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WORK HARDENING EFFECTS IN GELLAN GUM GELS¹

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ABSTRACT

Gellan gum is a bacterial polysaccharide that is marketed as a broad spectrum gelling agent. The shear and Young's moduli, and the fracture strength of gellan gels increase with increasing ionic strength, pass through maxima and then decrease to zero at higher ionic strength. The position of the maxima depend on the valency of added counterions and are virtually independent of polymer concentration. At low ionic strength the measured rheological parameters show small variability but these values become increasingly variable with increasing ionic strength. Stress relaxation experiments were carried out in order to examine the mechanical behaviour of gellan gels and to explain these effects. At low ionic strength the gels approximate to elastic solids whereas at high ionic strength the increased stress relaxation is colloid-like in behaviour. However, unlike colloidal dispersions, the magnitude of the stress relaxation decreases on successive applications of stress and the relaxation modulus increases. The gels work harden. Such behaviour is attributed to a heterogeneous structure within the gel.

INTRODUCTION

Gellan gum is the trivial name for the extracellular bacterial polysaccharide secreted by *Pseudomonas elodea*.² The polysaccharide is produced commercially by Kelco-AIL and marketed as a broad spectrum gelling agent. Structurally gellan is a linear anionic heteropolysaccharide based on a tetrasaccharide^{3,4} repeating unit: $\{ \rightarrow 3\text{-}\beta\text{-D-Glcp}\text{-}(1 \rightarrow 4)\text{-}\beta\text{-D-GlcpA}\text{-}(1 \rightarrow 4)\text{-}\beta\text{-D-Glcp}\text{-}(1 \rightarrow 4)\text{-}\alpha\text{-L-Rhap}\text{-}(1 \rightarrow)$. The native polysaccharide is partially esterified:⁵ the $(1 \rightarrow 3)$ linked D-Glc unit being partially substituted at C-2 with L-glycerate and at C-6 with O-acetate.⁵ A deesterified product can be produced by alkaline treatment of the broth followed by alcohol precipitation. Clarified products, freed

from bacterial cell debris, can be prepared by filtration of the hot fermentation liquor. The clarified, deesterified product is sold commercially under the tradename Gelrite.

Extensive X-ray diffraction studies of oriented fibres prepared from gellan gum gels suggest that gellan forms a 3-fold helical structure.⁶⁻¹⁴ Recent molecular modelling studies¹⁰⁻¹² show that gellan forms a left-handed 3-fold double helix. Deesterified regions of these double helices can crystallise into a trigonal unit cell and such crystallites are considered as models for the junction zones in gellan gum gels.¹⁵⁻¹⁷

Common monovalent and divalent salt forms of gellan gum will gel at sufficiently high polysaccharide concentrations. Gelation depends on the degree of esterification of the polysaccharide and the type and concentration of cations.¹⁸ The effects of common monovalent and divalent cations on the mechanical properties of gellan gels has been investigated.¹⁸⁻²¹ A systematic study²² suggests that the gelation may be sensitive to cation type as well as cation valency. A general feature is that as the ionic strength is increased then both the modulus and the fracture stress rise, pass through a maximum and then decrease to zero at higher ionic strength.¹⁹⁻²² The ionic strength at which such maxima occur is characteristic of the cation valency but independent of polymer concentration. The origins of such effects are obscure and form the basis for the present studies. In these studies effort has been concentrated upon studies of the effects of KCl on the mechanical properties of gellan gels.

RESULTS AND DISCUSSION

Measurements of fracture load versus KCl concentration are shown in Fig. 1. The fracture load increases with increasing polysaccharide concentration at a given ionic strength. For a given polymer concentration the fracture load initially increases with increasing ionic strength, reaches a maximum value at ~0.1—0.15M KCl (independent of polymer concentration) and then decreases to zero with further increase in ionic strength. Representative values of Young's modulus values were calculated from the same force—deformation curve. The modulus was determined by estimating the force required to cause a deformation of 0.1. The dependence of the Young's modulus upon polymer concentration is shown in Fig. 2. The modulus increases with increasing polysaccharide concentration at a given ionic strength. At a fixed polymer concentration the modulus shows a maximum value at KCl concentration of ~0.1—0.15M KCl, independent of gum concentration.

