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Texture properties of high and low acyl mixed gellan gels

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Abstract

The strength, deformability, and firmness of high acyl (H) and low acyl (L) mixed gellan gels were studied by compression tests. The gels were prepared with total polymer concentrations of 0.5, 1.0, and 1.5% at H/L weight ratios of 25/75, 50/50, 75/25, and calcium concentrations 2–80 mM. The mixed gels were much more deformable, with failure normal strains ranging from 0.6 to 1.5, but had similar strength compared to low acyl gellan gels. Both H/L ratio and total polymer concentration affected the textural properties, but H/L ratio was a more important factor. Maximum synergistic interaction was observed at H/L = 50/50. The mixed gels exhibited excellent texture properties compared to other common food gels. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Mixed gel; Gellan; High acyl; Low acyl; Stress; Strain; Modulus

1. Introduction

Gellan gum is a gel-forming polysaccharide produced by the microbe *Sphingomonas elodea* (formerly *Pseudomonas elodea*) (Kang, Veeder, Mirrasoul, Kaneko & Cottrell, 1982) and approved for food use by the FDA in 1992 (Pszczola, 1993). Gellan polymer consists of monosaccharides β-D-glucose, β-D-glucuronic acid and α-L-rhamnose in molar ratios of 2:1:1 (Sanderson, 1990) linked together to form a linear primary structure (Fig. 1). The native polymer is high acyl gellan (H) containing O-5-acetyl and O-2-glyceryl groups on the (1 → 3)-linked glucose residue (Fig. 1(a)). When exposed to alkali at high temperatures, both acyl groups are hydrolyzed and the deacylated form of low acyl gellan (L) is obtained (Fig. 1(b)). Low acyl gellan dissolves in water at temperatures above 90°C. The solutions form gels in the presence of cations when cooled to gelling temperatures (Tang, Tung & Zeng, 1997a). High acyl gellan solutions gel at much higher temperatures than low acyl gellan solutions. High acyl gellan gels are very weak because of the bulky acetyl and glyceryl groups that prevent close association between gellan polymer chains in double-helix formation and hinder compact packing of the cross-linked double helix. Their mechanical properties cannot be readily measured in compression tests. Only a few publications report on high acyl gellan gels (Baird, Talashek & Chang, 1992; Chandrasekaran & Thailambal, 1990; Chandrasekaran, Radha & Thialambal, 1992; Chandrasekaran, Radha & Giacometti, 1995; Morris, Gothard, Hember, Manning & Robinson, 1996; Sanderson, Bell, Clark & Ortega, 1988). Sanderson et al. (1988) reported that high acyl gellan gels are non-brittle and elastic, with a texture similar to the mixed gels of xanthan gum and locust bean gum. Baird et al. (1992) and Morris et al. (1996) reported that when acyl groups were progressively removed from the high acyl gellan chain, the gelling and mechanical properties of high acyl gellan gels approached that of low acyl gellan gels. Sanderson et al. (1988) reported intermediate textural properties between that of high and low acyl gellan gels when combining low acyl gellan with high acyl gellan to form mixed gels. A systematic study on the properties of mixed gels prepared from low and high acyl gellan is desirable to explore the full potential of gellan. Our objective was to study the effect of total polymer concentration, cation concentration, and the ratio of high to low acyl gellan on the mechanical properties of mixed gellan gels.

2. Materials and methods

2.1. Preparation of mixed gellan gels

High acyl gellan (H) Kelcogel LT100 and low acyl gellan (L) Kelcogel F were provided by NutraSweet Kelco Company (San Diego, CA). Weighed gellan powders were

