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The effect of degradation on κ-carrageenan/locust bean gum/konjac glucomannan gels at acidic pH

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ABSTRACT

The feasibility of textural and rheological modification of gels containing κ-carrageenan (KC) and locust bean gum (LBG) by addition of konjac glucomannan (KGM) was investigated. Special attention was paid to the effect of polysaccharide degradation during heating at acidic pH. The general effect of polysaccharide degradation was to decrease the Young's modulus, while the fracture strain in extension was scarcely affected unless the degradation was very severe.

Differential scanning calorimetry showed that the melting peak corresponding to dissociation of KC–KGM bonds decreased faster than the melting peak of KC-only bonds with increasing degree of polysaccharide degradation. The implication is that as degradation proceeds, fewer KGM molecules can interact with KC to form elastic bonds, and the excess of KGM which reinforces the existing elastic network and increases the fracture strain actually increases. For this reason, the fracture strain remains nearly unchanged with increasing degradation levels. A decrease in fracture strain is thus observed only at very severe degradations, where KC no longer forms a self-supporting gel by itself.

1. Introduction

κ-Carrageenan (KC) is a non-branched sulphated polysaccharide extracted from marine red algae, with the repeat unit β-D(1→3)-galactopyranose and 3,6-anhydro-α-D(1→4)-galactopyranose. Along with other marine red algae polysaccharides, it forms the second most used polysaccharide group in the food, chemical, pharmaceutical and cosmetic industries (Piculell, 2006), the first being starch and its derivatives. One popular way to modify the properties of KC-based gels in the food industry is to add non-gelling galactomannans, such as locust bean gum (Morris, 1990), with resulting gels showing higher fracture strains and less syneresis. The addition of konjac glucomannan, while less common, was shown to affect both the melting and rheological properties of KC-gels more strongly than LBG (Williams, Clegg, Langdon, Nishinari, & Phillips, 1992; Williams, Clegg, Langdon, Nishinari, & Piculell, 1993). Recent investigations of the nature of interactions and the resulting change in texture of ternary gels containing KC, LBG and KGM as a function of mixing ratio have revealed that two types of interactions are present between KC and LBG and also between KC and KGM (Brenner, Achayuthakan, & Nishinari, 2013; Brenner, Wang, Achayuthakan, Nakajima, & Nishinari, 2013). One interaction leads to formation of elastic bonds that are stronger than bonds between KC chains, with a weight ratio of about 1–5 (LBG to KC) or 1:7 (KGM to KC). Any excess KGM or LBG present beyond this concentration can interact with the elastic network in a different way, and this excess galactomannan or glucomannan increases the yield strain of the gels without increasing the elastic modulus. Thus, by changing the mixing ratios of KC, LBG and KGM, the Young's modulus may be fine-tuned, and the elasticity may be increased, yielding gels that can be extended to 6 times their original length (Brenner, Wang, et al., 2013).

The effect of polysaccharide thermal degradation on food quality has been long recognized (Fagerson, 1969). For the gels under study, acidification of the mixture post thermal treatment led to substantially higher Young's moduli than were obtained after heating the acidified solution (Brenner, Achayuthakan, et al., 2013). In the present study, we elucidate the effect of this thermal degradation on the non-linear rheology of the gels and compare the results with DSC endotherms.

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), Gel up J-4535

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(KC) and Vistop D-2050 (LBG). The sulphate group, cationic content and molecular weights of these gelling agents have been reported (Brenner, Achayuthakan, et al., 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%, and the sucrose content was 25 wt%. The concentrations of KC and LBG powders were kept equal, while the concentration of the KGM powder was varied. The ratio LBG/KC = 1 was chosen because according to Chen, Liao, Boger, and Dunstan (2001), the rupture stress in compression of LBG/KC gels in the presence of low KCl concentrations showed a peak around this ratio, while the shear modulus of the gels decreased at higher LBG:KC ratios Similar results were obtained in a previous investigation of our group (Brenner, Wang, et al., 2013). We will refer to the KGM powder content by its relative weight fraction of the total polysaccharide (gelling powder) content, χ_{KGM} ($\chi_{KGM} = C_{KGM}/1.2\%$). Values of χ_{KGM} in the range 0–0.5 were tested, allowing for a systematic study of the effect of KGM. No salt was added to the solution, so that apart from counter ions, the only salt present is KCl from the KC powder at concentrations between 5.5 and 11 mM. This series of gels imitates commercially available dessert jellies, in which both citric acid trisodium salt and anhydrous citric acid are common ingredients. The citric acid trisodium salt and anhydrous citric acid concentrations were fixed at 0.15 and 0.22 wt%, respectively. The resulting pH of the mixtures was 3.4–3.7, and increased slightly with increasing χ_{KGM}.

