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Polymer and Ion Concentration Effects on Gellan Gel Strength and Strain

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ABSTRACT

Failure stresses and strains were measured in compressive, tensile and torsional modes on gellan gels at four polymer (0.6–1.8% w/v) and seven Ca^{++} (1.5–60 mM) concentrations. Shear stresses at failure were equal in all three testing modes and proportional to gellan content. Low calcium gels increased linearly in strength with Ca^{++} concentration until it reached a level of about 0.5 calcium ions per repeat tetrasaccharide unit of gellan gum polymer. Gel strength decreased linearly with Ca^{++} at higher concentrations. Low calcium gels were extensible with failure strains decreasing as the logarithm of Ca^{++}; whereas high calcium gels were brittle and failed at a constant strain, the value of which was twice as high in compression and torsion as in tension.

Key Words: gellan, gels, extensibility, calcium, gel strength

INTRODUCTION

CARBOHYDRATE POLYMERS are important to the food industry due to demands for functional ingredients which impart thickening, gel formation and textural stability. Such ingredients are needed for replacement of fats and low molecular weight carbohydrates, particulary in low-fat and reduced calorie formulated foods. Gellan is a food approved (Anon., 1992) gelling agent that appears to have unique functional properties. However, information is needed about the polymer solution and gel properties before its full potential can be realized.

Gellan gum is an extracellular anionic polysaccharide secreted by the bacterium *Pseudomonas elodea*. Its monosaccharide units are β-D-glucose, β-D-glucuronic acid and α-L-rhamnose in molar ratios of 2:1:1 (Sanderson, 1990). The polysaccharide produces gels in the presence of cations, possibly due to the parallel alignment of left-handed double-helical polymers to form junction zones (Chandrasekaran et al., 1988) resulting in three dimensional networks. The mechanical properties of the gels depend on the structure of the networks so formed and are hence related to the polymer and ion concentrations. Moritaka et al. (1991) used small-displacement dynamic testing to study the effect of monovalent and divalent cations on the complex moduli of gellan gels. Rigidity of the materials was more sensitive to divalent than to monovalent cations.

Although small strain tests provide a useful means of studying gel structure, large deformation studies are of more practical importance since foods are subject to such deformations during processing and consumption. Of particular interest are the maximum stress and strain of a gel prior to failure in large deformation. Such properties reveal the strength and ultimate extensibility of the three dimensional gel network. Preliminary experimental results by Sanderson et al. (1987) have shown that the maximum stress and strain of gellan gel in compression were affected by both polymer and calcium ion concentration. Nussinovitch et al. (1990) reported that the strength and stiffness of gellan gels in compression increased with gum polymer concentration from 0.5 to 2.5% at a single ion concentration. Lelievre et al. (1992a) compared the stress and strain at failure in compression, tension and torsion using a single gellan polymer and calcium ion concentration. The stress at failure was the same in the three testing modes, whereas the corresponding strain, measured in tension, did not agree with results from the other procedures.

Our objective was to use torsional, compressive and tensile tests to investigate the effects of polymer and ion concentration on the strength and failure strain of gellan gels. Such information could be used to determine relationships between the structure and rheological properties of gels.

THEORY

TO SIMPLIFY the development of theory, stress-strain relationships were assumed to be linear. Experimental evidence has shown that for gellan gels, this approximation was valid over a wide range of strains (Gao et al., 1993).

Stress and strain equations for torsion specimens

Under a torsional load applied at both ends of a specimen (Fig. 1a), the maximum shear stress and strain occur at the surface of the narrowest section. Stress (τ_{max}) and strain (γ_{max}) at the failure site can be calculated as (Diehl et al., 1979):

$$\tau_{max} = \frac{2KM}{\pi r_{min}^3} \quad (1)$$

$$\gamma_{max} = \frac{2K\phi_s}{\pi r_{min}^3 Q_s} \quad (2)$$

where, M and r_{min} are the twisting moment and specimen minimum radius, respectively; ϕ_s is the angular deformation of

