

Gelling temperature, gel clarity and texture of gellan gels containing fructose or sucrose

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Received 10 January 2000; revised 11 April 2000; accepted 12 April 2000

Abstract

The effects of fructose and sucrose on the gelling temperature, clarity, and texture properties of gellan gels crosslinked with calcium or sodium ions were studied by dynamic rheological, visible light absorption, and compression tests. The gelling temperatures of gellan solutions generally increased due to the addition of sucrose, except when both cation and sucrose concentrations were high. Addition of fructose up to 35%w/v had no effect on the gelling temperatures. Incorporation of fructose and sucrose resulted in a marked increase in the gel clarity. At low cation concentrations, sucrose strengthened the gels; but at high cation concentrations, sucrose weakened the gels. Gels formed by slow cooling in air were more turbid and generally stronger than the gels formed by rapid cooling in water. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Gellan gel; Fructose; Sucrose; Gelling temperature; Clarity; Stress; Strain

1. Introduction

Gellan gum is a gel-forming polysaccharide secreted by the microbe *Sphingomonas elodea* (formerly *Pseudomonas elodea*) (Kang, Veeder, Mirrasoul, Kaneko & Cottrell, 1982) and approved by the US Food and Drug Administration in 1992 for food use (Pszczola, 1993). Linear gellan polymers consist of monosaccharides β -D-glucose, β -D-glucuronic acid and α -L-rhamnose in molar ratios of 2:1:1 (Sanderson, 1990). At high temperatures, gellan polymers in water solutions are in a disordered random coil state. When cooled to gelling temperatures, the polymers form double helices which aggregate to form junction zones. The presence of cations stabilizes the double helices and junction zones to form a three-dimensional gel network (Chandrasekaran, Puigjaner, Joyce & Arnott, 1988; Upstill, Atkins & Attwool, 1986).

Sugars are commonly used in food gels to provide desired functional properties. For example, high concentration of sugars were used to form high methoxyl pectin gels (Lopes da Silva & Goncalves, 1994; Ptitchkina, Danilova, Doxastakis, Kasapis & Morris, 1994; Rao & Cooley, 1993; Rao, Van Buren & Cooley, 1993). Addition of sugars

increased the dynamic Young's modulus and the melting point of κ -carrageenan gels (Nishinari, Watase, Williams & Phillips, 1990). Sucrose reduced the strength of κ -carrageenan/locust bean gum mixed gels, but increased the strength of alginate gels (Fizman & Duran, 1992). Sucrose increased the water holding capacity but reduced the strength of whey protein gels (Boye, Alli, Ramaswamy & Raghavan, 1997). Watase, Nishinari, Williams and Phillips (1990) observed that the dynamic elastic modulus of agarose gels increased with increasing concentration of sugars up to a certain amount, but decreased with excessive addition of sugars. The glass transition and rheological properties of gellan gels with sugars were reported by several researchers (Papageorgiou, Kasapis & Richardson, 1994; Sworn & Kasapis, 1998a,b). Papageorgiou et al. (1994) observed that increasing the concentration of sucrose to 50% gradually increased the gelling temperatures of gellan gels. Sworn and Kasapis (1998b) studied the effects of monomeric and dimeric sugars, and starch hydrolysates on the modulus and the yield stress and strain of gellan gels.

The sol–gel transition and rheological properties of gellan gels without sugars have been extensively investigated (Milas & Rinaudo, 1996; Miyoshi, Takaya & Nishinari, 1996; Morris, Tsiami & Brownsey, 1995; Nakamura, Tanaka & Sakurai, 1996; Okamoto & Kubota, 1996; Tang, Tung & Zeng, 1995, 1997a,b). Further investigation on the

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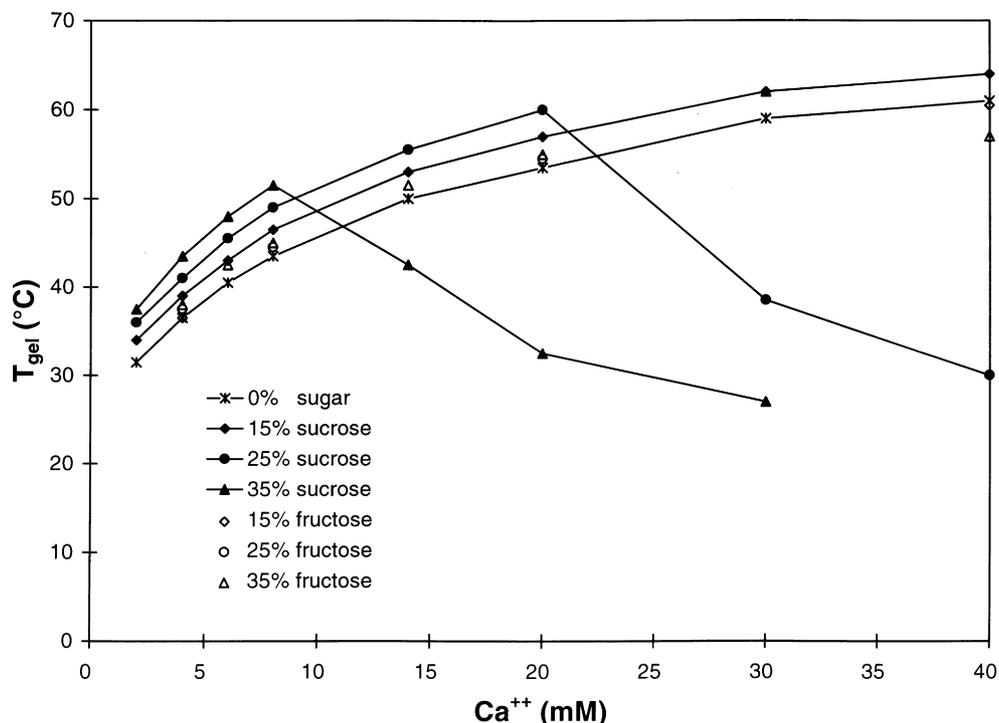


Fig. 1. Gelling temperatures of 0.6% gellan solutions containing calcium and sugar.

effect of sugars on gellan gels will provide useful information to the food industry. Our objectives were to study the gelling temperatures of gellan solutions, the clarity and large deformation failure properties of gellan gels as affected by the addition of fructose or sucrose. The effects of cooling methods on selected gel properties were also investigated.

2. Materials and methods

2.1. Gelling temperature

Deacylated gellan gum powder (KELCOGEL F) was provided by Kelco Biopolymers (San Diego, CA). Gellan powder at 0.6 and 1% w/v concentrations in final solutions was dispersed in distilled and deionized water in a 400 ml beaker with a magnetic stirrer. The mixtures were heated to the boiling point and the temperature was maintained for 30 s to fully hydrate the polymers. Fructose (ACS reagent) or sucrose (ACS reagent) was added to the hot solutions to prepare sugar concentrations of 15, 25 and 35% w/v in solutions, and the solutions were stirred for 30 s. Calcium chloride ('Baker Analyzed' reagent) or sodium chloride ('Baker Analyzed' reagent) was added to prepare solutions containing eight selected calcium concentrations (2–40 mM), or seven sodium concentrations (20–450 mM). The gelling temperatures were determined by dynamic rheological tests on a Bohlin Rheometer (Model VOR, Bohlin Rheology AB, Lund, Sweden) equipped with a coaxial cylinder

system C24.4HS. The dynamic testing was conducted at a frequency of 1 Hz and 0.5% strain amplitude in sinusoidal oscillation mode. During testing, the temperature of the solution was reduced from 80°C to 20°C at a constant rate of 0.6°C/min. The dynamic shear storage modulus (G') at each temperature (T) was recorded by a computer. The gelling temperature (T_{gel}) was determined by extrapolating a tangent line from the steepest slope for the portion of the $G'-T$ to intersect the abscissa and was averaged from two replicate tests. Details of testing method have been described previously (Tang et al., 1997a,b).