Four different dissolution methods were tested, referred to as M1–M4. For M1, First, the sucrose (25 wt%) and citric acid trisodium salt (0.15 wt%) were dissolved in MQ-grade water. Then, LBG, KC and KGM powders were added, in this order, under mechanical stirring at 70 °C. The solution was further heated at 80 °C for 40 min, followed by addition of anhydrous citric acid (0.22 wt%). The solution was poured into moulds and allowed to cure at 5 °C quickly after the anhydrous citric acid dissolution. For methods M2–M4, anhydrous citric acid (0.22 wt%) was added with the sucrose and citric acid trisodium salt, and the polysaccharides were added slowly and gradually under stirring at 45–50 °C. The solutions were further heated as follows: 65 °C for 30 min and 75 °C for 30 min (M2); 75 °C for 30 min and 85 °C for 30 min (M3); 45–50 °C for 90 min, 75 °C for 30 min and 85 °C for 30 min (M4). Following heating, the hot solutions were poured into moulds 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 to ring rupture (Kohyama, Iida, & Nishinari, 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. We have followed the newly suggested analysis, where the total engineering strain at its maximum, i.e., at the inner edge of the ring, is estimated (Brenner, Wang, et al., 2013). In this case the engineering extensional strain is estimated with:

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

where D is the distance the upper bar is raised and R_i is the initial inner radius of the ring (10.5 mm), while δ is a constant chosen so that the error in estimating the extensional strain is minimized (δ = 8.5 mm). Such an estimate is justified because the rupture was always observed from the inner edge toward the outer edge of the ring (Brenner, Wang, et al., 2013). Within our approximation, the raising speed used, 5 mm/s, corresponds to an extensional deformation rate $\dot{\varepsilon} = 0.15\ \ s^{-1}$. 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 et al. (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).

2.5. Intrinsic viscosity measurements

A KRK Ubbelohde viscometer (Vidrex, Fukuoka, Japan) was equilibrated at 30 ± 0.2 °C using a BR-61 uni-thermo bath (Yamato Scientific Co.). While the exact temperature was not determined to better accuracy than ±0.2 °C using a simple thermometer, the total fluctuation during each individual measurement, as well as between different measurements, was ensured to be within ±0.02 °C using a Beckmann thermometer (Nishinari et al., 1991). LBG solution in 0.05 M NaCl was prepared using protocols described in the text, with a resulting pH of 3.5. The specific viscosity, η_{sp}, was determined at different concentrations c. The intrinsic viscosity $[\eta]$ and Huggins coefficient k_H were determined using a linear expansion (Young, 1983):

$$\frac{\eta sp}{c} = [\eta] + k_H c[\eta]^2 \quad (2)$$

2.6. Shear viscosity measurements

The shear viscosity of concentrated solutions was determined using a Rheostress 600 (Thermo Scientific) rheometer with a cone (2°) and plate geometry. Solutions were loaded at room temperature and measured at 25 °C.

2.7. Extrusion test

The extrusion test was performed as previously described (Brenner, Hayakawa, et al., 2013; Brenner, Wang, 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. The measurement of the blank force, as well as recalculation of sensory scores from the extrusion data was as described elsewhere (Brenner, Hayakawa, et al., 2013; Brenner, Wang, et al., 2013).