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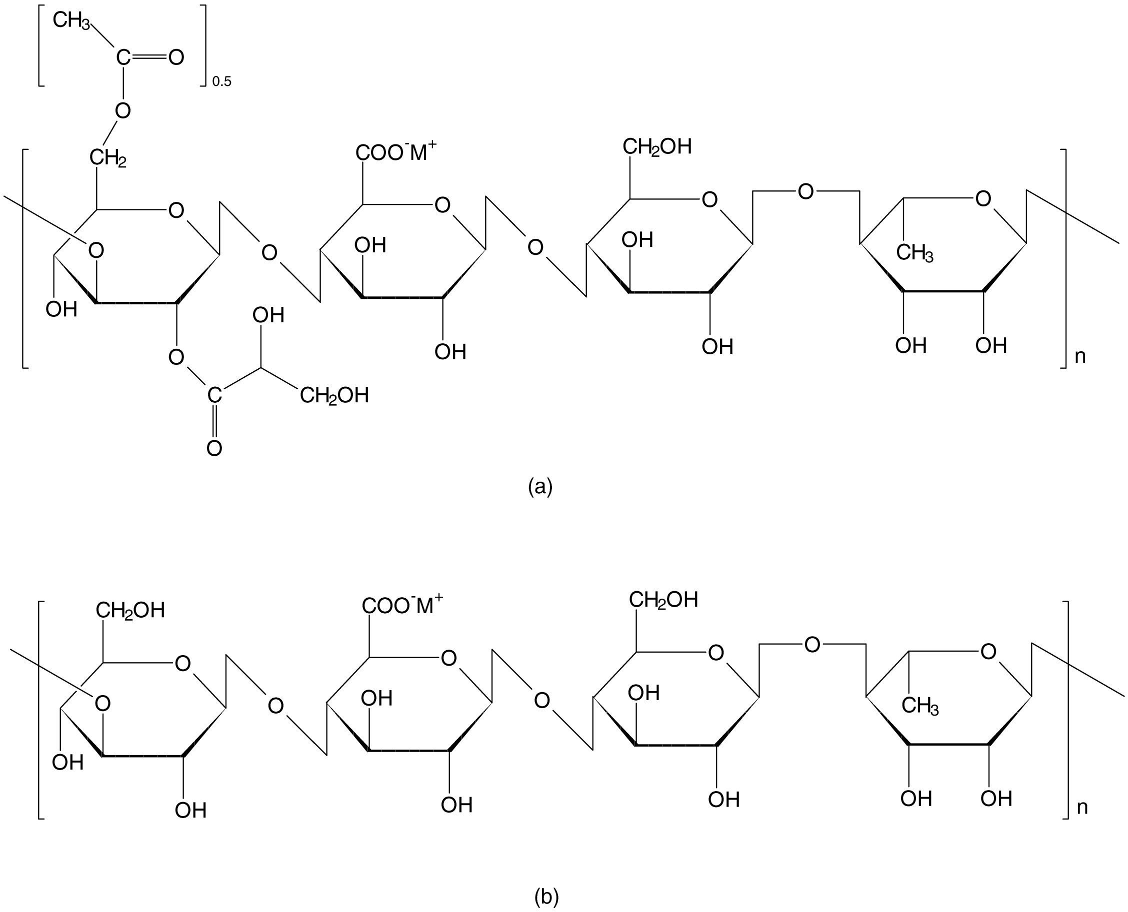

Fig. 1. The chemical structure of gellan gum: (a) native form (high acyl); (b) deacylated form (low acyl).

dispersed in deionized distilled water at 22°C. The mixtures were heated to 97–98°C and held for 1 min. Calcium chloride was added to the gellan solutions to prepare gels of 12 Ca^{++} concentrations between 2 and 80 mM. The solutions were stirred for 1 min and poured into stainless steel tubes (inner diameter 21 mm), which were preheated to 85°C to prevent partial gelling along the metal wall during pouring. The mixed gellan solutions started to form gels at temperatures between 70 and 84°C. These temperatures were much higher than gelling temperatures of low acyl gellan solutions

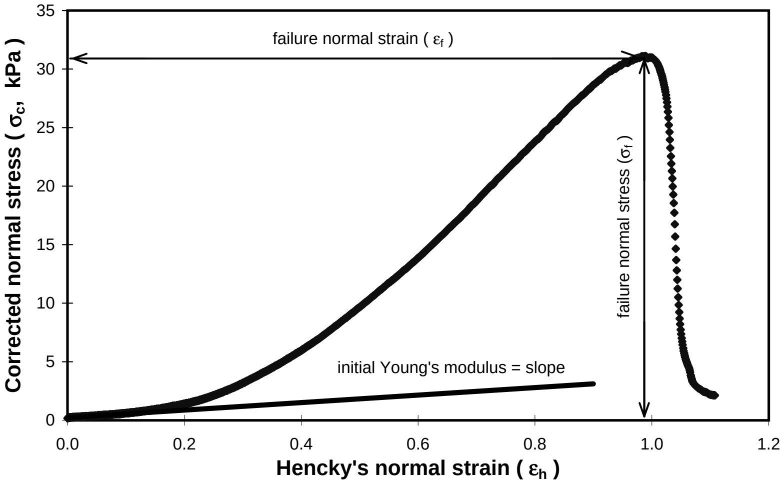

Fig. 2. Determination of initial Young’s modulus, failure stress and strain from compression tests.