2.2. Gel clarity

Gellan solutions were prepared as described in the previous section. After adding calcium chloride or sodium chloride, each solution was continuously stirred for 2 to 3 min and poured into six 4.5 ml 1×1 cm² square shape polystyrene cuvettes; three cuvettes were cooled in still air to room temperature (22°C), and other three cuvettes were cooled by placing them in cold running water (15°C).

All cuvettes containing the gels were stored at room temperature for 24 h. Light absorbance of the gellan gels was measured at $\lambda = 490$ nm with a spectrophotometer (Spectronic Model 501, Fisher Scientific, Pittsburgh, PA) using water as the reference. Preliminary scanning of gellan solutions and gels from UV-visible light region (190–800 nm) indicated an absorption peak at 290–296 nm in the UV region. Although the maximum absorbance peak may be appropriate for other quantitative analysis, such as

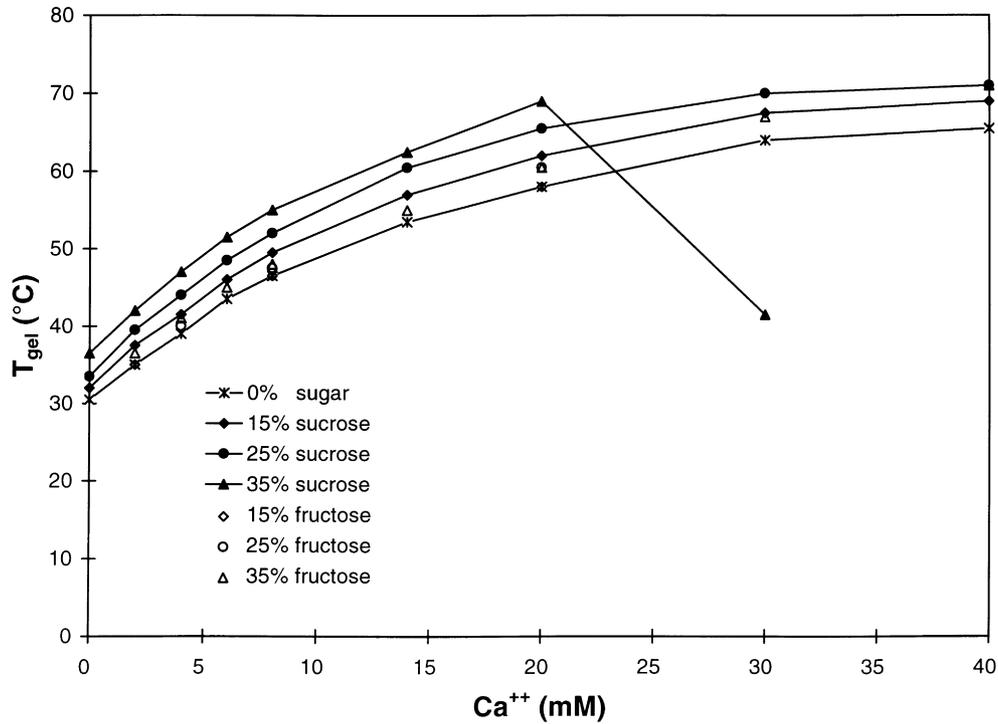


Fig. 2. Gelling temperatures of 1.0% gellan solutions containing calcium and sugar.

the determination of gellan concentration or other components, the absorbance peak at 290–296 nm could not be correlated to the visible clarity of the gels. In the visible region (400–800 nm), the absorbance was highest at the

lower end (400 nm). Thus 490 nm was selected as a reasonable compromise between having enough absorbance and avoiding the interference from UV region. The mean absorbance at 490 nm of gels cooled in air or in water was

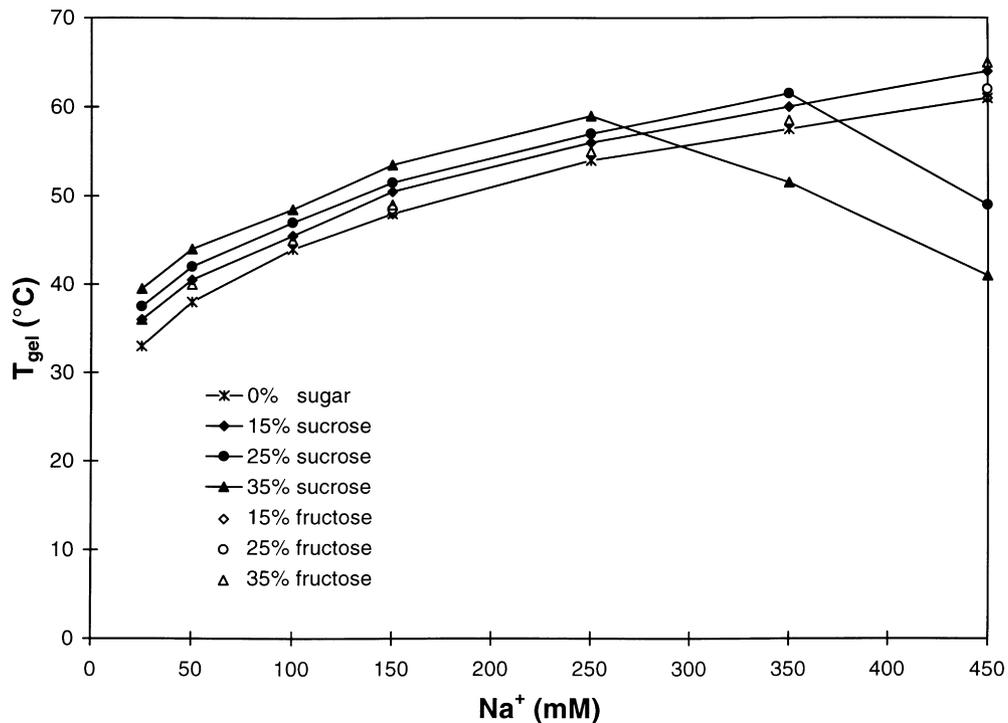


Fig. 3. Gelling temperatures of 0.6% gellan solutions containing sodium and sugar.

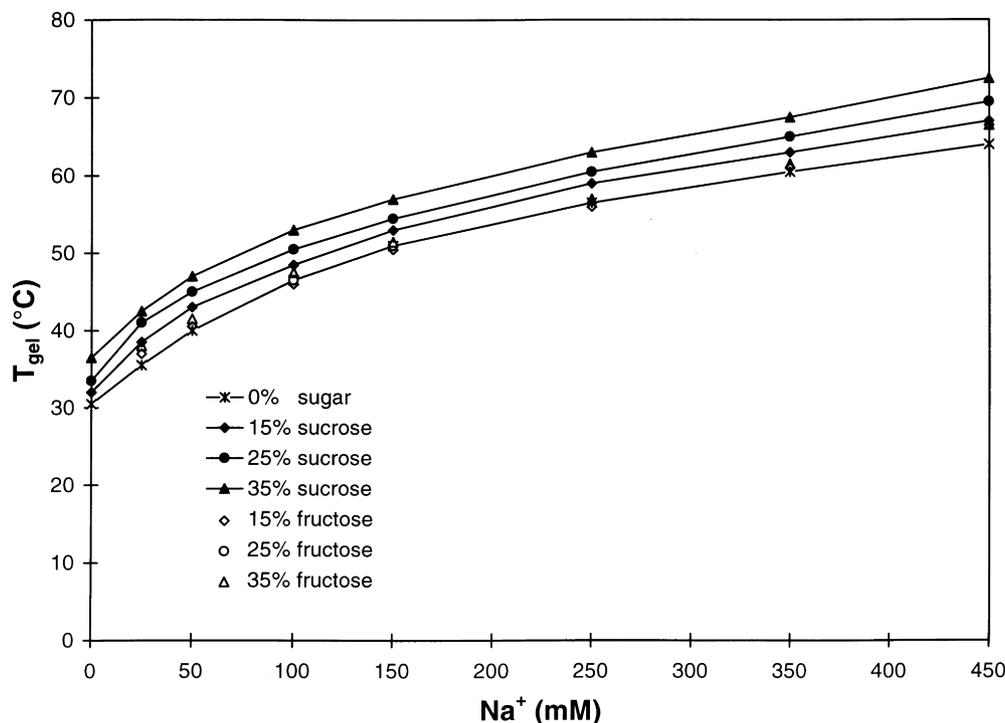


Fig. 4. Gelling temperatures of 1.0% gellan solutions containing sodium and sugar.

determined from three replicates. Small absorbance represents little turbidity and good clarity of the gels.

