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Compression strength and deformation of gellan gels formed with mono- and divalent cations

Juming Tang[a]*, Marvin A. Tung[b] & Yanyin Zeng[c]

[a]*Department of Biological Systems Engineering, Washington State University, Pullman, WA 99164-6120, USA*
[b]*Department of Food Science, University of Guelph, Guelph, ON N1G 2W1, Canada*
[c]*School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164-6120, USA*

The influence of divalent (Ca^{2+} and Mg^{2+}) and monovalent (Na^+ and K^+) cations on the failure stresses and strains in gels formed with gellan polymer were investigated. Gellan gels containing 0.6–2.2% polymer and varying cation concentrations were tested using large compressive deformation until failure. Maximal true shear stresses and corresponding shear strains represented gel strength and extensibility. At small cation concentrations, the strength of gellan gels increased while the extensibility decreased with cation concentrations. The strongest gels were obtained at cation levels corresponding to 0.5 cations per carboxylate group in the repeat gellan unit for gels crosslinked with divalent cations and 10 to 30 cations per repeat gellan unit for gels with monovalent cations. At optimum cation levels, gellan gels with Ca^{2+} were stronger than with Mg^{2+}, and gellan gels with K^+ were stronger than with Na^+. Above the optimum cation levels, gellan gels became brittle, and the strength of the gels decreased with increasing cation concentrations. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Gellan polymer, a newly food-approved anionic polysaccharide (Anon., 1992), is secreted by the bacterium *Pseudomonas elodea* during aerobic fermentation. The native polysaccharide contains approximately 6% *O*-acetyl groups and forms weak and deformable gels. The *O*-acetyl groups are lost during normal commercial extraction and the resulting deacetylated polysaccharide yields much stronger gels (Upstill *et al.*, 1986; Chapman *et al.*, 1987). Deacetylated gellan polymers consist of tetrasaccharide repeating units -3)-β-D-Glcp-(1→4)-β-D-GlcpA-(1→4)-β-D-Glcp-α-oL-Rhap(1→ (Fig. 1). These polymers produce gels in the presence of cations in water solutions, possibly through formation of 3-fold double helix followed by aggregation of the double-helical segments to form a three-dimensional network (Upstill *et al.*, 1986; Chandrasekaran *et al.*, 1988a). The carboxylate group (COO^-) in each repeat unit of the polymer helps to stabilize the double-helix conformation and strengthen the junction zones in the gel networks. The mechanical properties of the resulting hydrogels depend upon gellan polymer and cation

concentrations (Sanderson, 1990). They are also sensitive to the valency of the cations used in gel preparation. Divalent cations are more effective in facilitating crosslinking between gellan polymers. Using the small deformation dynamic testing method, Moritaka *et al.* (1991) showed that much higher concentrations of monovalent cations were required to form gels with storage moduli similar to the gels crosslinked with divalent cations. Sanderson and Clark (1984) suggested that maximum hardness required an approximate 25-fold increase in the molar concentration of monovalent cations as compared to using divalent cations. Chandrasekaran *et al.* (1988b) stated that 40 times more monovalent cations were needed to make gellan gels of strength similar to those with calcium ions.

Tang *et al.* (1994) studied the effects of polymer and Ca^{2+} concentrations on the strength and extensibility of gellan gels using large deformation tests. They reported that the maximum shear stresses of calcium–gellan gels at failure were the same when derived from either tension, torsion or compression experiments, and the failure shear strains in one test mode could be predicted from the other. There were two distinctive patterns of mechanical response, below and above a critical Ca^{2+} concentration at which the gel had maximum strength

*Author to whom correspondence should be addressed.