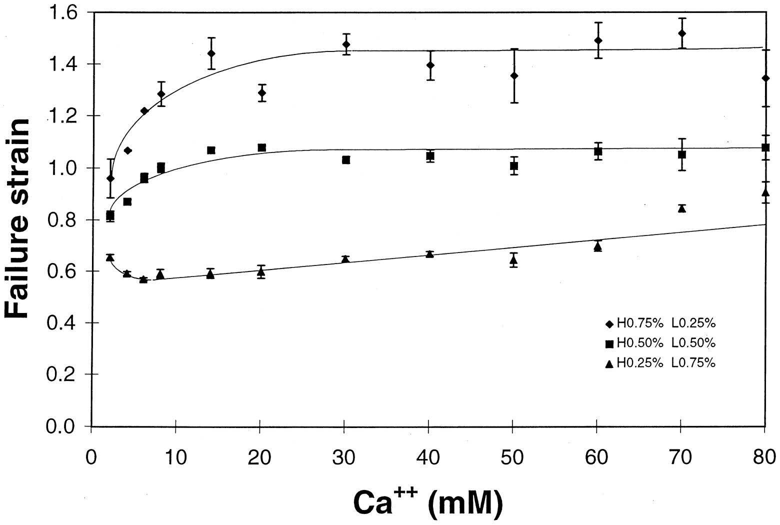

Fig. 3. The compressive deformability of mixed gellan gels with 1.0% total polymer concentration.

between 25 and 70°C (Tang et al., 1997a). The gels were set by cooling the tubes in running water at 15°C for 10 min. Gel samples were held at 22°C for 24 h before removal from the tubes, slicing, and compression testing.

2.2. Compression tests

Cylindrical gels 21 mm in diameter and 21 mm long were placed between lubricated flat metal surfaces fitted to The TA.XT2 Texture Analyzer (Texture Technologies Corp., Scarsdale, NY/Stable Micro Systems, Godalming, Surrey, UK). The gels were then compressed at a crosshead speed of 0.3 mm/s until failure. Assays were repeated six times using six different gels. The engineering stress (σ_{eng} = force/original cross-section area) and strain ($\varepsilon_{\mathrm{eng}}$ = reduction of length/original length) curves were obtained.

The cross-sectional area of the gels increased significantly under large compression before failure. Hencky's normal strain (ε_{h}) and the corrected stress (σ_{c}), which take into account the enlarged cross-sectional areas of the gels, were used to represent the true gel properties. Hencky's strain and the corrected stress were converted from engineering strain and stress by the following equations (Nussinovitch, Ak, Normand & Peleg, 1990; Tang, Tung & Zeng, 1996):

$$\varepsilon_{\mathrm{h}} = -\ln(1 - \varepsilon_{\mathrm{eng}}) \tag{1}$$

$$\sigma_{\mathrm{c}} = \sigma_{\mathrm{eng}}(1 - \varepsilon_{\mathrm{eng}}) \tag{2}$$

The failure strain (ε_{f}) and failure stress (σ_{f}) were determined from compression curves as shown in Fig. 2. A large failure strain corresponds to a very deformable gel and a large failure stress indicates a strong gel.

The gel firmness was characterized by the initial Young's

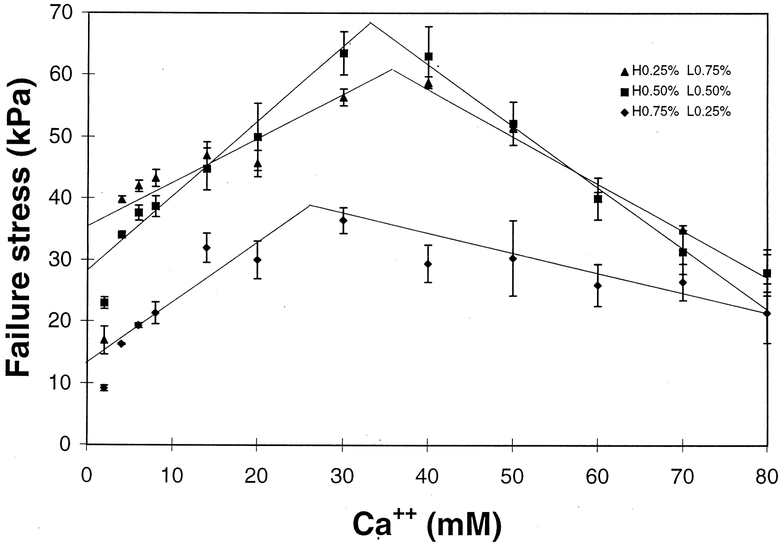

Fig. 4. The compressive strength of mixed gellan gels with 1.0% total polymer concentration.