2.8. 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

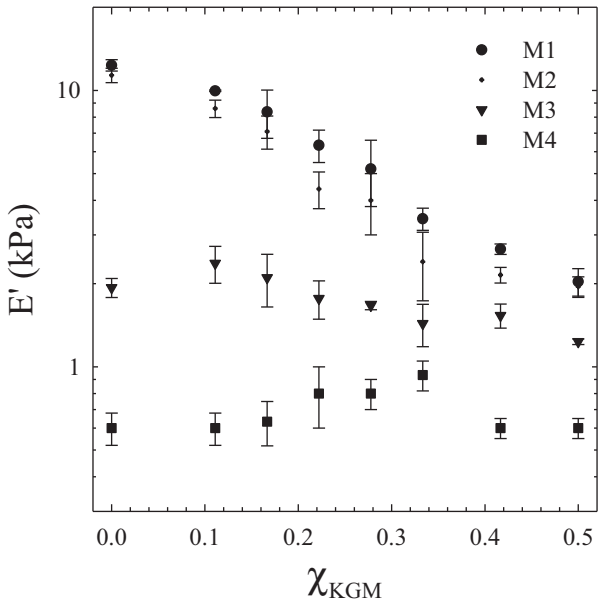

Fig. 1. Young's modulus of gels at 25 °C (F = 3 Hz) as a function of χ_{KGM} for different preparation methods (indicated in figure). Error-bars indicate one standard deviation.

Reproduced with modification from Brenner, Achayuthakan, et al. (2013) according to permission from John Wiley and Sons.

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.

3. Results and discussion

The Young's moduli of gels obtained using preparation methods M1–M4 have been given before (Brenner, Achayuthakan, et al., 2013) and are reproduced in Fig. 1. The main obvious effect of degradation is a strong decrease in E', while the general trend of a decrease in E' with increasing χ_{KGM} becomes much weaker, and a very weak peak in E' is observed for M3 and M4.

Fig. 2 shows the fracture strain ε_f (2A) and stress σ_f (2B) in the ring extension test. As seen from the figure, within the experimental error, we cannot conclude that there is any decrease in ε_f between M1 and M3. Thus, for these treatments, the decrease in σ_f reflects only the decrease in E'. However, for M4, a clear decrease in ε_f was found, leading to a more pronounced decrease in σ_f. The rather obvious conclusion that the decrease in E' corresponds to polysaccharide degradation was supported with measurements of the specific viscosity of KC, as shown previously (Brenner, Achayuthakan, et al., 2013). We have measured the specific viscosity of LBG in a similar manner, and the results are shown in Fig. 3. Degradation of LBG is obvious from the decrease in the intrinsic viscosity. However, the difference between the intrinsic viscosity of the M3 treated and M4 treated LBG is very small, in contrast with the case of KC. Furthermore, when we compare the non-treated LBG and LBG heated at 45 °C for 90 min, i.e., the difference between treatments M3 and M4, we also find a very small difference. The same observation can be made for a 0.5% KGM solution, as well as a 0.25% KGM–0.25% LBG solution, from the flow curves shown in Fig. 4. Because the degree of degradation of KGM and LBG is very similar for treatments M3 and M4, while this is not the case for KC, we tentatively suggest that the decrease in the fracture strain between treatments M3 and M4, which is seen in Fig. 2, owes to some critical degradation of KC. We observed for 0.6% KC solutions, that somewhere between heat-treatments M3 and M4,

