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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 $\Delta L/2 \approx D + (4\pi + 13 - 10.5\pi)\,\text{mm} = D - 7.4\,\text{mm}$. 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

$$\varepsilon = \frac{D - \delta}{\pi R_i} \tag{1}$$

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.