For the studies reported the cylindrical gels were removed from their moulds and cut into five test samples. The data shown in Figs. 1 and 2 are the mean of such

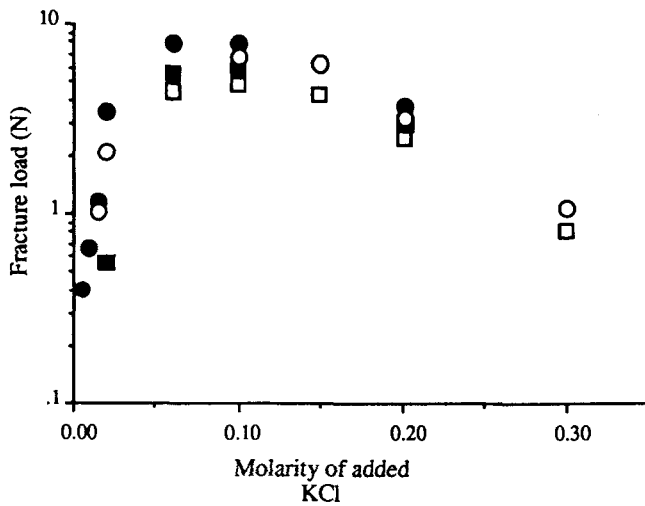


Figure 1. The effect of added KCl on the fracture stress of gellan gum gels. □-0.6%, ■-0.7%, ○-0.8% and ●-0.9% gellan.

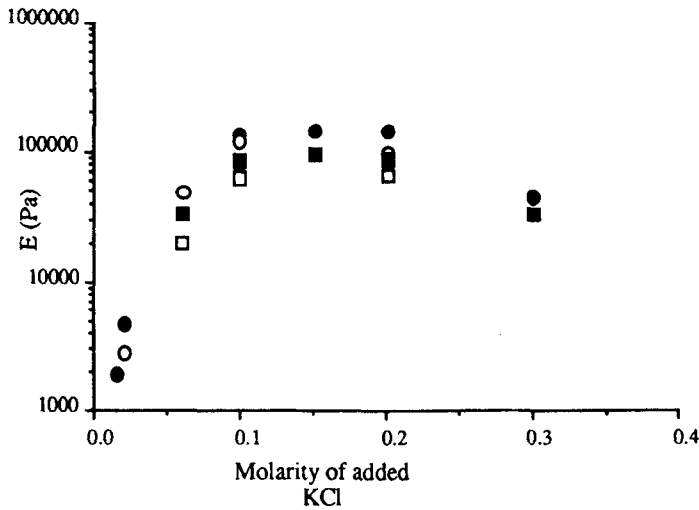


Figure 2. The effect of added KCl on the measured Young's modulus for gellan gum gels. □-0.6%, ■-0.7%, ○-0.8% and ●-0.9% gellan.

measurements. It was noticed that the variability between data on individual samples, and the reproducibility of data obtained on separately prepared gels, became worse with increasing salt content within the gels. The strain at fracture was seen to steadily decrease from its initial value of 0.5 for aqueous gellan gels to a value of 0.2 for 0.3M KCl gellan gels.

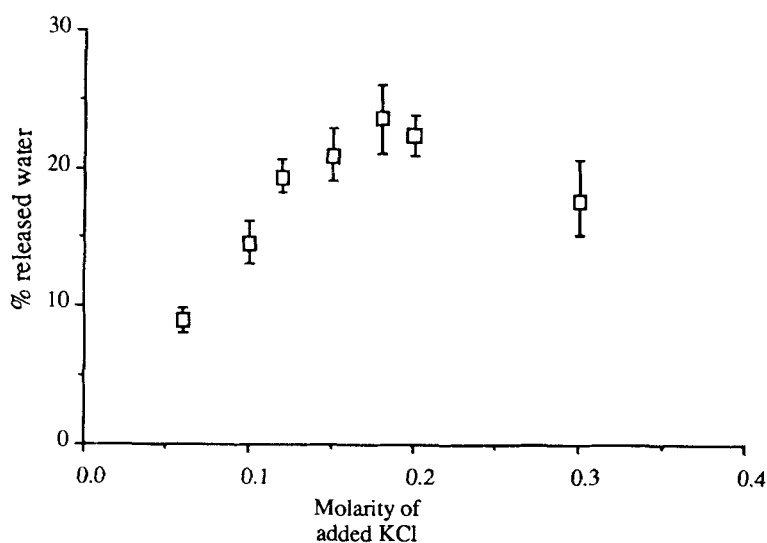


Figure 3. Percentage water loss from a 0.8% gellan gum gel under compression (0.09 strain) as a function of added KCl concentration.

The water loss from the gels after compression (Figure 3) was irreversible and peaked at an ionic strength corresponding to $\sim 0.15\text{M}$ KCl. The water holding capacity of the gels does depend markedly on the concentration of KCl and it is true that at higher salt levels syneresis is noticeable.