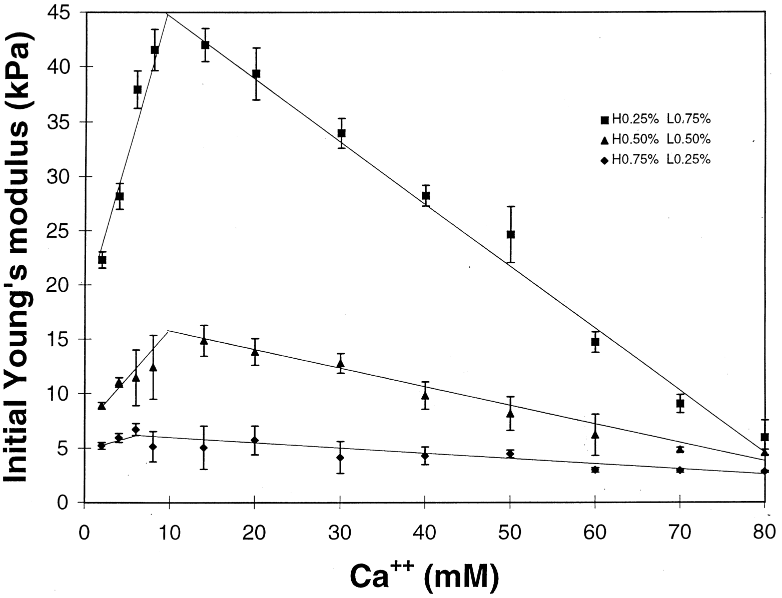

Fig. 5. The firmness of mixed gellan gels with 1.0% total polymer concentration.

modulus derived from the slope of the regression line of the corrected stress vs. Hencky's normal strain for strain not exceeding 6% (Fig. 2). A large value for Young's modulus indicates a firm gel.

3. Results and discussion

3.1. Influence of weight ratio of high and low acyl gellan

Fig. 3 shows the dependence of the failure strain of 1% mixed gels on calcium concentration at three high acyl (H) to low acyl (L) gellan ratios. In general, the failure strain increased with increasing H/L ratio. For the 1% gels with H/L = 50/50 and 75/25, the failure strain increased from 0.8 and 1.0 to reach a constant value of 1.0 and 1.5, respectively, as calcium concentration increased from 2 to 30 mM. The trend that failure strain increased with increasing calcium concentration was different from that observed with 1% low acyl gellan gels. Tang et al. (Tang, Lelievre, Tung & Zeng, 1994; Tang, Tung & Zeng, 1995; Tang et al., 1996) reported that the failure shear strains of 1% low acyl gellan gels decreased from 1.2 to reach a constant value of 0.4, which corresponded to failure normal strain from 0.8 to 0.3, when calcium concentration was increased from 2 mM to approximately 10 mM. For the gels with H/L of 25/75, the failure strain decreased slightly with increasing calcium concentration from 2 to 6 mM. With larger concentrations of calcium, the failure strain of mixed gels increased steadily. At an H/L ratio of 25/75, the behavior of the mixed gels is attributed to the large amount of low acyl gellan that dominated the gel properties.

Fig. 4 shows the failure stress of 1% mixed gels at three H/L weight ratios. The failure stress reached a peak at approximately 30 mM. This optimum calcium concentration was much higher than the 5 mM calcium concentration observed at the peak strength for 1% low acyl gellan gels (Tang et al., 1994, 1995, 1996).

Because low acyl gellan generally forms stronger gels than high acyl gellan, it is expected that mixed gels are stronger at low H/L ratios. This is generally true with a few exceptions as shown in Fig. 4. For example, the peak failure stress for the gels with H/L = 50/50 was larger than the peak failure stress for the gels with H/L = 25/75 (Fig. 4). A strong synergistic interaction may exist between low and high acyl gellan at the H/L ratio of 50/50. A DSC study of mixtures of high acyl and low acyl gellans showed two separate conformational transitions at temperatures that are characteristic of individual components (Morris et al., 1996). Hence Morris et al. (1996) suggested that the formation of double helices did not involve strands of both types. In other words, high acyl and low acyl gellans may form separate and interpenetrating polymer networks (IPN). The IPN structure can be full-IPN, i.e. both polymers are crosslinked; or semi-IPN, when only one type of polymer chains are crosslinked while the other type of chains are linear (Manson & Sperling, 1976). Full-IPNs are generally stronger and more deformable than semi-IPNs (Manson & Sperling, 1976). It is very likely that at the H/L ratio of 25/75 low acyl gellan polymers form a continuous matrix in the gel network, while a small amount of the high acyl gellan polymers are dispersed in the gel matrix. At the H/L weight ratio of 75/25, the discrete low acyl gellan polymers are dispersed in continuous high acyl gellan matrix. Both gels may have semi-IPN structures. At the H/L ratio of 50/50, however, high and low acyl gellan polymers may form continuous networks separately, resulting in full-IPN structures.