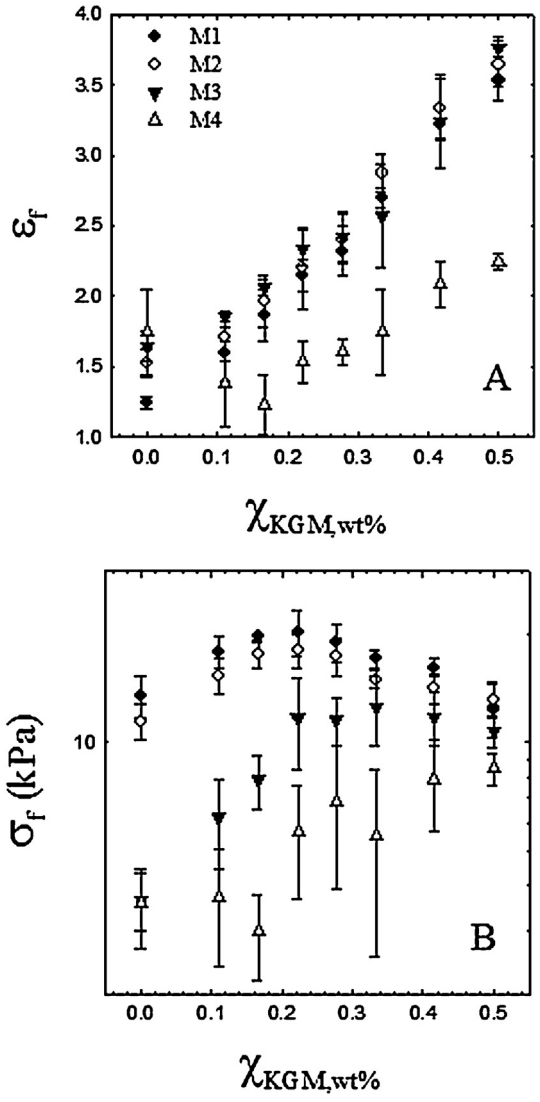

Fig. 2. Fracture strain ε_f (A) and stress σ_f (B) in ring extension tests ($\dot{\varepsilon} = 0.15\ \ s^{-1}$) at 25 °C as a function of χ_{KGM}. Error bars indicate one standard deviation.

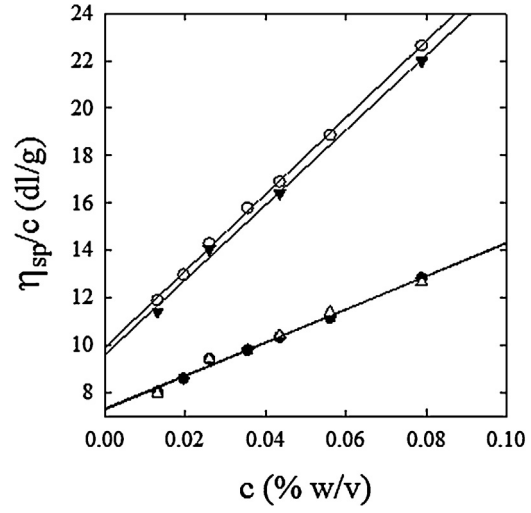

Fig. 3. Reduced viscosity of LBG at pH 3.5 in 0.05 M NaCl. Open circles, non-treated sample; filled triangles, 90 min at 45 °C; filled circles, M3; open triangles, M4. Solid lines are fits to Eq. (2).

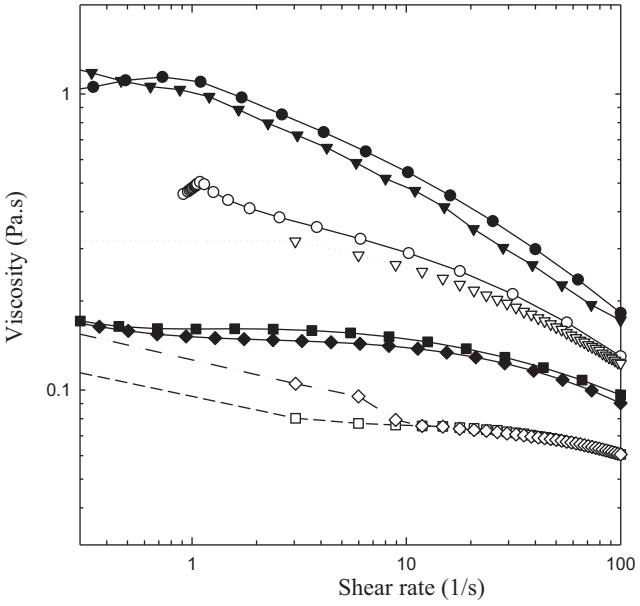

Fig. 4. Steady-state shear viscosity of 0.5% KGM (filled symbols) and 0.25% KGM-0.25% LBG (open symbols). Circles, non-treated samples; triangles, 90 min at 45 °C; squares, M3; diamonds, M4.

the solution no longer formed a self-supporting gel upon cooling. For the M4 treated mixed gels studied we observed that they were self-supporting and could be measured on the Rheolograph, but they were obviously slightly different in that the fracture strain was decreased. To clarify why the fracture strain did not decrease for treatments M1–M3 but only for M4, we performed DSC measurements on a sample containing 0.9% KC, 0.15% LBG and 0.15% KGM. As shown in a previous publication (Brenner, Wang, et al., 2013), at such a mixing ratio, the rheology and endotherms will be dominated by the interaction between KC and KGM. We chose this mixing ratio, which was not used for any of the gels studied herein (where $C_{KC} = C_{LBG}$) to ensure a high enough KC content and clear DSC endotherms. As shown in Fig. 5, the higher temperature endothermic peak, which corresponds to melting of mixed