Carboxylate group
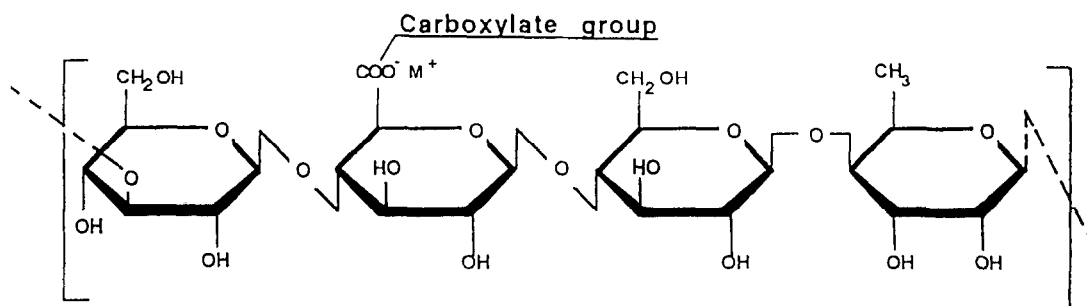
Gellan polymer repeat tetrasaccharide unit

Fig. 1. Deacetylated gellan polymer tetrasaccharide repeat unit.

for a given polymer concentration. The gels were soft and deformable below this critical Ca^{2+} level, but brittle above. They suggested this critical Ca^{2+} level may correspond to the state in which all the anionic sites in potential junction zones along the gellan polymers were occupied by cations, so that maximal interactions would take place within the gel network. Effects of monovalent cation concentrations on the mechanical response of gellan gels under large deformations are less clear. The purpose of this study was to gain a better understanding of the effects of divalent and monovalent cations on the strength and ultimate deformability of gellan gels using large deformation testing.

MATERIALS AND METHODS

Deacetylated gellan polymer powder, Kelcogel, was provided by Kelco Inc. (San Diego, CA, USA), along with its composition as listed in Table 1. Weighed amounts of gellan powder were dispersed in distilled deionized water at room temperature to form solutions with concentrations of 0.6–2.2% w/w for gels to be crosslinked with divalent cations, and of 0.6–1.8% w/w for gels formed with monovalent cations. These solutions were then heated with constant stirring on hot plates from room temperature

Table 1. Major components in the gellan polymer used in this study

Composition[a]	Weight in dry matter
Carbohydrates (dietary fibre)	85
Water	10
Sodium	0.3
Calcium	0.4
Magnesium	0.1
Potassium	4.9
Phosphorus	0.2

[a]Provided by the manufacturer, Kelco Inc., San Diego, CA.

to 90°C, so that the polymer powders were dissolved and the solutions became clear. Predetermined amounts of calcium chloride ($CaCl_2$) or magnesium chloride ($MgCl_2$) were added to the hot solutions to prepare dispersions containing divalent cations, ranging in concentration from 1.5 to 60 mM, while sodium chloride (NaCl) or potassium chloride (KCl) was added to make dispersions containing monovalent cations ranging in concentration from 25 to 600 mM. The hot solutions were poured into cylindrical stainless steel molds of 21 mm inner diameter and 140 mm length. The molds were fitted with rubber stoppers on both ends, immersed in running water at 15°C for 15 min, and held in air at room temperature (22°C) overnight to form consistent gels.

In the current study compression testing was used, as the sample preparation and measurement procedures for this method were far less time-consuming than for tension or torsion testing methods. In preparing specimens for compression tests, six cylindrical sections of 21 mm diameter and 20 mm length were cut from each gel when removed from its mold. These specimens were then compressed at a crosshead speed of 20 mm/min between Teflon plates in a mechanical testing machine (Model 1125, Instron Corporation, Canton, MA, USA) interfaced with an IBM microcomputer. The contact between the ends of the specimen and compressing surfaces were lubricated with a few drops of low viscosity oil to eliminate possible 'barrelling' caused by friction at the contact surfaces. The specimens were then compressed to failure. During the compression test, forces applied to the gel specimens increased with deformation imposed by the machine as a result of the moving crosshead. Compressive forces reached their peak values immediately before structural failure was observed in the gel samples. Each gel was characterized by extracting the mean values of engineering stress (σ_{eng} = force/original cross-section area) and strain (ε_{eng} = reduction in length/original specimen length) at the moment of failure from the

results of six test specimens. Because the gels underwent large deformations in these tests, it was necessary to calculate Hencky's stresses and strains from the engineering stresses and strains in order to represent the true stress and strain conditions at the moment of failure.