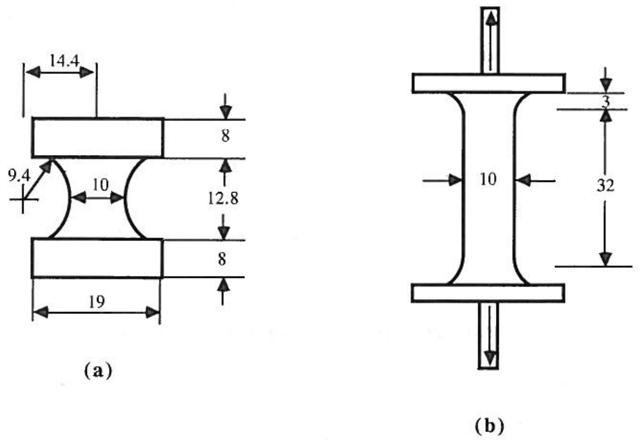

Fig. 1—(a) A capstan-shaped specimen used in torsion tests; (b) A dumbbell-shaped specimen used in tensile tests. Dimensions are shown in mm.

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the curved sector. K and Q_s are constants depending on the sample geometry. Equations for these two constants were reported by Diehl et al. (1979).

The end pieces have no effect on the stress at failure, but their deformation contributes to the total strain of the specimen. Assuming the two end pieces to be equivalent to a cylinder of radius r_{end} and total length L_{end}, the angular deformation of the end pieces are related to the twisting moment by (Timoshenko, 1958):

$$\phi_{end} = \frac{MQ_{end}}{G} \tag{3}$$

where G is the shear modulus, and

$$Q_{end} = \frac{L_{end}}{\pi r_{end}^4} \tag{4}$$

The total observed angular deformation, ϕ_t, of a capstan specimen equals the contribution from both the test section, ϕ_s, and the ends, ϕ_{end}:

$$\phi_t = \phi_s + \phi_{end} = \frac{M}{G}(Q_{end} + Q_s) \tag{5}$$

Thus,

$$\frac{\phi_s}{\phi_t} = \frac{Q_s}{Q_s + Q_{end}} \tag{6}$$

Substituting Eq. (4) into Eq. (6) yields:

$$\phi_s = \frac{Q_s}{Q_s + \dfrac{L_{end}}{\pi r_{end}^4}}\phi_t \tag{7}$$

Substituting for ϕ_s in Eq. (2) gives the equation required to calculate the shear strain:

$$\gamma_{max} = \frac{2K\phi_t}{\pi r_{min}^3 Q_s}K' \tag{8}$$

where,

$$K' = \frac{1}{1 + \dfrac{L_{end}}{\pi r_{end}^4 Q_s}} \tag{9}$$

K' is the correction factor for the end-piece effect, and it varies from 0 to 1, depending upon the magnitude of L_{end} and r_{end}, as well as the value of Q_s.

According to the stress and strain Mohr's circles (Hamann, 1983), torsion testing generates equal shear, compressive and tensile failure stresses in the specimen:

$$\sigma_{max} = \sigma_{true\ max} = \tau_{max} \tag{10}$$

and the normal strain is given by:

$$\varepsilon_{max} = \frac{\gamma_{max}}{2} \tag{11}$$

The true normal strain is (Nadai, 1937):

$$\varepsilon_{true\ max} = \frac{1}{2}\ln\left[1 + \frac{\gamma_{max}^2}{2} + \gamma_{max}\left(1 + \frac{\gamma_{max}^2}{4}\right)^{1/2}\right] \tag{12}$$

Stress and strain equations for compression specimens

In compression tests where specimen contact surfaces are lubricated, the magnitudes of true normal strains at failure in a cylindrical gel can be calculated as follows (Hamann, 1983):

$$\varepsilon_{true\ max} = -\ln\left[1 - \frac{\Delta L_{max}}{L}\right] \tag{13}$$

and the stresses for incompressible gels (Nussinovitch et al., 1990):

$$\sigma_{true\ max} = \frac{F_{max}(L - \Delta L_{max})}{\pi R^2 L} \tag{14}$$

where F_{max} is the compressive force at the moment of failure and ΔL_{max} is the corresponding deformation, R and L are the original radius and length of the gel specimen, respectively.