2.3. Compression testing

Only gellan gels containing sucrose were selected for compression tests in the current study, based on previous studies by Sworn and Kasapis (1998b) that found no effect on the modulus of gellan gels with the addition of 20% fructose. Gellan solutions were prepared with sucrose as described previously. After adding calcium chloride, the solutions were stirred continuously for 2 to 3 min and poured into metal tubes (inner diameter 21 mm) which were preheated to 80°C to prevent possible gelling of the solution along cold metal wall. Each solution was poured into two sets of tubes. One set was cooled in cold running water (15°C) for 15 min. The other set was cooled slowly in air. All tubes were stored at room temperature (22°C) for 24 h before the gel cylinders were removed from the tubes and sliced into disks of 21 mm length for compression testing.

The disc samples were compressed between two parallel lubricated flat Teflon plates that were fitted to an Instron (Model 1125, Instron Corporation, Canton, MA). The gels were deformed at a constant cross-head speed of 20 mm/min until failure. Tests were replicated six times. The true failure shear stress and strain were calculated as reported by Tang, Lelievre, Tung & Zheng (1994) and Tang et al. (1995).

3. Results

3.1. Gelling temperatures

The influence of gellan, sugar, and cation concentrations on the gelling temperatures of gellan solutions is shown in Figs. 1–4. Without sugars, the gelling temperature increased with increasing cation concentration, similar to results reported by Tang et al. (1997a,b). Fructose addition up to 35% (w/v) had little influence on the gelling temperatures. Addition of 10% increment of sucrose in the tested range (0–35% w/v), however, increased the gelling temperature by 1.5–3°C (Figs. 1–4). In general, the gelling temperature increased with increasing cation concentration, except when both sucrose and cation concentrations were very high. At high sucrose and cation concentrations, gelling temperatures reached a maximum and then dropped dramatically with additional cation or sucrose (Figs. 1–3). Similar to gellan solutions without sugar (Tang et al., 1997a,b), the gelling temperatures of gellan sugar solutions increased with increasing gellan concentration from 0.6 to 1.0% at fixed sugar and cation concentrations (Figs. 1–4). Increasing gellan concentration also shifted the maximum gelling temperature towards higher cation or sugar concentrations (Figs. 1 and 2). Although no maximum gelling temperature was observed in Fig. 4, we expected a maximum would be observed when sucrose or sodium concentration was increased beyond the current testing range.

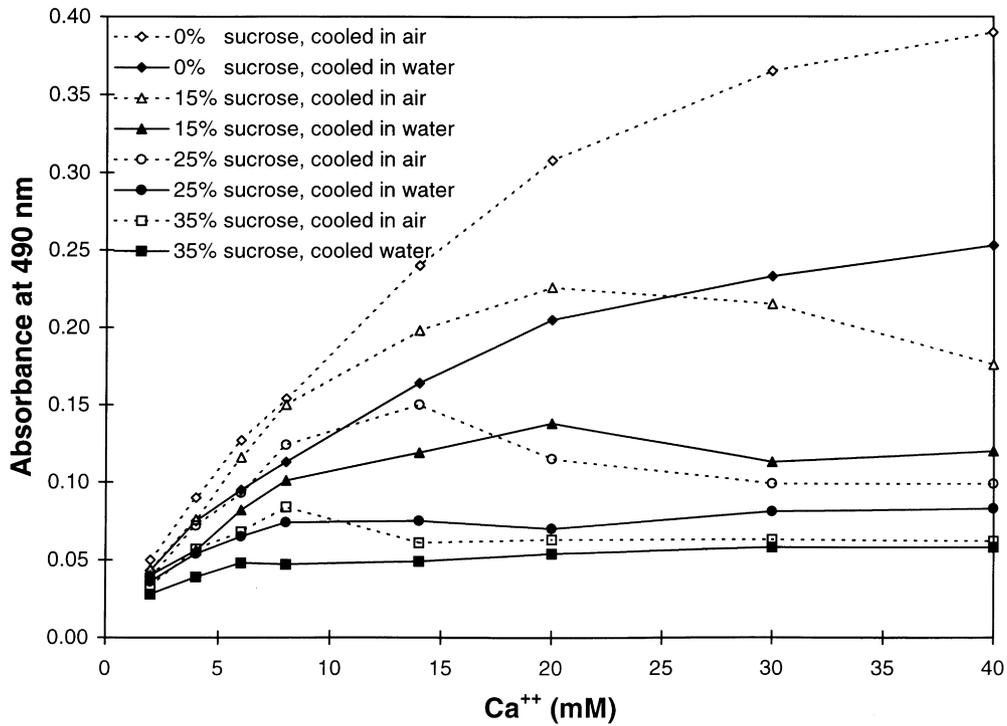


Fig. 5. Absorbance at 490 nm of 0.6% gellan gels containing calcium and sucrose.

3.2. Gel clarity

The influence of sucrose on gel clarity at selected gellan and cation concentrations are presented in Figs. 5–8.

Adding sucrose or fructose increased gel clarity, as indicated by lower absorbance at 490 nm. As cation concentration increased, the effect of sugar on gel clarity was more dramatic. Without sugars, the gels became less clear when

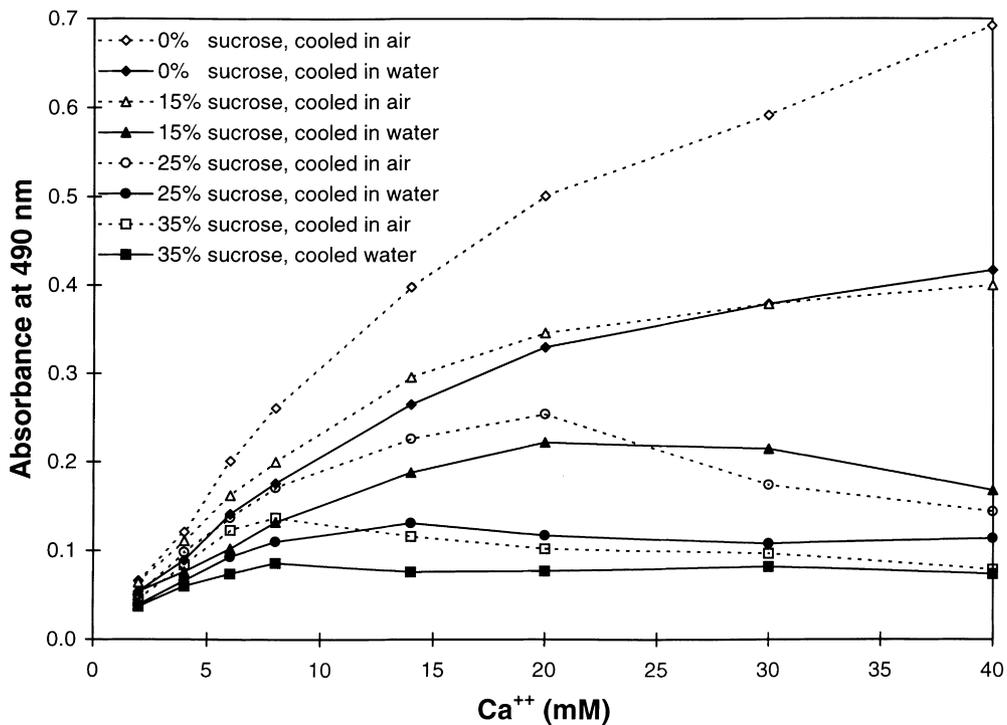


Fig. 6. Absorbance at 490 nm of 1.0% gellan gels containing calcium and sucrose.

