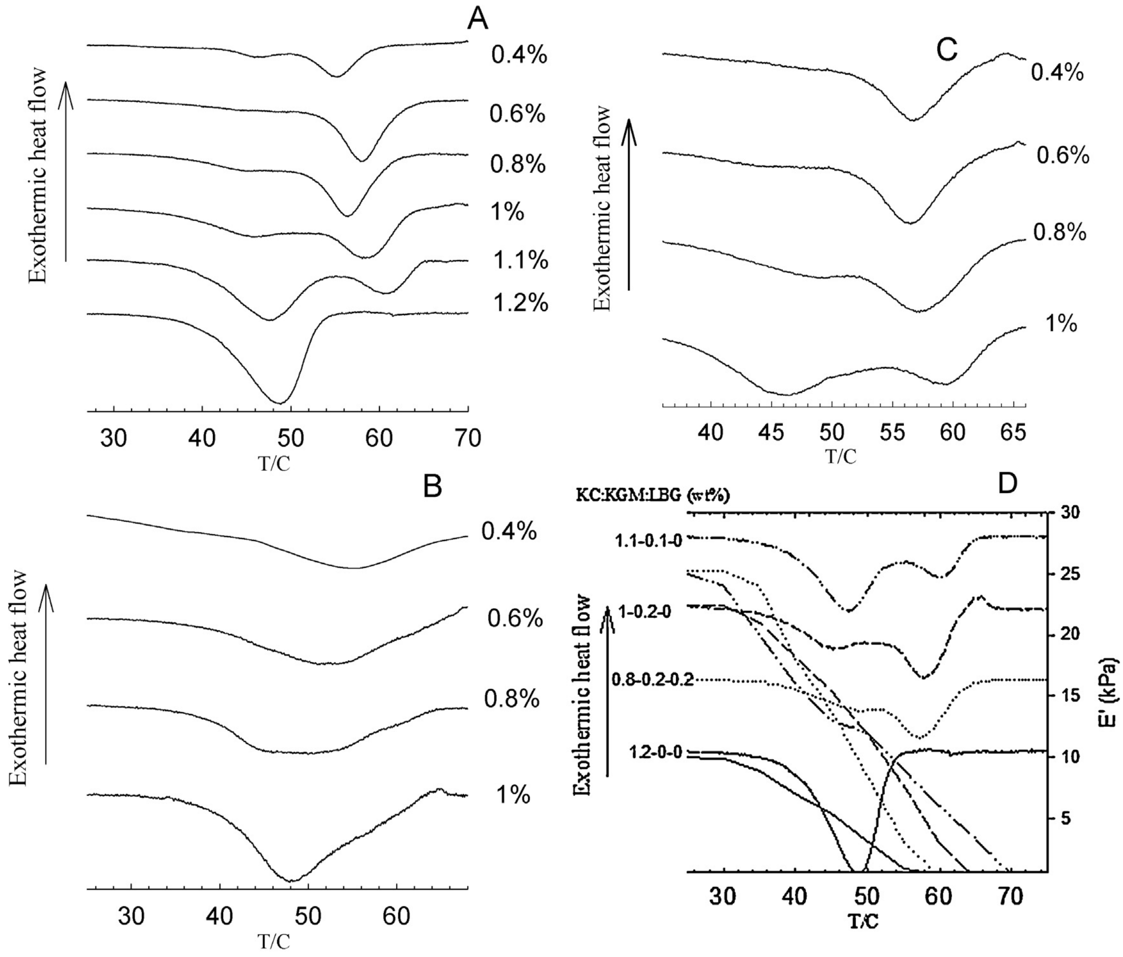

Fig. 5. DSC endotherms of gels heated at 1 °C/min. KC concentration is indicated in (A)–(C), and the total polysaccharide content is 1.2% in all cases. (A) KGM added KC samples, (B) LBG added KC samples and (C) 1:1 addition of LBG:KGM. In (D), the composition of each sample is indicated beside the endotherm with 3 numbers (C_{KC}, C_{KGM} and C_{LBG}), respectively, and the mechanical data (E') is given with the same line-type. The concentration of added K$^+$ was fixed to 22 mM for all samples.

of the two peaks for different KGM content establishes that the higher temperature peak corresponds to melting of mixed KC–KGM bonds, while the lower temperature peak corresponds to melting of KC–KC bonds. At KC:KGM ratios higher than 2:1 the higher temperature peak (normalized with amount KC) is still growing at the expense of the lower temperature peak with KGM addition, but at higher KGM contents their ratios stay roughly the same. The assignment of the higher temperature peak to the melting of KGM/KC mixed zones is in accord with the assignment by Williams et al. (1992) and Williams et al. (1993), but opposite to the order suggested by Kohyama et al. (1996). It appears that the source of the error in Kohyama et al. (1996) was the great variation in ionic content, especially K^+, between samples, as their KC sample contained 8% K^+ and 2% Ca^+ (w/w, %), so that the K^+ concentration strongly decreased with decreasing concentration of KC. In our investigations, we fixed the concentration of added K^+ by adding KCl to lower KC content gels, as explained in the experimental section.