Normalised stress relaxation data is shown in Fig. 4. The data was obtained on 0.8% gellan gum gels containing different levels of added KCl (0.01—0.08M). At low added salt concentration the gels show only a small level of stress relaxation. Essentially the gels approximate to elastic networks showing little energy dissipation on compression. The level of stress relaxation increases with increasing ionic strength until at the highest levels of added salt the stress relaxation is almost complete. In this instance the gels are behaving more like colloidal dispersions than elastic solids. The gels remain free standing. The relaxation results from a small but irreversible shrinkage of the gel from the upper platen accompanied by expulsion of fluid from the gel.

In order to study the effect of increasing normal force, or successive applications of the same normal force, on the structure of the gels the effects of such mechanical treatments on the shear modulus were monitored using a mechanical spectrometer. The data obtained on a 0.8% gellan gum gel containing 0.06M KCl is recorded in Table 1.

Both the applied and relaxed normal forces were monitored as a guide to the level of stress relaxation. It can be seen that as the applied normal force is increased the level of

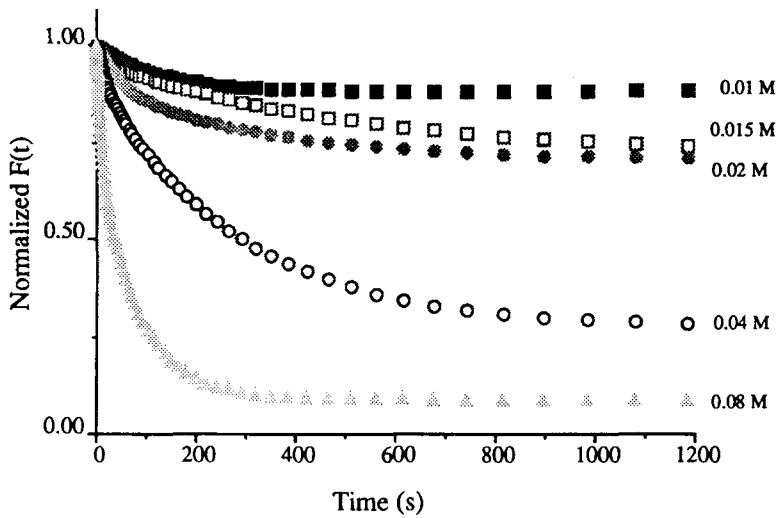


Figure 4. Normalised stress relaxation data for 0.8% gellan gum gels containing different levels of added KCl.

Table 1. Effect of successively applied normal force to gellan gum gels.

Applied Normal Force (N)	Relaxed Normal Force (N)	Shear Modulus G' (kPa)
0.04	nm ^a	2.3
0.2	0.08	2.6
1.0	0.2	2.9
1.0	0.4	3.3
1.0	0.6	3.8
1.0	0.6	4.1
1.0	0.8	5.1
1.0	0.8	5.5

a. nm not measured

stress relaxation decreases and the shear modulus of the gels increases. Similarly successive applications of the same applied normal force also lead to a decrease in the degree of stress relaxation and an increase in the shear modulus. In all these studies the time between reapplication of applied force was sufficiently large to allow the gels to relax completely. Thus these studies reveal that the gels work harden upon compression.

It is possible to draw a few general conclusions from the experimental data presented in this article. At low added salt concentrations it is reasonable to assume that

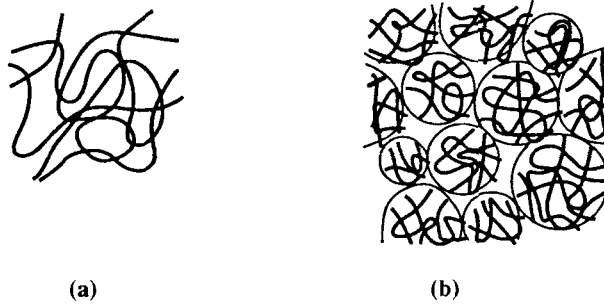


Figure 5. Schematic diagrams of the structure of gellan gum gels (a) Elastic network at low salt content. (b) Heterogeneous network at high salt content.

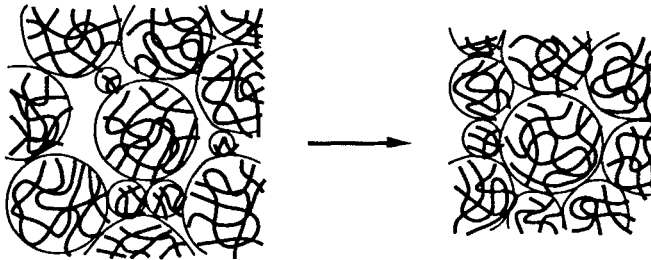


Figure 6. Schematic diagram illustrating irreversible shrinkage of gels upon compression. Repacking of 'microgels' during compression is suggested as a mechanism for work hardening.

increased level of salt promote helix-helix association leading to an increase in shear or Young's modulus and of fracture stress.