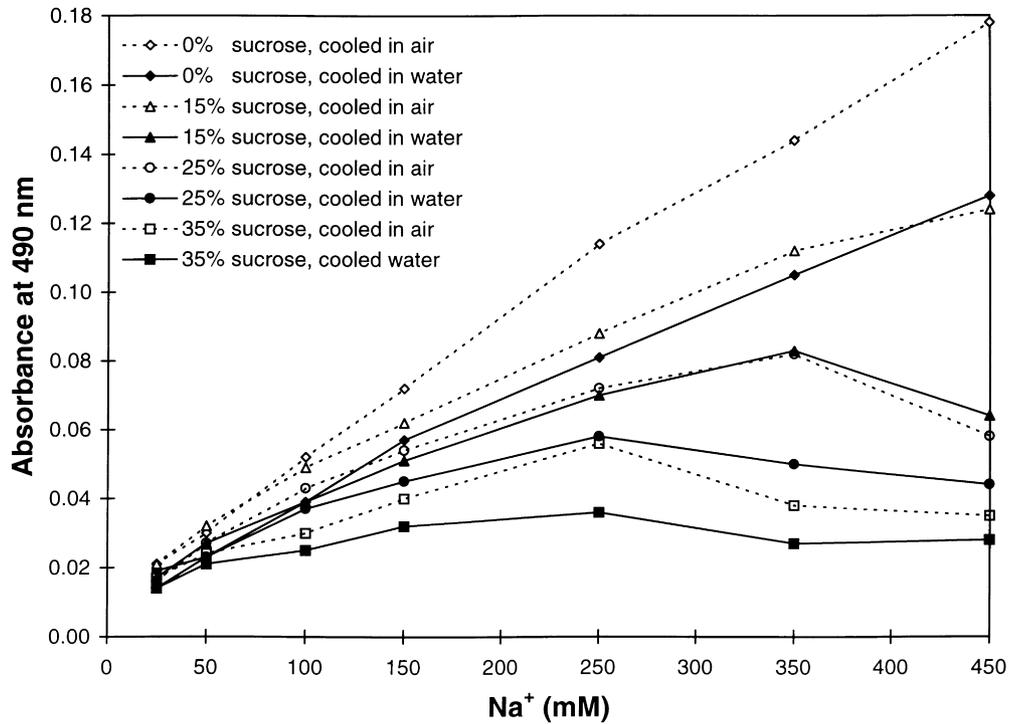


Fig. 7. Absorbance at 490 nm of 0.6% gellan gels containing sodium and sucrose.

Ca⁺⁺ or Na⁺ concentration was increased. At the presence of sucrose, the gel clarity initially decreased with increasing Ca⁺⁺ or Na⁺ concentration, but increased with excessive cation concentrations. Light absorbance at 490 nm

increased with increasing gellan concentration. That is, the gels became more opaque as gellan concentrations increased. In all cases, the gels cooled rapidly in cold water are clearer than the corresponding gels cooled slowly

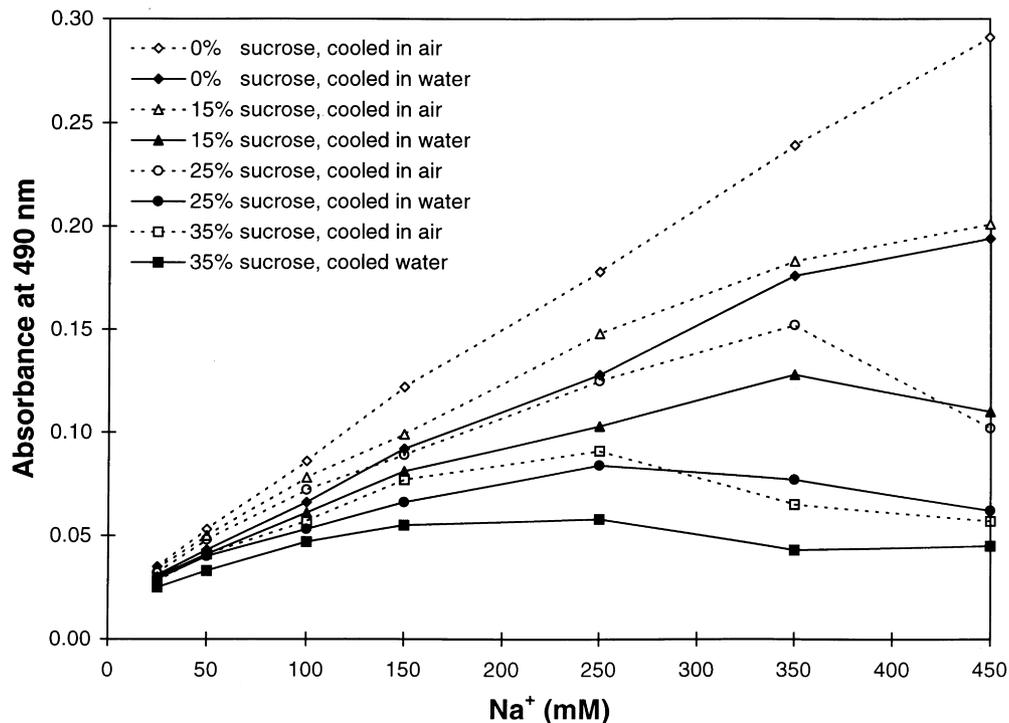


Fig. 8. Absorbance at 490 nm of 1.0% gellan gels containing sodium and sucrose.

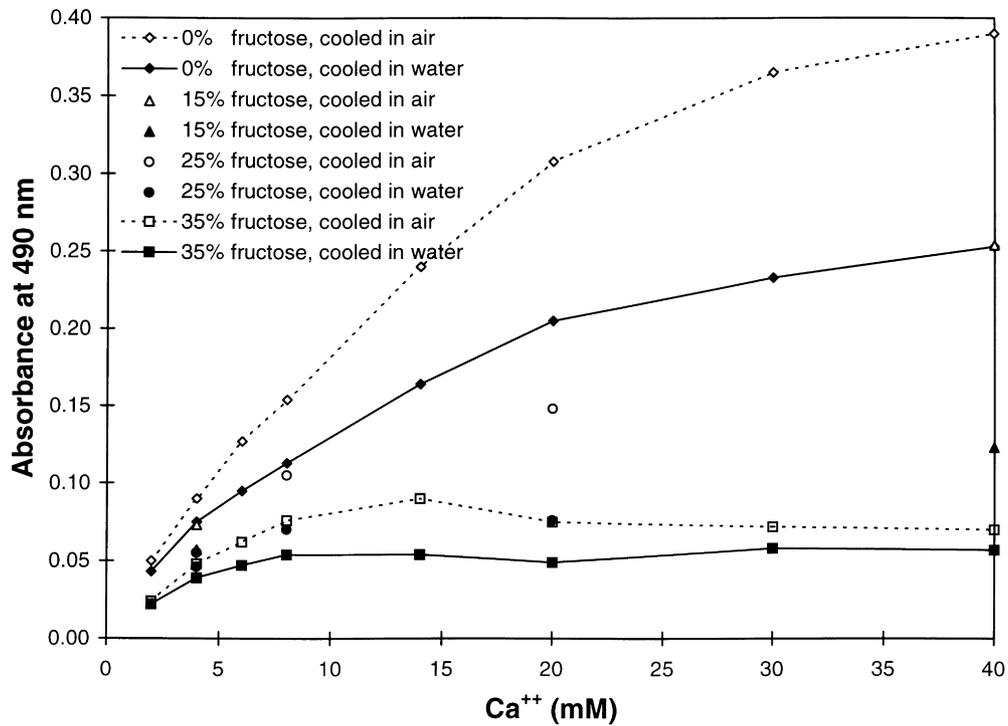


Fig. 9. Absorbance at 490 nm of 0.6% gellan gels containing calcium and fructose.

in air (Figs. 5–8). The effect of fructose on gel clarity was similar to sucrose (Figs. 9–12).