Hencky's normal strains (ε_h) in the cylindrical specimens were obtained from the following relation based on Hamann (1983):

$$\varepsilon_h = -\ln(1-\varepsilon_{eng}) \qquad (1)$$

Hencky stresses in gels (σ_h) were derived from the equation based on Nussinovitch *et al.* (1990), which assumed that the specimen volume remained constant by increasing the cross-sectional area while compressing the sample to a shorter length:

$$\sigma_h = \sigma_{eng}(1-\varepsilon_{eng}) \qquad (2)$$

The maximum shear strains (γ_{max}) and shear stresses were obtained from the normal strains and stresses by the following relations (Hamann, 1983):

$$v_{max} = (1 + v)\varepsilon_h \qquad (3)$$

$$\tau_{max} = \frac{\sigma_h}{2} \qquad (4)$$

Gellan gels were assumed to be incompressible under the loading conditions imposed by these tests, thus the Poisson's ratio (v) in equation (3) is equal to 0.5 (Juvinall, 1967).

RESULTS

The means of the maximum shear stresses and shear strains in six replicated gellan specimens during compression tests were used to reflect the strength and ultimate deformability of the gel samples. The effects of cation and polymer concentrations on the maximum shear stresses and strains of the gel samples were plotted in Figs 2–9. As the carboxylate group (COO^-) in each tetrasaccharide repeat unit of gellan polymer is believed to play a major role in gel forming, cation and carboxylate concentrations were expressed as ratios [cation]/[COO^-]. These ratios were calculated from the known amounts of cations originally in the gellan powder (Table 1) plus the added cations. For gels with added divalent cations, the amount of potassium in the powder was converted to an equivalent amount of divalent cations by a factor of 1/30. Likewise, for gels with added monovalent cations, divalent cations already in the gellan powder were converted to amounts of monovalent cations by multiplying by a factor of 30. In either case, the amounts of cations introduced with the polymer powder were only a small portion of the total cation concentration in the final gel samples.
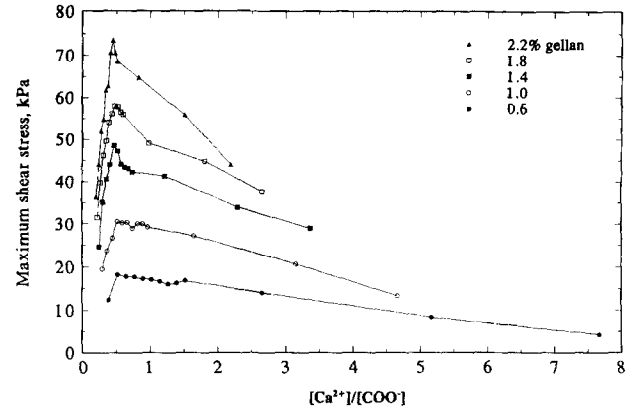

Fig. 2. Maximum shear stress at failure for calcium–gellan gels shown as a function of cation/carboxylate ratio at different polymer concentrations.
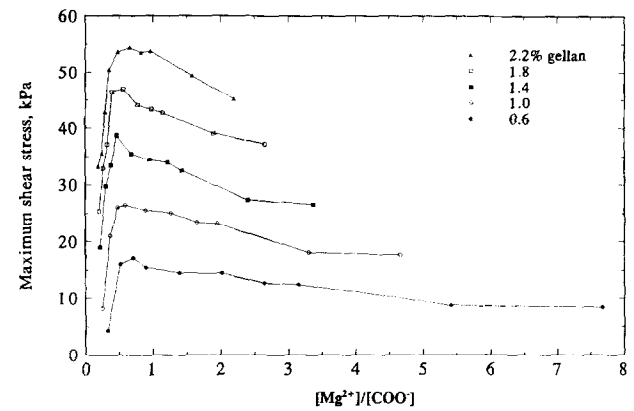

Fig. 3. Maximum shear stress at failure for magnesium–gellan gels shown as a function of cation/carboxylate ratio at different polymer concentrations.
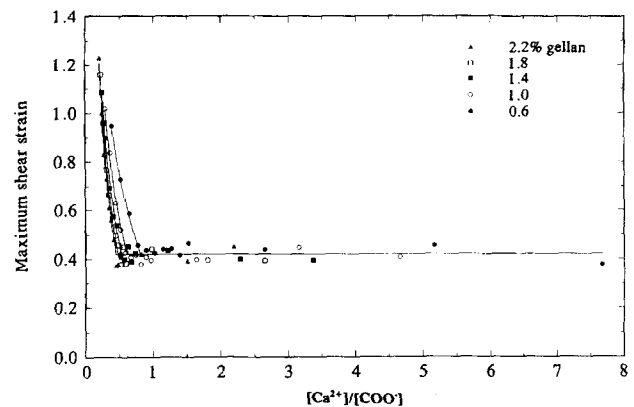

Fig. 4. Maximum shear strain at failure for calcium–gellan gels shown as a function of cation/carboxylate ratio at different polymer concentrations.