We disagree slightly with the language used in all three publications (Kohyama et al., 1996; Williams et al., 1992, 1993) in that we cannot claim that the KC–KC melting is present only when an “excess” of KC is present. Even at very high ratios of KGM to KC we find a lower temperature peak, and although it becomes broader and less distinct, the ratio of its enthalpy to that of the high-temperature peak remains roughly the same. It thus seems reasonable to suggest an equilibrium between formation of KC–KC and KC–KGM bonds, although this equilibrium obviously strongly favors formation of KC–KGM bonds.

Fig. 5B shows the results for binary KC–LBG solutions. As noted in other studies, the interaction between KC and LBG is weaker and does not lead to separate peaks (Goycoolea, Richardson, Morris, & Gidley, 1995; Williams et al., 1992, 1993), or to a very small additional peak (Goncalves et al., 1997). Fig. 5C shows the results for simultaneous addition of LBG and KGM to KC. As in the case of E', we see that the addition of KGM dominates the interaction in the system. Thus, the higher temperature peak is at a maximum at addition of 0.8%–0.2%–0.2% KC–LBG–KGM, just like it is at concentrations of 1%–0.2% for the KC–KGM system. For comparison, at an addition of 1%–0.1%–0.1% KC–LBG–KGM, the higher temperature peak is smaller. In Fig. 5D, we show the mechanical melting of several gels along with their DSC endotherms. The ratio of the two endothermic peaks can be reflected in slightly different decrease patterns of E' with increasing temperature, for instance, the steep decrease in E' for the 1.1% KC + 0.1% KGM sample starts a few degrees Celsius lower than for the 1% KC + 0.2% KGM sample. Nevertheless, the total effect on the melting profile is weak and amounts to only several degrees Celsius, in keeping with other reports in the literature (Brenner, Achayuthakan, et al., 2013; Kohyama et al., 1993, 1996).

3.4. Sensory properties from extrusion tests

Sufficient addition of galacto- or glucomannan to KC leads to gels that do not fracture in compression (Brenner, Achayuthakan, et al., 2013). In such cases, it makes no sense to try and obtain parameters that correlate with sensory properties and can differentiate between samples from compression tests (Barrangou, Drake, Daubert, & Foegeding, 2006a; Barrangou, Drake, Daubert, & Foegeding, 2006b; Truong & Daubert, 2000; Truong & Daubert, 2001), such as the instrumental Texture Profile Analysis (Bourne, 2002; Szczesniak, 1963). As shown recently, robust correlation of certain mouth-feel properties may be achieved with empirical parameters obtained from an extrusion test (Brenner, Hayakawa, et al., 2013). In this publication, we will not show the forces (stresses) measured in the extrusion test, but will instead show directly recalculated texture properties, using the robust relations recently proposed (Brenner, Hayakawa, et al., 2013).