3.3. Compression behavior

In the low calcium concentration region (2–4 mM), the

failure stress (corresponding to gel strength) increased with increasing sucrose concentration for 0.6 and 1.0% gellan gels (Table 1). In contrast, in the high calcium region (30–40 mM), the failure stress decreased with increasing sucrose concentration (Table 1). When both calcium and sucrose concentrations were high, the 0.6% gellan gels

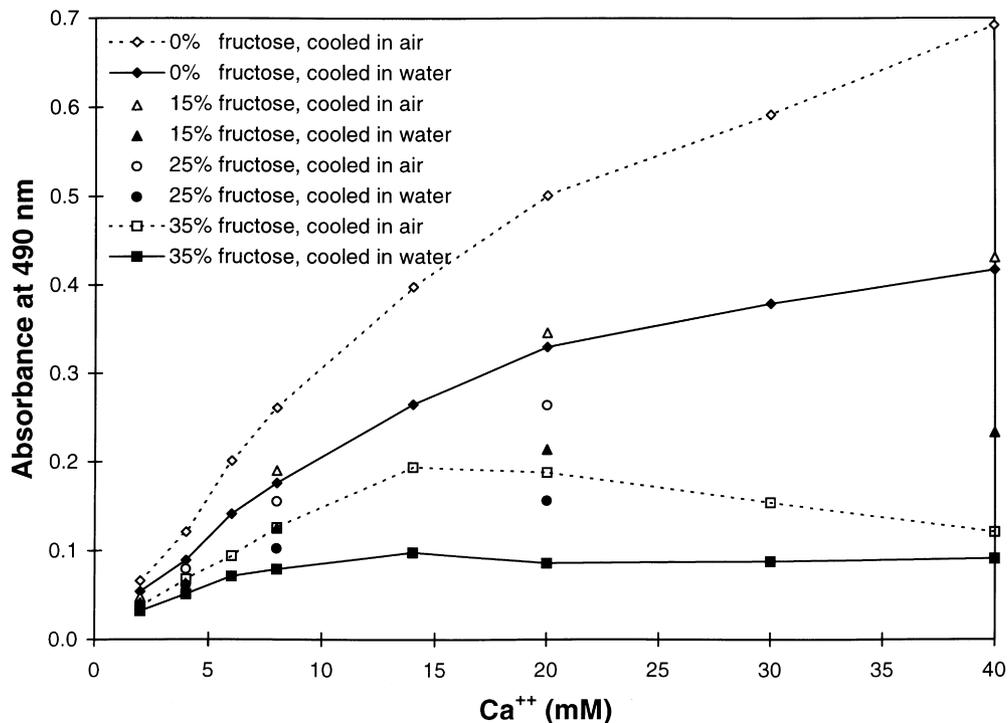


Fig. 10. Absorbance at 490 nm of 1.0% gellan gels containing calcium and fructose.

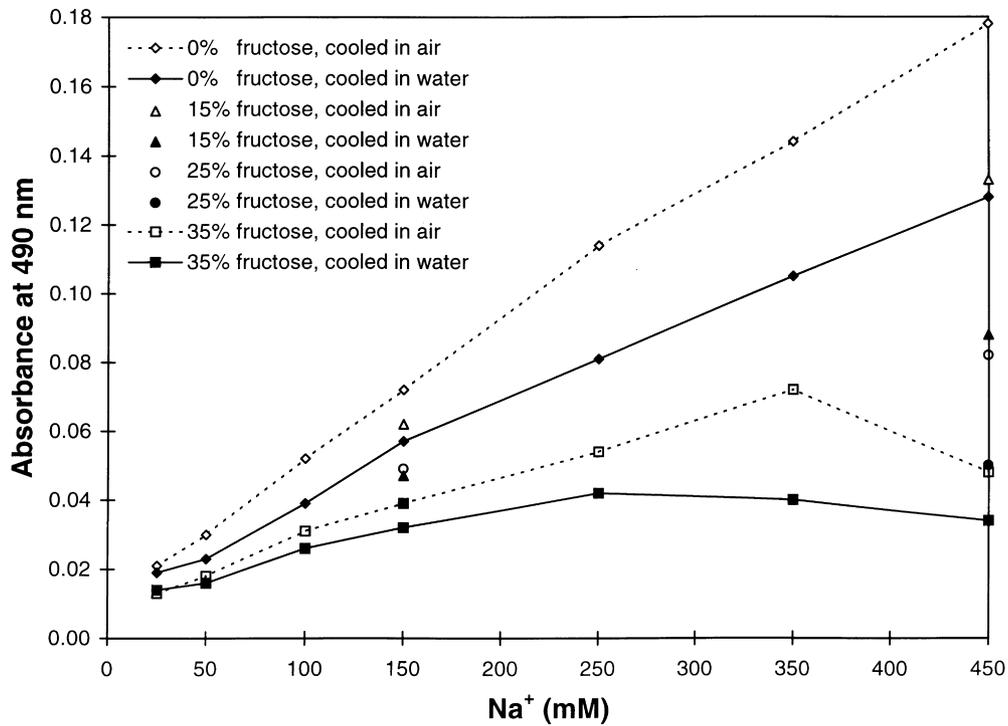


Fig. 11. Absorbance at 490 nm of 0.6% gellan gels containing sodium and fructose.

became too weak to be used in compression tests. In the intermediate calcium region (6–20 mM), the function of sucrose changed from strengthening the gels to weakening the gels when either calcium or sucrose concentration was

increased (Table 1). The different influences of sucrose at various calcium regions for 1% gellan gels cooled in water was shown in a 3D surface plot (Fig. 13). With a few exceptions, the gels rapidly cooled in water were weaker than the

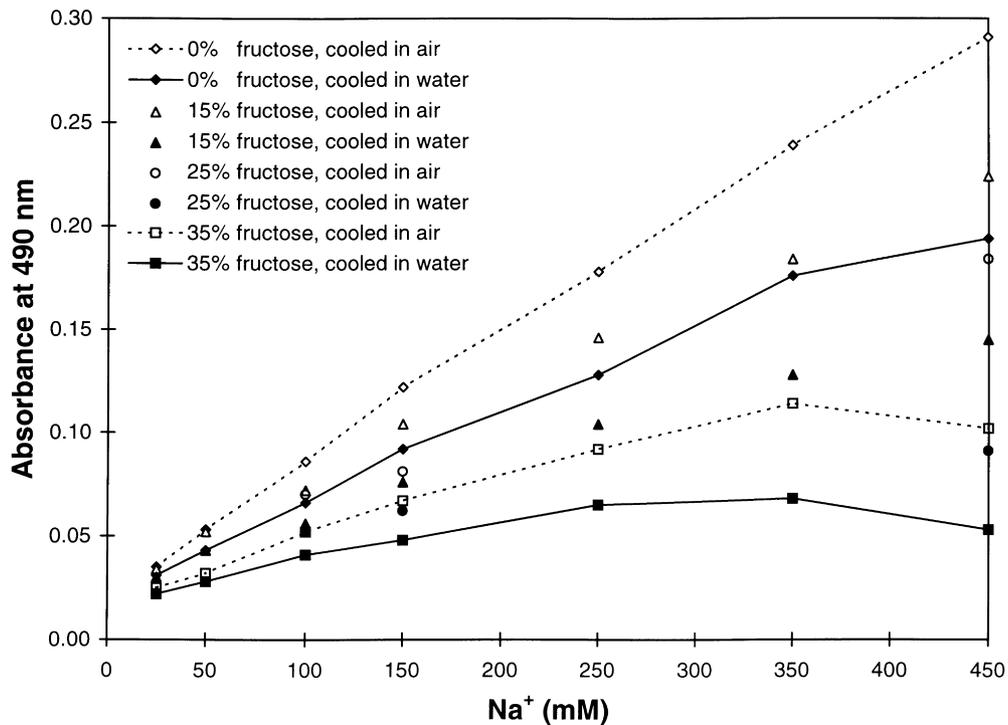


Fig. 12. Absorbance at 490 nm of 1.0% gellan gels containing sodium and fructose.

corresponding gels slowly cooled in air as indicated by the smaller failure stresses (Table 1).