Gellan gels with divalent cations

The strength of gellan gels increased with polymer concentration at all divalent cation levels (Figs 2 and 3). The same observations were made with gels crosslinked with monovalent cations (Figs 6 and 7). It is likely that
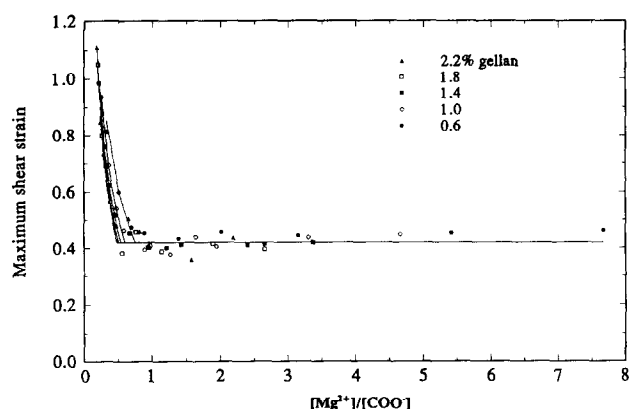
Fig. 5. Maximum shear strain at failure for magnesium–gellan gels shown as a function of cation/carboxylate ratio at different polymer concentrations.
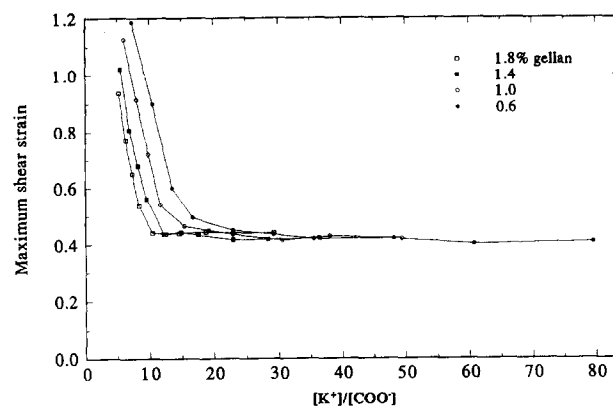

Fig. 8. Maximum shear strain at failure for potassium–gellan gels shown as a function of cation/carboxylate ratio at different polymer concentrations.
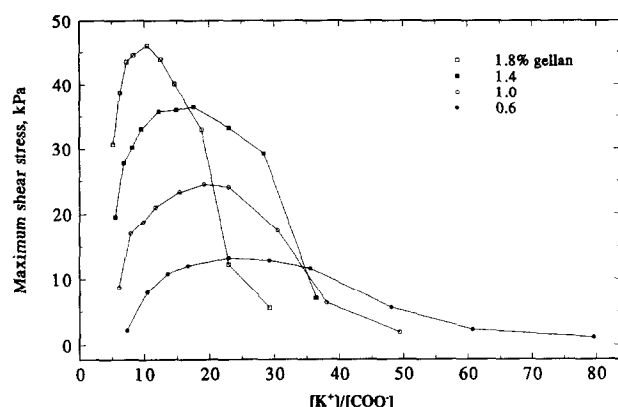

Fig. 6. Maximum shear stress at failure for potassium–gellan gels shown as a function of cation/carboxylate ratio at different polymer concentrations.
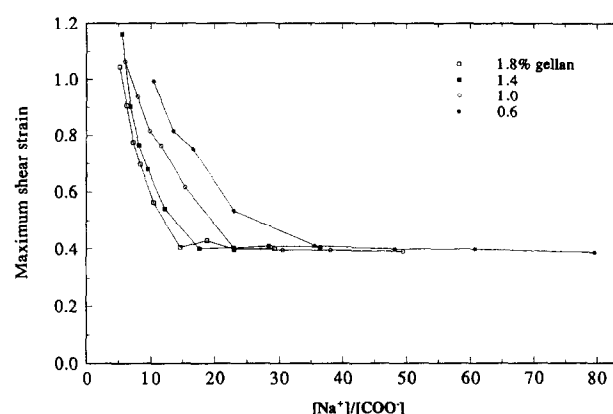