Gellan gels exhibited viscoelasticity (Nussinovitch et al.,

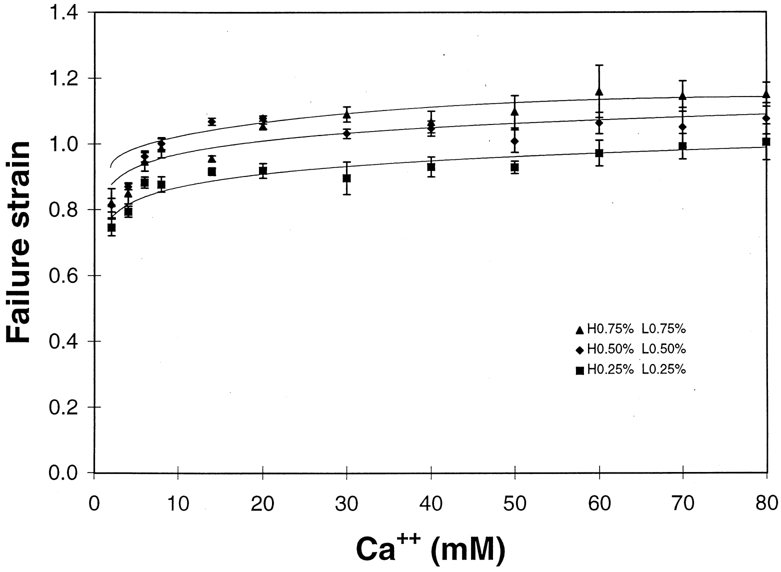

Fig. 6. The compressive deformability of mixed gels with equal weight of high and low acyl gellan.

1990). Tang, Tung, Lelievre and Zeng (1997b) observed that gellan gels followed linear stress–strain relationships in small strains (<0.04). They also studied the suitability of the Mooney–Rivlin constitutive equation, from the rubber theory (Treloar, 1975), and its various modifications, in modeling the stress–strain curves of gellan gels in tension, compression and torsion at large strains. None of those equations was found satisfactory. Therefore, only the linear portions of the small strains in the stress–strain relationships, e.g. in Fig. 2, were used to derive the initial Young's moduli for further analyses.

Young's modulus of mixed gels at 1% polymer concentration initially increased with increasing calcium concentration up to a maximum value and then decreased with further increase in calcium concentration (Fig. 5). The optimum calcium concentration corresponding to the maximum modulus for each H/L weight ratio was about 10 mM, much smaller than the optimum calcium concentration (around 30 mM) for failure stress (Fig. 4).

At a given calcium concentration, the initial Young's modulus of mixed gellan gels increased with decreasing H/L ratio (Fig. 5). It is clear from Figs. 4 and 5 that the initial Young's modulus of mixed gels followed a different trend from that of failure stress with respect to H/L ratio. For example, the failure stresses of gels with H/L = 50/50 at 30 mM Ca^{++} were greater than that at H/L = 25/75, while the initial Young's moduli for gels with H/L = 25/75 were much higher than with H/L = 50/50. Therefore, gels with similar failure strength may exhibit very different firmness.

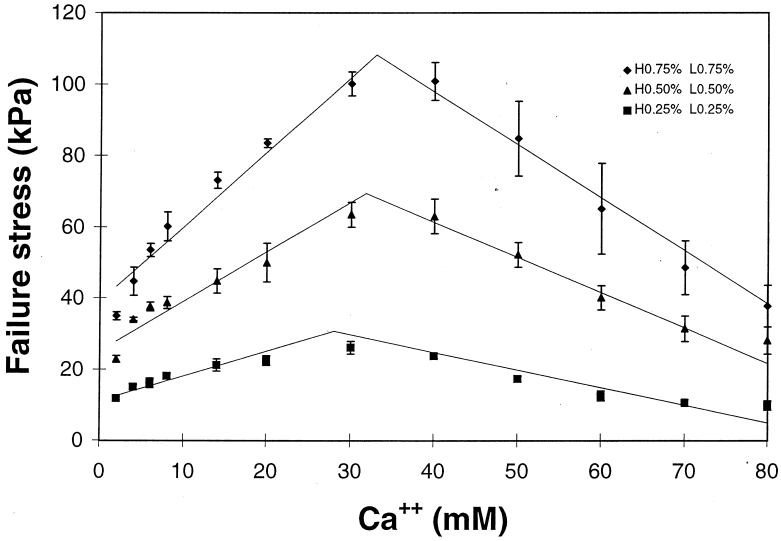

Fig. 7. The strength of mixed gels with equal weight of high and low acyl gellan.