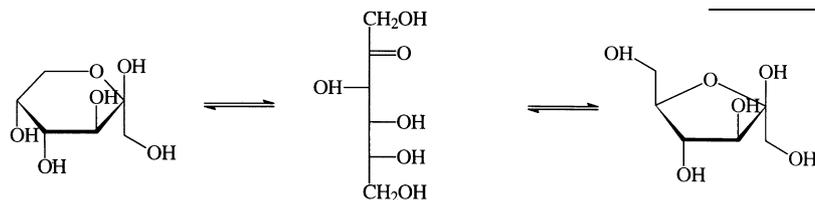
The influence of sucrose on the compressive failure strain was less clear (Table 2). Except for a few cases, the gels rapidly cooled in water were more deformable than the corresponding gels slowly cooled in air as indicated by the greater failure strains (Table 2).

4. Discussion

4.1. Influence of sugars on gelling temperatures

Sucrose can be readily crystallized in aqueous solutions under proper conditions. In the crystal structure, the hydroxyl groups of sucrose, except O-4, form intramolecular and intermolecular hydrogen bonds (Brown & Levy, 1963). In concentrated aqueous solutions, sucrose molecules tend to be packed in an orderly fashion. Sucrose is a disaccharide containing glucose and fructose residues. Gellan molecules also contain glucose residues. The glucose units in gellan chains may replace the glucose units of sucrose molecules in the ordered sucrose molecular packing. Thus orderly packed sucrose molecules may have a stabilizing effect on the orderly packed gellan double helix in aqueous solutions. This stabilizing effect of sucrose on the ordered conformation of gellan gum was reported by Papageorgiou et al. (1994). As a result, increasing sucrose content of gellan gels generally resulted in a higher gelling temperature.

In contrast, due to rapid conversion among pyranose-keto-furanose structures:



fructose cannot be crystallized in aqueous solutions. Fructose was long known as “uncrystallized glucose”, “sucrose liquid” or “uncrystallizable sugar” before Jungfleisch and Lefranc obtained crystalline solids in 1881 by leaving the syrup with absolute alcohol at 0°C for a few days (Barry & Honeyman, 1952). The randomly packed fructose molecules do not exhibit the stabilization effect to the orderly packing of gellan molecules. Adding fructose to gellan solutions, therefore, had little effect on gelling temperatures.

Cations at moderate concentrations have a stabilizing effect on the orderly packed gellan double helices and strengthen the gellan gels. But excessive cations may hinder the orderly packing of gellan helices and weaken gellan gels (Tang et al., 1994, 1995; Tang, Tung & Zeng, 1996). Tang et al. (1994, 1995, 1996, 1997a,b) observed that excessive cations decreased gellan gel strength, but did not decrease gellan gelling temperatures. The maximum calcium concen-

tration in those studies was, however, only 40 mM (Tang et al., 1997a,b). In the current study, we observed that a 1% gellan solution containing 100 mM Ca^{++} had a gelling temperature of 30°C, much lower than the gelling temperature (65°C) of 1% gellan solution with 40 mM Ca^{++} , indicating that excessive cation may also reduce the gelling temperatures of gellan solutions.

Sucrose exhibits similar stabilizing effect as the cations in gellan solutions and gels. Excessive sucrose concentrations may also destabilize gellan gels. Therefore, when both cation and sucrose concentrations were high, the gelling temperature of gellan solutions and the strength of resultant gels decreased.

4.2. Influence of sugars and cooling methods on gel clarity

Sugar by itself cannot increase the clarity of water solution. The absorbance of a 35% sucrose solution at 490 nm is 0.006 when pure water was used as reference. That is, the sugar solution is slightly more turbid than pure water, possibly due to light scattering effect of sucrose molecules.

The reason for increased clarity in gellan gels with added sugars may be explained by reduced optical contrast between the polymer and the medium, i.e. by their reduced difference of refractive indices. In gellan gels, the orderly packed junction zones have higher density and larger refractive indices than randomly dispersed gellan coils or sugar solutions. These junction zones scatter light much like discrete particles. Assuming that a dilute solution contain N identical particles per ml, the turbidity (τ) of the solution due to light scattering is related to the volume of individual

particles by the following equation (Heller, 1959):

$$\tau = 24\pi^3 \left[\frac{(\epsilon_2 - \epsilon_1)^2}{(\epsilon_2 + 2\epsilon_1)^2} \right] \frac{V^2 N}{\lambda^4} \quad (1)$$

where ϵ_1 , ϵ_2 are the optical dielectric constants of medium and particles, respectively; V is the volume of a single particle; λ is the wavelength of the incident light. Eq. (1) does not consider secondary scattering and applies only to dilute solutions. However, Eq. (1) is useful to elucidate some important factors affecting gel turbidity.

The particle volume is related to the cubic order of particle diameter (D). That is,

$$\tau \propto V^2 \propto D^6 \quad (2)$$

The size of a small molecule such as sucrose is about 1 nm (Brown & Levy, 1963), the radius of gyration of a

Table 1
True failure shear stress (kPa) of gellan gels at selected calcium and sucrose concentrations

Gellan (%w/v)	Ca ⁺⁺ (mM)	Sucrose (%w/v)					
		15		25		35	
		Cooling medium					
		Air	Water	Air	Water	Air	Water
0.6	2	14.6	9.9	16.5	12.2	17.6	14.6
	4	14.5	13.3	17.8	16.4	19.5	17.9
	6	15.6	15.6	15.5	14.6	15.9	16.4
	8	13.7	15.4	14.6	17.1	14.0	12.9
	14	11.0	13.3	13.5	10.5	2.7	2.7
	20	10.1	11.5	9.2	4.9	1.2	1.9
	30	8.9	5.5	2.6	3.1	^a	^a
	40	5.4	3.5	^a	^a	^a	^a
1.0	2	22.1	15.4	24.3	18.2	27.1	20.7
	4	27.3	22.7	28.8	25.0	33.1	29.5
	6	24.8	23.9	28.6	25.3	31.4	30.8
	8	24.3	25.3	28.2	30.6	25.5	24.8
	14	21.3	26.4	23.0	24.6	22.6	12.7
	20	19.2	27.4	21.2	13.1	8.1	6.6
	30	15.9	13.5	14.2	7.1	2.2	4.8
	40	16.2	7.9	5.9	5.0	1.9	2.2

^a Gel was too weak to test.

common polymer molecule is on the order of 100 nm (Kratochvil, 1972). Eq. (2) indicates that, when compared with polymers, the light scattering from small molecules is negligible unless the small molecules overwhelmingly outnumber the polymers. When compared with polymer gels, even the light scattering from polymer solution is negligible. For example, it was observed that when a polymer (e.g. methyl cellulose) solution became a physically crosslinked gel, the intensity of the scattered light increased

hundreds of times (Mao, Liu, Huglin & Holmes, 1998). Tang et al. (1997a) observed that when gellan solutions became gels, the light absorbance at 490 nm increased from near zero to a significant amplitude and the dramatic increase in absorbance was used to determine the gelling point. Therefore, although sugar molecules may scatter light, their contribution to the turbidity in a gel system is too small compared to the turbidity resulting from gelation of gel components.