Fig. 9. Maximum shear strain at failure for sodium–gellan gels shown as a function of cation/carboxylate ratio at different polymer concentrations.
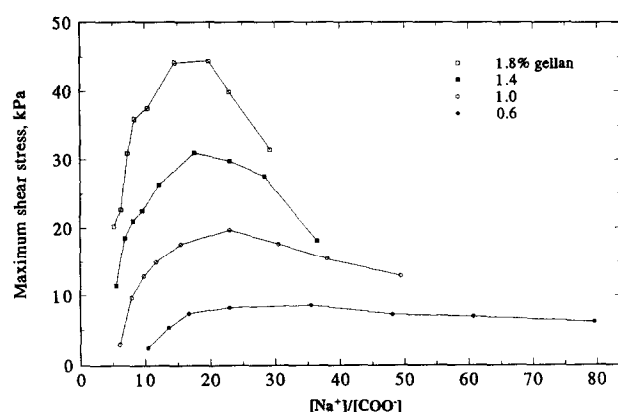

Fig. 7. Maximum shear stress at failure for sodium–gellan gels shown as a function of cation/carboxylate ratio at different polymer concentrations.

higher polymer concentrations resulted in greater crosslink densities in the gel networks, thus, stronger gels.

When the divalent [cation]/[carboxylate] ratio was less than 0.5, the strength of gellan gels increased

sharply with increasing cation concentrations (Figs 2 and 3) to reach a peak value at about 0.5 [cation]/ [carboxylate] for all gellan levels. This is in general agreement with the findings of Tang *et al.* (1994). At the maximal strength for each polymer concentration, gels with Ca^{2+} were 1.1–1.4 times stronger than the corresponding gels crosslinked with Mg^{2+}. When the [cation]/[carboxylate] ratio was larger than 0.5, gellan gels were weakened by additional added cations. The calcium gel strength was reduced at greater rates than magnesium gels (Figs 2 and 3). At values near 3.0 for the [cation]/[carboxylate] ratio, the two gels had fallen to comparable strength, and above this ratio, calcium gels were generally weaker than the corresponding magnesium gels.

Gellan gels can be deformed to a relatively large extent at very low divalent cation levels. For instance, the failure shear strains at 0.2 [cation]/[carboxylate] were comparable to the failure shear strains of fish gels and egg white gels (1.0–1.2; Hamann, 1983). When the [cation]/[carboxylate] ratios were smaller than 0.5, calcium gels were deformed to larger strains before

failure than magnesium gels, and the maximum shear strains in both gels decreased sharply with increasing cation concentrations (Figs 4 and 5). The failure shear strains of gellan gels reached minimum values of about 0.4 at [cation]/[carboxylate] ratios between 0.5 and 0.8. Above these cation levels, the failure shear strains of calcium and magnesium gels remained at virtually the same value of 0.4.

It was observed during the tests that the specimens generally fractured at an angle of about 45° from the principal axis of the cylinder at cation levels below 0.5 [cation]/[carboxylate], and in the direction of the cylinder axis at above 0.5 [cation]/[carboxylate]. Thus, the gels failed in the planes of maximum shear stress in the former instances, and along planes of maximal tensile stress in the latter.

Gellan gels with monovalent cations

The strengths of monovalent ion–gellan gels as reflected by the failure shear stress in each sample during compression tests are presented in Figs 6 and 7, as functions of monovalent [cation]/[carboxylate]. Similar to gels crosslinked with divalent cations, gellan gels with K^+ and Na^+ showed maximum strengths at particular levels of cation concentration. However, the peaks in the strength of these gels were much broader than for gels with divalent cations. The [cation]/[carboxylate] ratios at the maximum strength were also much larger than 0.5 as was found for Ca^{2+} and Mg^{2+} gels. As gellan concentrations were reduced from 1.8 to 0.6% w/w, the optimum [cation]/[carboxylate] ratios changed from 10 to 22 with K^+ and from 15 to about 30 with Na^+. At the maximum gel strength, the gels with potassium ions were stronger than the corresponding gels formed with sodium ions. However, the strength of the former gels decreased at a faster pace with increasing cation concentrations beyond the optimal cation levels, especially in gels of 1.8% w/w polymer concentration (Fig. 6).