Stress and strain equations for tension specimens

Lelievre et al. (1992b) demonstrated that when the height of the end pieces in a dumbbell specimen was reduced to 1/10 of the length of the test section (Fig. 1b), the end effects were negligible. In this case, the equation for true normal stress and strain can be obtained from the following equations:

$$\varepsilon_{true\ max} = \ln\left[1 + \frac{\Delta L_{max}}{L}\right] \tag{15}$$

$$\sigma_{true\ max} = \frac{F_{max}(L + \Delta L_{max})}{\pi R^2 L} \tag{16}$$

In both compression and tension modes, the true shear stress and strain are related to the true normal stress and strain by (Hamann, 1983):

$$\tau_{true\ max} = \frac{\sigma_{true\ max}}{2} \tag{17}$$

$$\gamma_{true\ max} = \varepsilon_{true\ max}(1 + \nu) \tag{18}$$

The Poisson's ratio, ν, is about 0.5 for most food gels (Hamann, 1983).

MATERIALS & METHODS

MECHANICAL TESTING of gellan gels was conducted at gellan gum levels: 0.6, 1.0, 1.4 and 1.8% w/v, and calcium ion concentrations: 1.5, 3, 4.5, 6, 24, 42 and 60 mM. All tests were carried out in six replicates.

Preparation of gellan gels

Gellan gum powder (KELCOGEL, Kelco Div. of Merck & Co. San Diego, CA) at different gum concentrations (0.6 to 1.8% w/v) was dispersed in deionized distilled water using a magnetic stirrer. The solution was heated to 90°C to give a clear gellan gum solution. Calcium chloride at different concentrations (1.5 to 60 mM) was added to the hot gellan gum solution so that crosslinks could be formed on cooling. The gellan solution was filled into molds at 60°C, and the gels were set by cooling in running water at 15°C for 15 min. Samples were held overnight at 22°C before stress-strain measurements.

Torsion test

Test samples (Fig. 1a) were prepared in a mold (Lelievre et al., 1992a). For these specimen dimensions, constants K and Q_s in Eq. (1) and (2) were 1.08 and $8.45 \times 10^6 m^{-3}$, respectively (Diehl et al., 1979), and K' in Eq. (8) was calculated as 0.871. The flat ends of a specimen were glued to plastic disks using cyanoacrylate glue (Navickis and Bagley, 1983). The disks were then attached to a Bohlin rheometer (Model VOR, Bohlin Rheology AB, Lund, Sweden) in a manner analogous to that described for Brookfield (Wu et al., 1984) and Ferranti-Shirley (MacDonald et al., 1990) viscometers. The specimens were twisted at a constant strain rate of $0.0583\ s^{-1}$.

Compression test

Cylindrical test specimens of 21 mm diameter and 20 mm length were compressed between lubricated flat teflon surfaces fitted to a mechanical testing machine (Model 1125, Instron Corporation, Can-

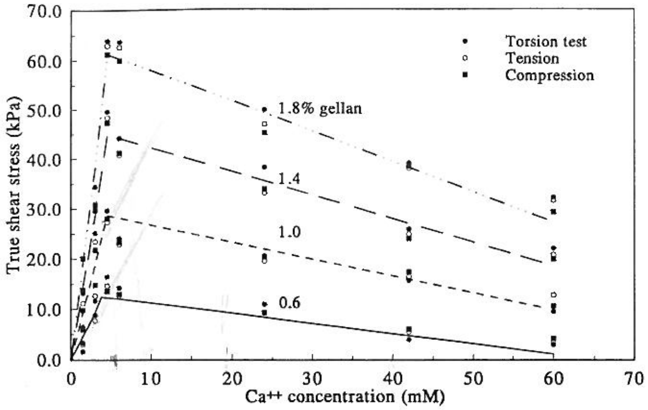


Fig. 2—True failure shear stresses relation to calcium ion concentration in different modes.

ton, MA) interfaced with an IBM microcomputer. The gels were deformed at a constant crosshead speed of 20 mm/min.