The optical dielectric constant in Eq. (1) is related to the refractive index (n) by,

$$\epsilon = n^2 \quad (3)$$

Sucrose concentration at 35%w/v is approximately 31%w/w. The refractive indices of 31%w/w sucrose solution and pure water at 589 nm and 20°C are 1.3830 and 1.3330, respectively (Anon, 1996). The refractive index data of gellan is not available. The refractive indices for common polymers are approximately 1.5. For example, the refractive indices for polymethyl methacrylate, polyethyl methacrylate and poly-*n*-butyl methacrylate at 633 nm and 25°C are 1.4878, 1.4822 and 1.4800, respectively (Huglin, 1972). The refractive index of starch at 589 nm and 25°C is 1.53 (Tabor, 1972). Assuming that the refractive index of gellan (n_2) is 1.53, it may be calculated for gellan-water system ($n_1 = 1.3330$ for water as medium),

$$\frac{(\epsilon_2 - \epsilon_1)^2}{(\epsilon_2 + 2\epsilon_1)^2} = \frac{(1.53^2 - 1.3330^2)^2}{(1.53^2 + 2 \times 1.3330^2)^2} = 9.15 \times 10^{-3}$$

and for gellan-35% sucrose aqueous solution system ($n_1 = 1.3830$ for 35% sucrose solution as medium),

$$\frac{(\epsilon_2 - \epsilon_1)^2}{(\epsilon_2 + 2\epsilon_1)^2} = \frac{(1.53^2 - 1.3830^2)^2}{(1.53^2 + 2 \times 1.3830^2)^2} = 4.82 \times 10^{-3}$$

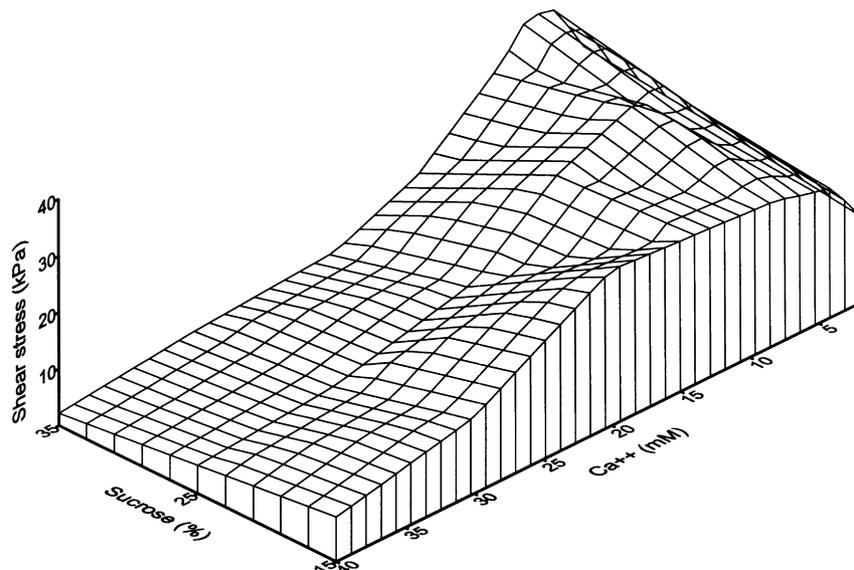


Fig. 13. True failure shear stress (kPa) of 1.0% gellan gels cooled in water containing calcium and sucrose.

Table 2
True failure shear strain of gellan gels at selected calcium and sucrose concentrations

Gellan (%w/v)	Ca ⁺⁺ (mM)	Sucrose (%w/v)					
		15		25		35	
		Cooling medium					
		Air	Water	Air	Water	Air	Water
0.6	2	0.55	0.86	0.62	0.88	0.59	0.86
	4	0.37	0.54	0.42	0.57	0.43	0.61
	6	0.38	0.45	0.35	0.40	0.35	0.48
	8	0.42	0.44	0.41	0.45	0.34	0.55
	14	0.53	0.46	0.37	0.55	0.33	0.39
	20	0.46	0.47	0.37	0.61	0.29	0.39
	30	0.35	0.63	0.43	0.67	^a	^a
	40	0.36	0.51	^a	^a	^a	^a
1.0	2	0.60	0.87	0.62	0.88	0.61	0.90
	4	0.39	0.54	0.39	0.56	0.43	0.62
	6	0.38	0.46	0.33	0.41	0.37	0.52
	8	0.36	0.37	0.36	0.45	0.31	0.38
	14	0.51	0.42	0.37	0.32	0.32	0.49
	20	0.54	0.42	0.39	0.53	0.49	0.67
	30	0.39	0.48	0.37	0.70	0.43	0.74
	40	0.36	0.47	0.43	0.68	0.40	0.46

^a Gel was too weak to test.

Above calculations indicated that if the number (N) and the dimensions (D) of the junction zones are equivalent in both solutions, the turbidity of sugar gel should be about half of water gel, due to the reduced optical contrast between the polymer and the medium.

The refractive index of 31%w/w fructose aqueous solution at 589 nm and 20°C is 1.3821 (Anon, 1996), very close to the refractive index of sucrose aqueous solution at equivalent concentration (1.3830). Therefore, fructose may have similar effect as sucrose and addition of fructose could make gellan gels clearer (Figs. 9–12).

Increased clarity of gellan gels by adding sugars may also be attributed to the increased viscosity in sugar solutions that hinders the gellan double helices to join junction zones. The viscosity of 31%w/w sucrose or fructose solutions are about three times as high as the viscosity of water (Anon, 1996). Mao, Tang and Swanson (1999) reported that at the beginning of gelation (at the gelling point), the length of a junction zone along the strand of gellan chains in calcium stabilized gellan gel was 5.63 nm. The length of the junction zones after full gelation of gellan gels were as large as 70 nm (Nakajima, Ikehara & Nishi, 1996). Therefore, during the gelation process, except for forming new junction zones, gellan double helices migrated and were orderly packed to the existing junction zones. Increasing the viscosity of the medium hinders such migration and causes the size of the junction zones of sugar gels to be smaller than that of water gels. According to Eq. (1), the turbidity is proportional to the 6th power of the size. Therefore, sugar gels are clearer than corresponding water gels.

Gellan gels that were cooled rapidly in running water

were clearer than the gels cooled in air (Figs. 5–12). It is possible that when a gel was slowly cooled in air, the gelling process took longer time, the gellan double helices had more time to migrate and join the existing junction zones than the gels rapidly cooled in water. Thus the size of the junction zones of gels slowly cooled in air were larger than the junction zones of gels rapidly cooled in water. Larger junction zones resulted in more turbid gels. In addition, increased junction zone sizes also increased gel strength. Therefore, the failure stress of gels slowly cooled in air were usually higher than that of gels rapidly cooled in water (Table 1).

4.3. Influence of sucrose on gel texture

As discussed earlier, sucrose exhibits a stabilizing effect on formation and packing of gellan double helices in a similar manner as cations. Excessive sucrose also hinders the aggregation of gellan double helices and reduces the size of the junction zones. This was confirmed by Fiszman and Duran (1992) that both resistance to rupture and firmness of 1% alginate gels were improved by the addition of sucrose up to 40%, but additional sucrose beyond 40% reduced the firmness of the gels.