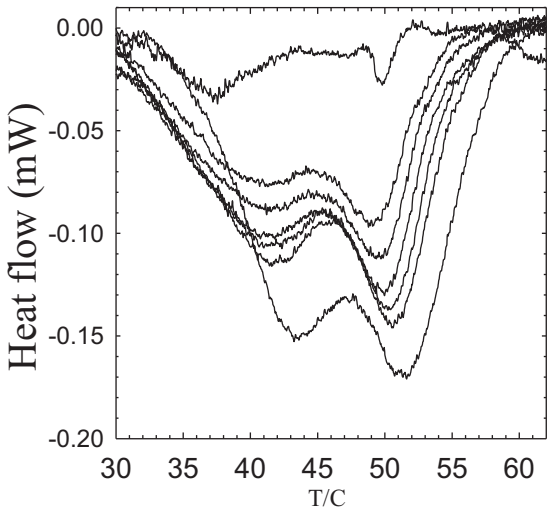

Fig. 5. DSC heating endotherms of a mixed polysaccharide solution (C_{KC} = 0.9%, C_{KGM} = 0.15%, C_{LBG} = 0.15%, pH = 3.5). The solution was heated from 5 °C to 80 °C and then cooled back at 1 °C/min. The bottom 6 curves represent heating cycles 1–6, with curves becoming less endothermic with each repetition. The top-most curve was obtained for a sample heated 6 times and then left for 15 h at 70 °C.

KC–KGM bonds (Brenner, Wang, et al., 2013), decreases faster than the lower temperature peak, which corresponds to melting of KC-only bonds. The ratio of the areas of the endothermic peaks changed from 1:1.3 to 3:1 (low to high temperature peaks) after 6 heating cycles and 15 h at 70 °C. This finding ties in very nicely with our observation that in the initial stages of polysaccharide degradation, the fracture strain does not decrease. We recall that KGM and LBG interact with KC to form elastic bonds, and when excess KGM or LBG are present, they reinforce the elastic network and increases the fracture strain (Brenner, Wang, et al., 2013). The molecular picture invoked in an accompanying publication (Brenner, Wang, et al., 2013) is that the LBG or KGM forming the elastic bonds can connect crystalline domains of double KC helices (Morris, 1995). The excess galacto- or glucomannan interact with the bound chains without forming new elastic bonds, and enhance their ability to deform. Because, as degradation advances, relatively fewer KGM chains are interacting with KC, i.e., the lower temperature peak is growing relative to the higher temperature peak, more KGM chains are present as excess and reinforce the elastic network, thus increasing the fracture strain. In practice, we can say that not only are the domains of crystalline packed KC helices becoming smaller with increasing degradation, which is trivial and follows directly from the total decrease in the enthalpy of the endotherm, but also the sites compatible for KGM or LBG become scarcer, i.e., the smaller crystalline zones are less compatible for LBG or KGM binding, and the LBG and KGM can bind them and form new elastic bonds to a lesser degree. This leaves more excess KGM and LBG that may interact with the elastic network without forming new elastically active bonds, and only increase the deformability of the network. This effect probably counteracts the expected effect of a lower fracture strain for gels formed by shorter chains (Mitchell, 1979, 1980; Ward & Cobbett, 1968). Indeed, for treatments M2 and M3, we suspect that there might even be a slight increase of the ε_f with increasing degradation, although we cannot conclude it definitively, because it is within the experimental error, see Fig. 2.

The gels under study do not fracture under compression (Brenner, Achayuthakan, et al., 2013). For such foods, it has been pointed out (Barrangou, Drake, Daubert, & Foegeding, 2006a, 2006b; Truong & Daubert, 2000, 2001) that correlation of the rheology with texture attributes should not be attempted through the two-cycle compression test known 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; Brenner, Wang, 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; Brenner, Wang, et al., 2013). 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, Achayuthakan, et al., 2013; Brenner, Hayakawa, et al., 2013; Brenner, Wang, et al., 2013). For the M1 gels, the firmness is roughly a constant up to $\chi_{KGM} \approx 0.2$, and then decreases weakly with increasing χ_{KGM}. This is reflected in an increase in the extrusion force with increasing force up to intermediate χ_{KGM} values, reminiscent of the increase in the extensional fracture stress, see Fig. 2B, and the monotonously decreasing E' (Brenner, Achayuthakan, et al., 2013). The firmness of all gels decreased with increasing degree of degradation, as seen particularly for M3 and M4. The extensibility is a sensory measure of the deformability. The extensibility (Fig. 6B) of M1 gels increases monotonously with increasing KGM content, as expected from the increase in fracture strain shown in Fig. 2A. The extensibility increases slightly with the advance of degradation for M2 and M3,