Tensile test

The mold system described by Langley et al. (1986) was used to prepare dumbbell-shaped samples for tensile tests. The dumbbell end pieces were cut to 3 mm to reduce the end effect (Fig. 1b). Nylon disks with cylindrical shafts normal to the disk surface were glued on both ends of the specimen using cyanoacrylate glue. The assembly was then mounted in the Instron machine by gripping the nylon attachment shafts with drill chucks fixed to the load cell and crosshead and the samples were deformed at a speed of 20 mm/min.

RESULTS & DISCUSSION

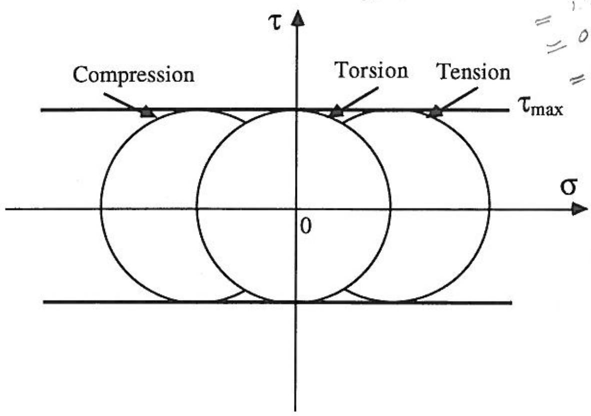
TESTING DATA from six replicates at each polymer and calcium concentration gave a coefficient of variation (C.V., %) value of <5 for compression, <9 for tension and <7 for torsion. Means of these replicates were used in the figures and statistical analyses.

Failure stress and strain in three testing modes

In all cases, the gellan gels failed in the direction of maximum tensile stress, except in compression tests below certain critical Ca^{++} ion levels. In those cases, the specimens fractured at an angle of about $\pi/4$ radians from the cylinder axis, which was in the direction of the maximum shear stress.

At any given gellan and ion concentration, no significant difference ($p>0.05$) was observed among the failure shear stresses obtained by the three different testing methods (Fig. 2), while the shear strain measured in tension was about half that of the compression and torsion cases. As a typical example, where the gellan concentration was 1.0% and the calcium concentration 24 mM, failure stresses were 20.7 ± 0.2, 20.4 ± 0.1 and 19.7 ± 0.9 kPa for torsion, compression and tension, respectively. The corresponding failure strains were 0.42 ± 0.01, 0.45 ± 0.01 and 0.20 ± 0.07. These results demonstrated that the disagreement among failure strain in the three testing modes reported previously (Lelievre et al., 1992a) applies over a wide range of polymer and ion concentrations.

A general stress condition within the gels at failure could be best represented using Mohr's circle (Ugural and Fenster, 1981). If compressive stress is considered negative and tensile positive, and each circle represented one test method, a plot of τ and σ at failure in different planes of the same specimen element would appear as shown in Fig. 3. The three circles of equal radius indicate that the gels failed when shear stresses reached essentially the same value, regardless of testing mode.



5k kPa ⇒ $5\times1000\frac{N}{m^2}\times\frac{\pi D^2}{4}=$

$=5\times1000\frac{Nf}{m^2}\times\frac{\pi\times21^2 mm^2}{4\times1000^2\frac{mm^2}{m^2}}=$

$=1.732N$

$=0.176 kgf$

$=\frac{0.176 kgf}{0.467\frac{kgf}{lbf}}$

$=0.378 lbf$

⇓

3.78% of 10lb load cell

Fig. 3—Mohr's circles for failure stresses in different modes.

Failure stress-composition relationships

In general, the values of failure shear stress were functions of both calcium ion concentration and gellan concentration. At all calcium levels, failure shear stresses increased with polymer concentration in a linear manner (Fig. 2). The same trend was reported by Sanderson (1990) over a range of gellan concentration from 0.25 to 1.5% at 7 mM Ca^{++}. Higher polymer concentrations probably corresponded to higher crosslink densities, thus, increased strength of the gel structure. The failure shear stress increased with calcium concentration up to a critical ion level (Fig. 2). Beyond that level, the shear stress decreased gradually in a linear manner.