Gellan gels with K^+ and Na^+ were relatively deformable before failure at low cation concentrations, and the maximum shear strains were reduced from over 0.9 to a constant value of about 0.4 when the [cation]/[carboxylate] ratios increased from about 5 to 40 and above. It is noteworthy that the points where the shear strains approached 0.4 in Figs 8 and 9 match closely the [cation]/[carboxylate] ratios at the maximum strength of each gel in Figs 6 and 7.

Gellan gels formed with monovalent cations generally fractured in the plane of maximum shear stress (45° from the longitudinal axis of the cylinder) below the optimum ion levels, and in the planes of maximum tensile stress (0° from the cylinder axis) above the optimum ion levels. At the extremely high cation levels, e.g. above 450 mM, gels also often fractured in the planes of maximum shear stress.

DISCUSSION

It may be possible that divalent cations established direct polyanion–cation–polyanion interactions between the carboxylate groups of adjacent double helices in gellan gels (Chandrasekaran *et al.*, 1988*a, b*). A small number of these interactions (or crosslinks) could form a junction. It is likely that at low cation concentrations, a relatively small number of crosslinks were formed due to limited availability of cations and thus, the gel structures were weak and flexible. The polymers could accommodate additional cations to increase crosslinks at the junction zones. As a result, both the strength and rigidity of the gel would increase with increasing cation concentration. Maximum strength was reached when all the possible crosslinks were built and the maximal number of complete junction zones were formed with just sufficient divalent cations. This occurred when the stoichiometric requirement of the carboxylate groups in gels were satisfied, namely, when the divalent [cation]/[carboxylate] ratio was equal to 0.5 as shown in Figs 2 and 3. The difference between the strength of gels with Ca^{2+} and Mg^{2+} at the maximum strength may be related to the difference in cation sizes, as Ca^{2+} ions are about 1.5 times the size of Mg^{2+} ions (Chang, 1991). Larger Ca^{2+} cations might provide stronger binding forces at the junctions and, therefore, result in stronger gels than with Mg^{2+}. When more than 0.5 [cation]/[carboxylate] divalent cations were present during gelation, excessive cations might have competed for anionic sites and imposed repulsive forces to prevent the formation of crosslinks. These forces would increase with greater amounts of excessive cations, thereby reducing the number of crosslinks in the junction zones and weakening the gel structure. In these cases, the larger Ca^{2+} might provide stronger repulsive forces to reduce the strength of gels to a greater extent than smaller Mg^{2+}.

Monovalent cations helped crosslinking in the double helices indirectly, with the help of water molecules. They might have formed polyanion–cation–water–cation–polyanion linkages between adjacent helices (Chandrasekaran *et al.*, 1988b) or other linkages by shielding the electrostatic repulsion of the carboxylate groups (Moritaka *et al.*, 1991). This may explain in part why maximum gellan gel strengths were achieved at much higher monovalent [cation]/[carboxylate] ratios than with divalent cations, and why broader peaks in gel strength were observed in Figs 6 and 7. The binding forces in these junctions should be weaker than the direct polyanion–cation–polyanion interactions. Therefore, gels with K^+ and Na^+ were generally weaker than gels with Ca^{2+} or Mg^{2+}. Similar to divalent cations, excessive monovalent cations present in solutions during gelation may inhibit the formation of crosslinks by imposing repulsive forces between polymer molecules, and thereby weaken the gel structure. This may be

increasingly true at large polymer concentrations for a given [cation]/[carboxylate] ratio (Figs 8 and 9), as the density of cations in solutions before gelling is proportional to polymer concentration. The difference between the strength of gels with K^+ and Na^+ may also be a result of the size difference between the cations, as K^+ are about 1.4 times as large as Na^+ (Chang, 1991).

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