When the calcium concentration was smaller than stoichiometric concentration to neutralize the negative charges in the gellan chains, adding sucrose should stabilize gellan double helices. Therefore, gellan gel strength increased with increasing sucrose concentration. On the other hand, at high calcium concentrations the amount of calcium was more than adequate to stabilize the gellan double helices, and

the excess calcium hindered the aggregation of gellan double helices. In such situations adding sucrose could only hinder the growth of junction zones. Therefore, with excess calcium concentrations, gellan gel strength decreased with increasing sucrose concentrations.

5. Conclusions

Adding fructose up to 35%w/v to 0.6 and 1.0% gellan solutions exhibited little effect on the gelling temperatures. The addition of 10% increment of sucrose increased the gelling temperatures by 1.5–3°C. But when both cation and sucrose concentrations were high, the gelling temperatures of gellan solutions were decreased by the addition of sucrose. The different effects of sucrose and fructose on the gelling temperatures of gellan solutions can be attributed to the different ability of these two sugars to stabilize orderly packing of gellan double helices in water solutions. Adding sucrose or fructose increased gellan gel clarity by reducing the differences in refractive index between gellan polymer and the medium, i.e. by reducing the optical contrast between gellan and the surrounding environment. The higher viscosity of sugar solutions might also contribute to gel clarity because viscous media hindered the growth of the junction zones. Sucrose exhibited similar effect as cations to stabilize the orderly packing structure of gellan. But like cations, excessive sucrose also hindered the formation and growth of junction zones. Thus at low cation concentrations, sucrose strengthened gellan gels; but at high cation concentrations, sucrose weakened the gels. Gellan gels formed by slow cooling in air were more turbid and stronger than the gels formed by rapid cooling in water due to the prolonged gelation time that increased the dimension of junction zones.

Acknowledgements

These studies were supported by the USDA NRI Competitive Grant Program, by Washington State Agricultural Research Center, and by the Natural Sciences and Engineering Research Council of Canada. We thank Kelco Biopolymers for providing the gellan gum.

References

Anon (1996). Density, refractive index, freezing point depression, and viscosity of aqueous solutions. In D. R. Lide & H. P. R. Frederikse, *CRC handbook of chemistry and physics, 1996–1997* (77th ed). (pp. 8.56–8.87). Boca Raton, FL: CRC Press.

Barry, C. P., & Honeyman, J. (1952). Fructose and its derivatives. In C. S. Hudson, M. L. Wolfrom & S. M. Cantor, *Advances in carbohydrate chemistry* (pp. 53–98). 7. New York: Academic Press.

Boye, J. I., Alli, I., Ramaswamy, H., & Raghavan, V. G. S. (1997). Interactive effects of factors affecting gelation of whey proteins. *Journal of Food Science*, 62, 57–65.

Brown, G. M., & Levy, H. A. (1963). Sucrose: precise determination of

crystal and molecular structure by neutron diffraction. *Science*, 141, 921–923.

Chandrasekaran, R., Puigjaner, L. C., Joyce, K. L., & Arnott, S. (1988). Cation interactions in gellan: an-X-ray study of the potassium salt. *Carbohydrate Research*, 181, 23–40.

Fizman, S. M., & Duran, L. (1992). Effects of fruit pulp and sucrose on the compression response of different polysaccharides gel systems. *Carbohydrate Polymers*, 17, 11–17.

Heller, W. (1959). Elements of theory of light scattering. 1. Scattering in gases, liquids, solutions, and dispersions of small particles. *Records of Chemical Progress*, 20, 209–233.

Huglin, M. B. (1972). Specific refractive index increments. In M. B. Huglin, *Light scattering from polymer solutions* (pp. 165–332). New York: Academic Press.

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.

Kratohvil, P. (1972). Particle scattering functions. In M. B. Huglin, *Light scattering from polymer solutions* (pp. 333–384). New York: Academic Press.

Lopes da Silva, J. A., & Goncalves, M. P. (1994). Rheological study into the aging process of high methoxyl pectin/sucrose aqueous gels. *Carbohydrate Polymers*, 24, 235–245.

Mao, R., Liu, Y., Huglin, M. B., & Holmes, P. A. (1998). Dynamic light scattering from polymer gels: spring-rotor model. *Polymer International*, 45, 321–326.

Mao, R., Tang, J., & Swanson, B. G. (1999). Gelling temperatures of gellan solutions as affected by citrate buffers. *Journal of Food Science*, 64, 648–652.

Milas, M., & Rinaudo, M. (1996). The gellan sol–gel transition. *Carbohydrate Polymers*, 30, 177–184.

Miyoshi, E., Takaya, T., & Nishinari, K. (1996). Rheological and thermal studies of gel–sol transition in gellan gum aqueous solutions. *Carbohydrate Polymers*, 30, 109–119.

Morris, V. J., Tsiami, A., & Brownsey, G. J. (1995). Work hardening effects in gellan gum gels. *Journal of Carbohydrate Chemistry*, 14, 667–675.

Nakajima, K., Ikehara, T., & Nishi, T. (1996). Observation of gellan gum by scanning tunneling microscopy. *Carbohydrate Polymers*, 30, 77–81.

Nakamura, K., Tanaka, Y., & Sakurai, M. (1996). Dynamic mechanical properties of aqueous gellan solutions in the sol–gel transition region. *Carbohydrate Polymers*, 30, 101–108.

Nishinari, K., Watase, M., Williams, P. A., & Phillips, G. O. (1990). κ -Carrageenan gels: effect of sucrose, glucose, urea, and guanidine hydrochloride on the rheological and thermal properties. *Journal of Agricultural and Food Chemistry*, 38, 1188–1193.

Okamoto, T., & Kubota, K. (1996). Sol–gel transition of polysaccharide gellan gum. *Carbohydrate Polymers*, 30, 149–153.

Papageorgiou, M., Kasapis, S., & Richardson, R. K. (1994). Glassy-state phenomena in gellan-sucrose-corn syrup mixtures. *Carbohydrate Polymers*, 25, 101–109.

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

Ptitchkina, N. M., Danilova, I. A., Doxastakis, G., Kasapis, S., & Morris, E. R. (1994). Pumpkin pectin: gel formation at unusually low concentration. *Carbohydrate Polymers*, 23, 265–273.

Rao, M. A., & Cooley, H. J. (1993). Dynamic rheological measurement of structure development in high-methoxyl pectin/fructose gels. *Journal of Food Science*, 58, 876–879.

Rao, M. A., Van Buren, J. P., & Cooley, H. J. (1993). Rheological changes during gelation of high-methoxyl pectin/fructose dispersions: effect of temperature and aging. *Journal of Food Sciences*, 58, 173–176 (also p. 185).

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

Sworn, G., & Kasapis, S. (1998a). The use of Arrhenius and WLF kinetics

- to rationalise the mechanical spectrum in high sugar gellan systems. *Carbohydrate Research*, 309, 353–361.
- Sworn, G., & Kasapis, S. (1998b). Effect of conformation and molecular weight of co-solute on the mechanical properties of gellan gum gels. *Food Hydrocolloids*, 12, 283–290.
- Tabor, B. E. (1972). Preparation and clarification of solutions. In M. B. Huglin, *Light scattering from polymer solutions* (pp. 1–25). New York: Academic Press.
- 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 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 temperature of gellan solutions containing calcium ions. *Journal of Food Science*, 62, 276–280.
- Tang, J., Tung, M. A., & Zeng, Y. (1997b). Gelling properties of gellan solutions containing monovalent and divalent cations. *Journal of Food Science*, 62, 688–692.
- Upstill, C., Atkins, E. D. T., & Attwood, P. T. (1986). Helical conformations of gellan gum. *International Journal of Biological Macromolecules*, 8, 275–288.
- Watase, M., Nishinari, K., Williams, P. A., & Phillips, G. O. (1990). Agarose gels: effect of sucrose, glucose, urea, and guanidine hydrochloride on the rheological and thermal properties. *Journal of Agricultural and Food Chemistry*, 38, 1181–1187.