The least squares method was used to correlate failure shear stress with gellan and calcium ion concentrations. The best fit model is presented as Eq. (19) for the three test modes at calcium concentrations below the critical levels, and as Eq. (20) at calcium concentrations above the critical levels.

$$\tau_{max} = (-1.36 + 6.2x_g)\,x_c \quad (x_c < x_{cr},\ R^2 = 0.93) \qquad (19)$$

$$\tau_{max} = -12.0 + 41.8x_g - 0.262x_gx_c \qquad (20)$$
$$(x_c \geq x_{cr},\ R^2 = 0.95)$$

where, τ_{max} is the failure shear stress (kPa), x_g is the gellan gum concentration (%, w/v), and x_c the calcium ion concentration (mM). The critical levels of calcium ions (x_{cr}) had a value around 6 mM. The goodness of fit of Eqs. (19) and (20) to the experimental data is demonstrated in Fig. 2.

Failure strain-composition relationships

At each polymer concentration, the failure strain decreased exponentially with an increase in Ca^{++} concentration, until Ca^{++} reached the same critical level as for stresses (see Fig. 4 to 6). Above that level, the failure shear strain became independent of ion concentration. Failure shear strains also increased linearly with increased polymer concentration below the critical ion levels. Above that level, the strains became independent of gellan concentrations.

The nonlinear regression procedure in SAS (SAS Institute, Inc., 1985) was used to fit the failure shear strain data at ion concentrations below the critical levels. The failure shear strain relationships expressed in Eq. (21) had coefficients of variation of 2.5% for compression tests and 3.4% for torsion tests:

$$\gamma_{max} = \gamma^*_{max} + 1.24\log\left(\frac{x_{cr}}{x_c}\right) \qquad (x_c < x_{cr}) \qquad (21)$$

where, γ^*_{max} is the failure shear strain above the critical calcium level χ_{cr}, which has a value of 0.43 in compression and torsion

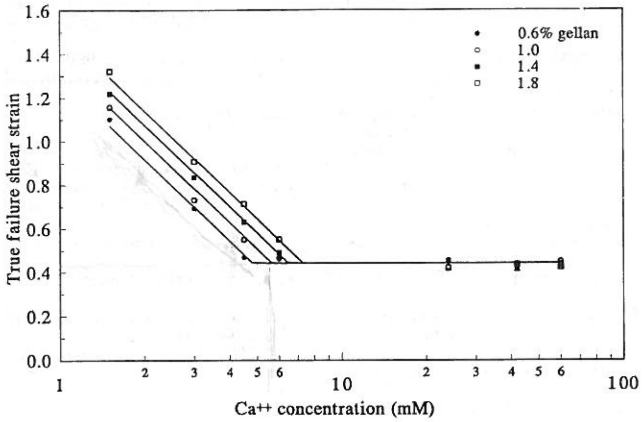


Fig. 4—True failure shear strains related to calcium ion concentration in compression tests.

tests. Note that the critical level of calcium ion varied with gellan polymer concentration according to:

$$x_{cr} = 3.5 + 2.1x_g \text{ for } 0.6 \le x_g \le 1.8\% \text{ (w/v)} \qquad (22)$$

A model for the failure shear strain in tensile testing could also be obtained by multiplying the right hand side of Eq. (21) by a factor of 0.51. This equation fits the data with a C.V. value of 4.4%.

Interpretation of the critical calcium level

The value of the critical Ca^{++} level, as indicated by the inflection in the curve for failure shear strain (Fig. 4), increased from 4.6 to 7.1 mM, when the gellan concentration increased from 0.6 to 1.8% (w/v). These values correspond to 0.40 to 0.72 calcium ions per repeat tetrasaccharide unit of gellan gum polymer. Each repeat unit has a carboxylate group and provides an anionic site for 0.5 divalent calcium cations (Sanderson, 1990). Therefore the critical ion level may correspond to a state in which the numbers of calcium ions were barely adequate to link the anionic sites in the junction zones of the polymer network. Below the critical ion level, added ions help to form junction zones and thus increase the strength of the gel. Above that level, additional ions may occupy the anionic sites, prevent linkages forming between adjacent polymer chains and introduce repulsive forces in the junction zone. As a result, the gel structure may be weakened as shown by our mechanical testing experiments.