However, the peaks in modulus and fracture stress suggest an additional effect due to added KCl which reduces the modulus and introduces weaknesses into the gel which facilitate fracture. It is suggested that these effects arise due to the appearance of an increasingly heterogeneous structure with increasing level of added salt. At low salt concentrations it is envisaged that the junction zones arise upon cooling due to spontaneous nucleation. However, with increasing salt content the polysaccharide becomes progressively insoluble and the aqueous samples, even at high temperatures, become increasingly dispersions of incompletely dissolved aggregates. These aggregates will act as heterogeneous nuclei leading to the growth of microgels which interconnect to form a weakened network structure.

Extreme schematic pictures of the suggested gel structure at low and high added salt are shown in Fig. 5. At low salt levels the enhancing effect of added KCl on helix-

helix association predominates and both modulus and fracture stress increase. At high added salt the weakening effects of increased microgel-microgel contacts predominates and both mechanical parameters decrease. The maximum in mechanical properties arises because of the competition between these two effects. The effect of large inhomogeneities is much stronger on fracture force than on the Youngs' modulus, and this may explain the difference in their dependence on KCl concentration.

The work hardening effects and stress relaxation can be explained by such a model. If the inter microgel-microgel contacts are weaker than the polymer-polymer linkages within the elastic network, then applied stress will be concentrated at these microgel-microgel contact points. Breakage of such interactions would allow better packing of microgels, irreversible shrinkage and water loss, leading to increased modulus. This effect is illustrated schematically in Fig. 6. Further, such effects should be enhanced at higher added salt levels as the polysaccharide becomes progressively insoluble.

A feature of food products prepared from gellan gum is the unusual flavour release properties of the gels. Such an heterogeneous model could account for this behaviour. Biting would concentrate stress at the weaker linkage points leading to fracture and the release of microgels with a high surface area for flavour release.

CONCLUSIONS

Detailed rheological studies on gellan gum gels containing various levels of added KCl have identified unusual work hardening behaviour in such gels. Such effects have been attributed to the presence of an heterogeneous gel structure. Such a model can account for the observed maximum in fracture stress and moduli upon increasing the level of added salt, the stress relaxation behaviour and work hardening of the gels, and the loss of water from the gel structure upon compression.

EXPERIMENTAL

A commercial sample of Gelrite (Kelco-AIL) was used without further purification. The commercial preparation procedure results in a product predominantly in the potassium salt form.

Gellan gum gels were prepared by the following procedure. Gellan gum was dispersed in water contained in sealed glass tubes and the dispersions heated in a water

bath at 100 °C for about 30 min. Agitation was used to aid the initial dispersion and wetting of the powdered sample. KCl solutions of appropriate concentration were prepared and heated to 90 °C in sealed tubes. Gellan samples and KCl solutions, of appropriate amounts, were mixed at 90 °C and kept at this temperature in sealed glass containers for 30 min. These samples were then poured into appropriate moulds, covered with 'Parafilm' to inhibit water loss by evaporation, allowed to cool to room temperature and left standing for 24 h before testing.

Compression studies were carried out at room temperature using cylindrical test samples of diameter 13 mm and typical length 15 mm. The compressive forces were applied along the symmetry axis of the sample. Force—deformation curves were obtained using an Instron 1122 Universal Testing Machine and parallel plate geometry (diameter 17 mm). A crosshead speed of 10 mm min⁻¹ was employed and the force—time response curve recorded graphically. Stress relaxation studies were carried out using the same apparatus and samples. A low standard force of 0.2 N was used, applied at a crosshead speed of 1 mm min⁻¹. Typically, the induced compressive strain was 0.004.

Small deformation oscillatory studies were made using an Instron 3250 Mechanical Spectrometer and parallel plate geometry (diameter 40 mm). The gel moulds were plastic petri dishes (gel diameter 52 mm and approximate height 1.5 mm). The gels were retained within the plastic mould which was fixed to the bottom platen of the spectrometer. Mechanical tests were carried out at a fixed frequency (2 Hz) and using a low strain sweep (0.001 — 0.01), the limits of linearity for viscoelastic behaviour. Experiments were conducted to assess the effect of increasing the applied normal force and successive applications of the same normal force, upon the measured shear modulus.

During excessive compression it was noticed that water was released from the gels. The water loss was monitored for 0.8% gellan gels containing different levels of KCl (0.06—0.3M KCl). The gels were studied at constant strain (0.09). Filter paper was used to collect the released water and weighed before and after compression of the gels. The weight of released water was used, together with the weight of gel sample prior to compression, to calculate the percentage loss of water. Mean values of five experiments were recorded.

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