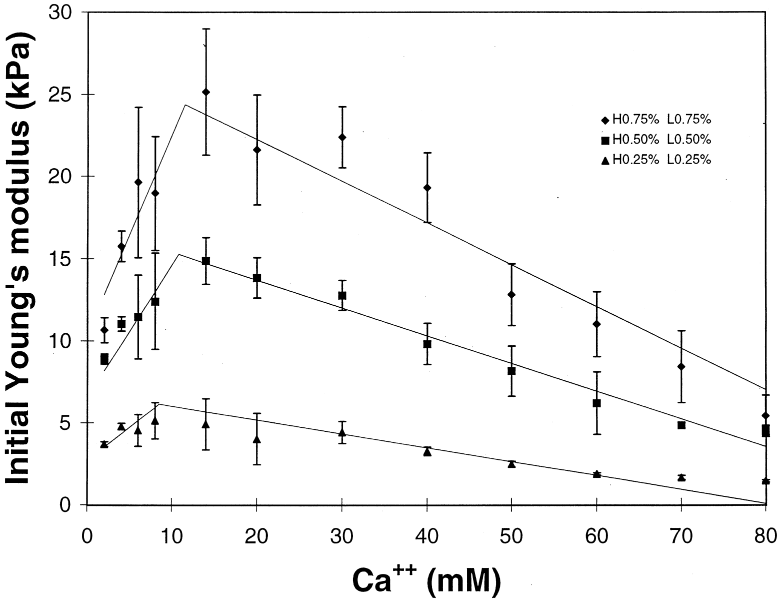

Fig. 8. The firmness of mixed gels with equal weight of high and low acyl gellan.

3.2. Influence of total polymer concentration

At H/L = 50/50, failure strains of the mixed gels increased from 0.7 to 0.9 at low calcium levels and from 1.0 to 1.2 at high calcium levels as total polymer concentrations increased from 0.5 to 1.5% (Fig. 6). Thus failure strains increased slightly with total polymer concentrations, similar to low acyl gellan gels at low calcium concentrations (Tang et al., 1994, 1995). At each total polymer concentration, the failure strain, however, increased with calcium concentration, which was the opposite of the reported observations with low acyl gellan gels (Tang et al., 1994, 1995).

Although increasing the polymer concentration will normally increase the deformability (strain) of low acyl gellan gels at low calcium concentrations (Tang et al., 1994, 1995), increasing the absolute amount of low acyl gellan in the mixed gels may decrease the deformability. For example, the failure strains of gels at every tested calcium concentration were reduced when the high acyl gellan concentration was fixed at 0.75% and the low acyl gellan was increased from 0.25% (top curve of Fig. 3) to 0.75% (top curve of Fig. 6). For the deformability of the mixed gellan gels, therefore, the H/L ratio is a more important factor than the total polymer concentration.

The effects of calcium and total polymer concentrations on the failure stress and initial Young's modulus of mixed gels with equal amounts of high and low acyl gellan are presented in Figs. 7 and 8, respectively. Similar to the low acyl gellan gels (Tang et al., 1994, 1995), the failure stress of mixed gels increased linearly with added Ca^{++} up to an optimum calcium concentration, then decreased linearly with further added Ca^{++}. At all studied calcium concentrations, the failure stress of mixed gels increased with increasing total polymer concentration.

The optimum calcium concentration (X_σ) and the corresponding peak failure stress (σ_p) for each total polymer concentration (X_g) were estimated from Fig. 7 and presented in Table 1. The peak failure stresses of the mixed gels are comparable to the peak stresses of low acyl gellan gels (Tang et al., 1994, 1995). The optimum calcium concentrations of the mixed gels (around 30 mM) are, however, much higher than the optimum calcium concentrations (around 5 mM) at similar polymer concentrations when only low acyl gellan was used (Tang et al., 1994, 1995).

The firmness of the mixed gel initially increased linearly with calcium concentration, then decreased linearly with further added calcium (Fig. 8). This trend was similar to the trend for the failure stresses as shown in Fig. 7. The optimum calcium concentrations (X_E) corresponding to the peak Young's modulus (E_p) were estimated from Fig. 8 and also listed in Table 1. X_E is only about one third of X_σ for each polymer concentration.