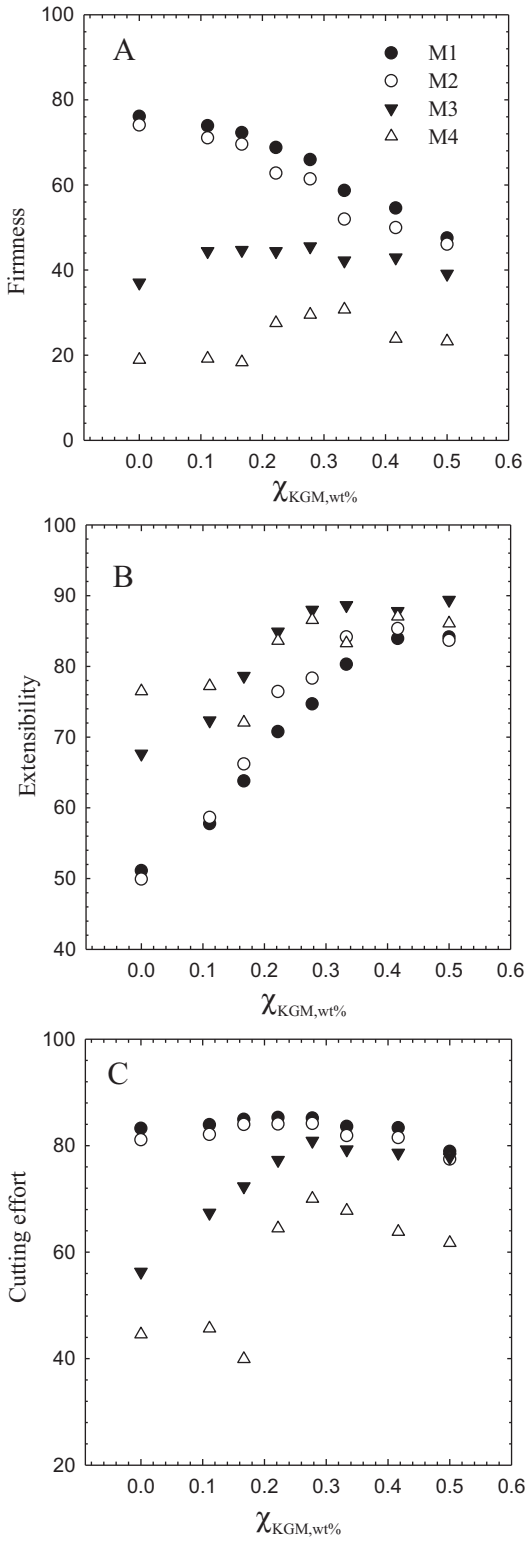

Fig. 6. Sensory scores (0–100) for gels, recalculated from extrusion test data and the Young's modulus. (A) firmness, (B) extensibility (a measure of deformability), (C) cutting effort. The heat treatments are as indicated in 6A.

but decreases again for M4, which checks with our findings for the fracture strain in Fig. 2A. The recalculated effort-of-cutting scores of the gels are given in Fig. 6C. The peak at around $\chi_{KGM} \approx 0.25$ is again reminiscent of the peak in σ_f (Fig. 2B). The effect of degradation is to decrease the cutting effort of the gels, especially for treatments M3 and M4.

4. Conclusions

A series of gels simulating dessert jellies containing κ-carrageenan, locust bean gum and konjac glucomannan was prepared. Polysaccharide degradation due to heating at acidic pH was confirmed for all three polysaccharides. The degradation of κ-carrageenan was responsible for the marked decrease in E'. The sensory extensibility (deformability) and fracture strain in extension of the gels were hardly affected by degradation, unless it was very severe, in which case κ-carrageenan did not form a self-supporting gel. The reason was that fewer konjac glucomannan chains interacted with κ-carrageenan to form elastic bonds once the latter was degraded, and thus the konjac glucomannan could to a greater degree reinforce the elastic network and increase the fracture strain. While degradation hardly affected the sensory extensibility (deformability), the cutting effort and firmness decreased monotonously with increasing polysaccharide degradation.

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