CONCLUSIONS

HIGHER FAILURE STRESSES were found in gellan gels at higher polymer concentrations. At a given level of polymer and ion concentration, no difference was observed in failure shear stress from torsional, compressive and tensile tests. The corresponding failure strain was also not different in torsional and compressive modes. Failure strain in tensile testing was about half that of the other two modes. The effect of Ca^{++} concentration on failure properties was characterized by a critical Ca^{++} level at each polymer concentration, with distinctive mechanical behavior below and above that level. The critical Ca^{++} level may correspond to the state when maximum linkages were made at junction zones of the gel network. These results provide a general guideline for formulating gellan gels with a broad range of textural properties. Brittle gels of various strengths could be obtained with different polymer concentrations at calcium ion concentrations above the critical ion level. Extensible gels of a desired strength could be achieved at a given polymer concentration at relatively low calcium ion concentrations.

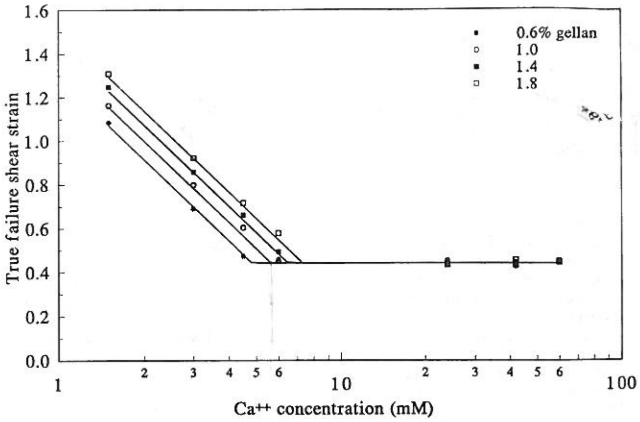


Fig. 5—True failure shear strains related to calcium ion concentration in torsion tests.

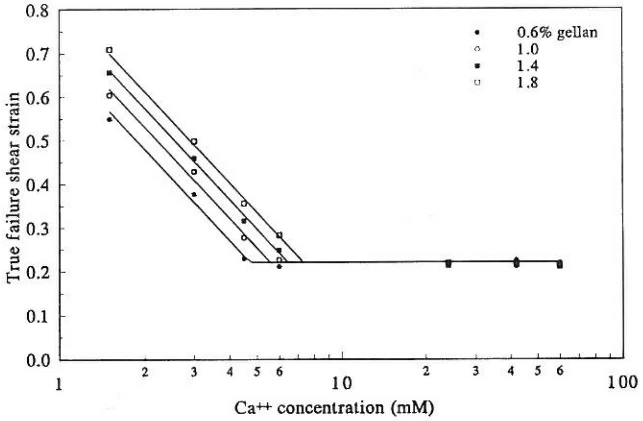


Fig. 6—True failure shear strains related to calcium ion concentration in tension tests.

NOMENCLATURE

F	Force (kN)
G	Shear modulus (kPa)
K	Specimen shape factor
K′	Correction factor for the end pieces of torsion specimens
L	Initial specimen length (m)
ΔL	Deformation (m)
M	Twisting moment (kNm)
Q	Specimen shape factor (m^{-3})
r_{min}	Torsion specimen minimum radius (m)
R, r	Specimen radius (m)
γ	Shear strain
ϵ	Normal strain
ν	Poisson's ratio
τ	Shear stress (kPa)
σ	Normal stress (kPa)
ϕ	Angular deformation (rad)
x_c	Calcium ion concentration (mM)
x_{cr}	Critical calcium ion concentration (mM)
x_g	Gellan gum concentration (%, w/v)
Subscript	
end	Specimen end pieces
max	Engineering failure stress or strain
s	Curved sector of a specimen
t	Total
true max	True or Hencky's failure stress or strain during the test

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