Although increasing polymer concentration normally increases gel firmness (Fig. 8), increasing the absolute amount of high acyl gellan in the mixed gels may sometimes reduce gel firmness. For example, when low acyl gellan

Table 1
The optimum calcium concentrations for failure stress (X_σ), for initial Young's modulus (X_E), and the corresponding peak failure stress (σ_p), peak initial Young's modulus (E_p) of the mixed gels with equal amount of high acyl and low acyl gellan

	Failure stress		Initial Young's modulus	
X_g(%)	X_σ (mM)	σ_p (kPa)	X_E (mM)	E_p (kPa)
0.5	28	31	9	6
1.0	32	69	11	15
1.5	33	108	12	24

Table 2
Failure properties of mixed high and low acyl gellan gels and of selected food gels

Gel type	Failure stress (kPa)	Failure strain	Ref.
Mixed gellan gel, 1% total polymer			This work
H/L = 25/75, 8 mM Ca^{++}	43.3 ± 1.4	0.59 ± 0.02	
30 mM[a]	56.4 ± 1.3	0.65 ± 0.01	
60 mM	40.4 ± 0.8	0.70 ± 0.02	
H/L = 50/50, 8 mM Ca^{++}	38.7 ± 1.7	1.00 ± 0.02	
30 mM[a]	63.5 ± 3.5	1.03 ± 0.01	
60 mM	40.1 ± 3.4	1.06 ± 0.03	
Low acyl gellan, 1% polymer[b]			Tang et al., 1995
3 mM Ca^{++}	46.0	0.55	
5 mM[a]	61.0	0.38	
20 mM	54.0	0.28	
Egg white gel[b]	27.8 ± 5.7	0.77 ± 0.09	Hamann, 1983
Fish gel[b]	40.0 ± 4.8	0.68 ± 0.06	Hamann, 1983
Gelatin gel, 7% polymer[c]	29.2	1.11	Takahashi and Nakazawa, 1992
Agar gel, 1.2% polymer[c]	32.8	0.46	Takahashi and Nakazawa, 1992
Mixed gellan gel, 1.5% total polymer, H/L = 50/50, 30 mM Ca^{++}[a]	100.2 ± 3.3	1.09 ± 0.02	This work
Carrageenan gel, 1.75% polymer[b]	40.5 ± 0.4	0.50 ± 0.01	Mirza and Lelievre, 1992
Carrageenan (CA) and locust bean gum (LBG) mixed gels, 1.75% total polymer, CA/LBG = 60/40[b]	60.3 ± 0.7	1.09 ± 0.03	Mirza and Lelievre, 1992

[a] At or near the optimum calcium concentration.
[b] Data were converted from original reported true failure shear stress and strain.
[c] Data were converted from original reported engineering stress and strain.

concentration was fixed at 0.75% and high acyl gellan concentration was increased from 0.25% (top curve of Fig. 5) to 0.75% (top curve of Fig. 8), the firmness of the mixed gellan gels was significantly reduced. This result again suggests that the weight ratio of high acyl to low acyl gellan is more important in controlling gel texture properties than the total polymer concentration.

3.3. Comparison with selected food gels

Table 2 lists the properties of several high and low acyl mixed gellan gels, together with those of selected food gels reported in the literature. When compared to low acyl gellan gels at the optimum calcium concentrations, the mixed gel with H/L = 25/75 and 1% total polymer concentration had a higher deformability (the failure strain increased from 0.38 to 0.65) but slightly reduced strength (the failure stress decreased from 61.0 to 56.4 kPa). The mixed gel with H/L = 50/50 at 1% total polymer concentration had much improved deformability without the loss of strength (the failure strain became 1.03 and stress 63.5 kPa). Table 2 also indicates that the strength and the deformability of mixed gellan gels formed at 1% total polymer concentration with H/L = 50/50 and at 30 mM Ca^{++} were better than the listed egg white gel, fish gel, gelatin gel at 7% polymer concentration, agar gel at 1.2% polymer concentration, and carrageenan (CA) gel at 1.75% polymer concentration. The only gel with comparable strength and deformability was the mixed gel of CA and locust bean gum (LBG) at 1.75% total polymer concentration with CA/LBG = 60/40. This CA/LBG gel, however, has much less strength than the mixed gellan gel at 1.5% total polymer concentration with H/L = 50/50. The excellent texture properties of the mixed high and low acyl gellan gels are evident.