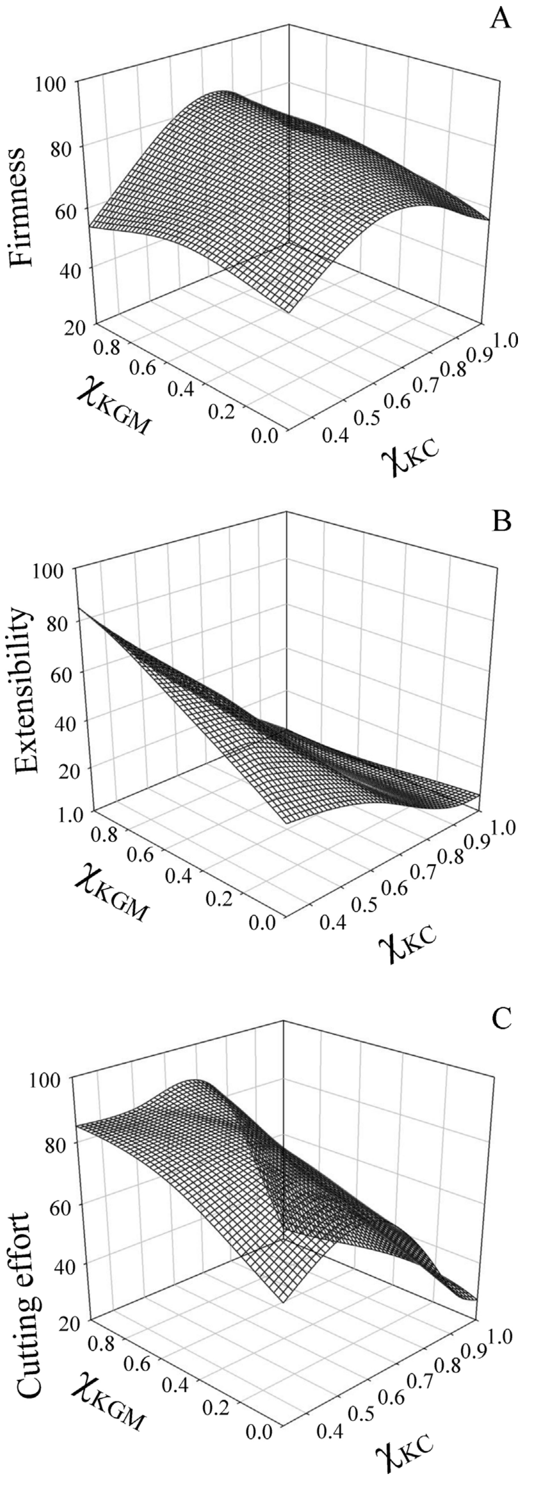

Fig. 6. Sensory scores (0–100) for gels, recalculated from extrusion test data and the Young’s modulus. (A) firmness, (B) extensibility (a measure of deformability), and (C) cutting effort.

Fig. 6A shows the recalculated firmness of the gels. The firmness, defined as the force required for small deformation between the tongue and the hard palate, correlates very well with a logarithmic sum of the extrusion force and E' (Brenner, Hayakawa, et al., 2013). The firmness of the gels shows a peak at intermediate additions of gluco- or galactomannan, reflecting the opposing trends of an increase in extrusion force and large deformation forces and the decrease in E' with decreasing KC content well beyond the stoichiometric mixing ratios with LBG and KGM. The firmness is virtually independent of the added polysaccharide in this case, with addition of LBG or KGM (or a mixture) at the same concentration to KC leading to virtually the same firmness scores.

The sensory extensibility is a sensory measure of deformability, defined as the extent to which the gel can be deformed between the tongue and the hard palate, and correlates with the ratio of the extrusion force and E' (Brenner, Hayakawa, et al., 2013). As shown in Fig. 6B, the extensibility of the gels increases monotonously with increasing galacto- or glucomannan, and the increase is stronger for KGM. This is as expected from the ring extension test, but could not be predicted from compression tests, because no fracture of the gels with the higher galacto- or glucomannan content is observed in compression.

The cutting-effort, evaluated by the force needed to cut gels with the molar teeth, correlates directly with the extrusion force (Brenner, Hayakawa, et al., 2013). As shown in Fig. 6C, the cutting-effort increases with increasing LBG or KGM content, and levels out for χ_{KC} levels below about 0.7. A small decrease in the cutting-effort is observed for addition of LBG but not of KGM at very low χ_{KC} values. Gels with slightly higher or similar firmness, higher deformability and which require longer oral processing time may thus be obtained by addition of LBG, KGM, or a combination of both to KC.

4. Conclusions

The presence of a synergy-like peak in the Young's modulus was found for both KC–LBG and KC–KGM gels. The excess of either galacto- or glucomannan reinforces the elastic network and increases the fracture strain and stress considerably. In terms of the sensory perception, this leads to more deformable gels that require higher effort of mastication, but are of a similar firmness.

The molecular picture invoked is that of two types of interactions in the gels. Crystallite zones are connected by either LBG or KGM, which do not necessarily attach at the same place. The connection possibilities for LBG are a bit larger than those for KGM. Once all the LBG or KGM have reacted with crystalline zones of KC, any excess LBG or KGM bind to the LBG or KGM chains present in the 3D elastic network, without making any new elastic connection points. These excess chains are thus not elastically active but dissipate stress and strongly increase the fracture strain of the gels.

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