4. Conclusion

The mixed gellan gels studied in this research were much more deformable and exhibited similar compressive strength, compared to low acyl gellan gels at similar polymer concentrations. Deformability of mixed gels normally increased with increasing calcium concentrations. The relationship of gel strength to polymer and calcium concentrations was similar to the gel strength of low acyl gellan gels. An optimum calcium concentration, about 30 mM for mixed gels studied, was observed that corresponded to the maximum gel strength. The maximum gel strength increased with total polymer concentration. At the optimum calcium concentration of about 30 mM, mixed gels made of an equal amount of low acyl and high acyl gellan polymers were the strongest, and the gel deformability was about four times that of low acyl gellan gels. The firmness of the mixed gellan gels increased with total polymer concentration and the proportion of low acyl gellan. The maximum firmness was observed in mixed gels with around 10 mM calcium concentration. The weight ratio of H/L played a more important role in the textural properties of mixed gels than the total polymer concentration.

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References

Baird, J. K., Talashek, T. A., & Chang, H. (1992). Gellan gum: effect of composition on gel properties. In G. O. Phillips & P. A. Williams & D. J. Wedlock (Eds.), *Gums and stabilisers for the food industry 6*, (pp. 479–487). Oxford: IRL Press.

Chandrasekaran, R., & Thailambal, V. G. (1990). The influence of calcium ions, acetate and L-glycerate groups on the gellan double-helix. *Carbohydrate Polymers*, *12*, 431–442.

Chandrasekaran, R., Radha, A., & Thailambal, V. G. (1992). Roles of potassium ions, acetyl and L-glyceryl groups in native gellan double helix: an X-ray study. *Carbohydrates Research*, *224*, 1–17.

Chandrasekaran, R., Radha, A., & Giacometti, A. (1995). Molecular modeling of substituted polysaccharides. *Carbohydrate Polymers*, *28*, 49–59.

Hamann, D. D. (1983). Structure failure in solid foods. In M. Peleg & E. B. Bagley (Eds.), *Physical properties of foods*, (pp. 351–383). Westport, CT: AVI Publishing.

Kang, K. S., Veeder, G. T., Mirrasoul, P. T., Kaneko, T., & Cottrell, I. W. (1982). Agar-like polysaccharide produced by a Pseudomonas species: production and basic properties. *Applied Environmental Microbiology*, *43*, 1086–1091.

Manson, J. A., & Sperling, L. H. (1976). *Polymer blends and composites*, New York/London: Plenum Press, chap. 8.

Mirza, I., & Lelievre, J. (1992). Effect of sample dimensions and deformation rate on the torsional failure of dumbbell shaped gels. *Journal of Texture Studies*, *23*, 57–67.

Morris, E. R., Gothard, M. G. E., Hember, M. W. N., Manning, C. E., & Robinson, G. (1996). Conformational and rheological transitions of welan, rhamsan and acylated gellan. *Carbohydrate Polymers*, *30*, 165–175.

Nussinovitch, A., Ak, M. M., Normand, M. D., & Peleg, M. (1990). Characterization of gellan gels by uniaxial compression, stress relaxation and creep. *Journal of Texture Studies*, *21*, 37–49.

Pszczola, D. E. (1993). Gellan gum wins IFT's food technology industrial achievement award. *Food Technology*, *47* (9), 94–96.

Sanderson, G. R. (1990). Gellan gum. In P. Harries (Ed.), *Food gels*, (pp. 201–232). New York: Elsevier Science.

Sanderson, G. R., Bell, V. L., Clark, R. C., & Ortega, D. (1988). The texture of gellan gum. In G. O. Phillips & P. A. Williams & D. J. Wedlock (Eds.), *Gums and stabilisers for the food industry 4*, (pp. 219–229). Oxford: IRL Press.

Takahashi, J., & Nakazawa, F. (1992). Effects of dimensions of agar and gelatin gels on palatal pressure patterns. *Journal of Texture Studies*, *23*, 139–152.

Tang, J., Lelievre, J., Tung, M. A., & Zeng, Y. (1994). Polymer and ion concentration effects on gellan gel strength and strain. *Journal of Food Science*, *59*, 216–220.

Tang, J., Tung, M. A., & Zeng, Y. (1995). Mechanical properties of gellan gels in relation to divalent cations. *Journal of Food Science*, *60*, 748–752.

Tang, J., Tung, M. A., & Zeng, Y. (1996). Compression strength and deformation of gellan gels formed with mono- and divalent cations. *Carbohydrate Polymers*, *29*, 11–16.

Tang, J., Tung, M. A., & Zeng, Y. (1997a). Gelling properties of gellan solutions containing monovalent and divalent cations. *Journal of Food Science*, *62*, 688–692, also p. 712.

Tang, J., Tung, M. A., Lelievre, J., & Zeng, Y. (1997b). Stress–strain relationships for gellan gels in tension, compression and torsion. *Journal of Food Engineering*, *31*, 511–529.

Treloar, L. R. G. (1975). *The physics of rubber elasticity*, 3rd Ed. Bristol, UK: Oxford University Press.