ELSEVIER
0144-8617(94)00037-9
Carbohydrate Polymers 25 (1994) 101-109

0144-8617/94/$07.00

Glassy-state phenomena in gellan–sucrose–corn syrup mixtures

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(Received 26 April 1994; revised version received 29 June 1994; accepted 1 July 1994)

The method of dynamic oscillation was employed to investigate changes in the mechanical properties of deacylated gellan gels in the presence of sucrose–corn syrup blends. The effect of sugar, at concentrations between 0 and 50% in the mixture, is to raise gradually the gelling temperature and the mechanical strength of the gellan network. However, there is a sharp increase in thermal stability (formation of a structure at the highest experimentally accessible temperature of 90°C) and substantial reduction in shear modulus development at 60% co-solute in the system which is discussed in terms of a disproportionate conformational ordering and diminishing water-supported, intermolecular junction zones of the gellan strands in a low solvent environment. The dramatic change in physical properties of the gellan–solute blends at 90°C produces a spectacular temperature dependence of the in-phase and out-of-phase viscoelastic components during subsequent cooling. Thus, the high-solids gellan network undergoes transformation from a rubber-like consistency to a glassy state in the manner observed for entangled networks of high molecular weight synthetic polymers. The onset of glass transition is enhanced by increasing amounts of sugars, occurring at about 37°C for the 0·5% gellan plus 85% solute system at an experimental frequency of 10 rad/s. Mechanical spectra of sucrose–corn syrup mixtures at this concentration remain Newtonian at 5°C, the lowest experimentally accessible temperature. According to the time–temperature superposition principle, vitrification of the above gellan sample commences at ≈17 Hz at 90°C. Following the empirical procedure developed by Williams, Landel and Ferry, the temperature at which the gellan–solute glass forms (*Tg*) was found to be close to the vitrifiication temperature of a sucrose preparation at 15% moisture content (≈ −25°C).

INTRODUCTION

The acylated form of gellan gum is an extracellular polysaccharide secreted by the bacterium *Pseudomonas elodea*. Alkaline conditions during preparation of the commercial product cause the removal of the acetyl group and the L-glyceryl substituent, attached to the oxygen atoms (6) and (2) of the 3-linked residue in the repeat sequence, thus producing a linear tetrasaccharide with the following structure (Jansson *et al.*, 1983; O'Neill *et al.*, 1983):

→ 3)-β-*D*-Glcp-(1 → 4)-β-*D*-GlcpA-(1 → 4)-
β-*D*-Glcp-(1 → 4)-α-*L*-Rhap-(1 →

Under non-gelling conditions, i.e. in the presence of bulky organic counterions such as the tetramethylammonium salt, gellan undergoes a thermally reversible conformational transition involving two disordered coils at high temperature and a left handed, three-fold coaxial helical structure at temperatures below the transition point (Crescenzi *et al.*, 1987; Chandrasekaran *et al.*, 1988). Gelation is promoted by cation-mediated aggregation of the intertwined helical chains and is heavily dependent upon both the ionic strength and the identity of the cation (Grasdalen & Smidsrød, 1987). A finite concentration of each ion is required to induce gelation and as ionic strength is increased further, gel strength increases through to a maximum. Increase in ionic concentration beyond the maximum gives rise to a progressive reduction in gel strength and ultimately no gel is formed (Sanderson & Clark, 1983). The dramatic effect of salt on the properties of gellan structure allows the formation of systems with a wide range of textural properties, i.e. from fairly soft and non-brittle to firm and very brittle gels (Papageorgiou *et al.*, 1994*a*). For all practical purposes, the amounts of monovalent and

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divalent cations present in market products (typically Na^+, K^+ or Ca^{2+}) result in thermally irreversible gels (Watase & Nishinari, 1993; Papageorgiou *et al.*, 1994*a*). However, a superior flavour release is guaranteed, since the small amounts of polymer (0·05–1%) employed in the gellan-structured commercial products release water instantaneously upon mastication (Morris, 1993). Over the last decade gellan gum has been developed as a versatile ingredient for food applications either as the sole texturising agent or in combination with other hydrocolloids (Sanderson *et al.*, 1988; Sanderson & Ortega, 1993). Recently, the effect of Ca^{2+} and Mg^{2+} ions on the structural properties of alginate–gellan water dessert gels was investigated. Results suggest that changes in salt composition transform the preparation from an alginate continuous-phase dispersion with elastic properties to a product where gellan coexists with alginate as a supporting matrix (bicontinuous system), imparting a shorter mouthfeel to the gel (Ortega *et al.*, 1994; Papageorgiou *et al.*, 1994*b*). Substitution of gelatin for alginate in the composite mixture produces table jellies that are thermally stable at high ambient temperatures (Shim, 1985; Wolf *et al.*, 1989). Detailed examination of the exclusion phenomena between the two biopolymers at acidic pH reveals that gellan encapsulates the gelatin inclusions in a continuous matrix thus preventing them from welding together at temperatures as high as 50°C (Papageorgiou *et al.*, 1994*a*). An obvious continuation of the above work is to explore the macroscopic understanding of functional properties in single and mixed gellan gels in the presence of co-solutes. With the view of facilitating the development of existing, or potentially important, new confectionery products this work illustrates the use of dynamic mechanical measurements for providing a deeper insight into the effect of sucrose and corn syrup on the physical properties of gellan gels.

MATERIALS AND METHODS

The deacylated gellan gum (Kelcogel; batch number 77109A) was kindly supplied by Kelco Division of Merck and Co., Inc. Atomic absorption analysis produced the following data for the two major monovalent cations (M^+) of the gum: K^+: 31079 ppm; and Na^+: 1633 ppm. The potassium and sodium content of the sample was converted to percentage of the polymer stoichiometric requirement as follows: The M^+ concentration was reworked in mg/g by dividing the ppm values by 1000. Then, the actual amount of polymer present (G mg/g) was calculated by subtracting the moisture (mg/g) and the total M^+ content (the level of divalent ions was found to be about a tenth of the monovalent content) from the value of 1000 mg/g. Finally, the M^+ content was expressed relative to the concentration of carboxyl groups on the polymer taken as 100 (i.e. as a percentage of the stoichiometric requirement of the gellan gum). The formula weight for the repeat unit of gellan ion (without acyl substituents) was taken as 645. Thus the equivalent weight of an ion of mass M and valency V (in this case equal to 1) required was therefore $W = GM/645V$ (mg/g). If the actual concentration of the ion was I mg/g, the percent stoichiometry $= 100I/W = I(64500V/M)/G$. The factors by which the ionic content (mg/g) was multiplied to give the percent stoichiometry were therefore $1650/G$ for K^+ and $2806/G$ for Na^+. According to this procedure the total M^+ content was estimated to screen 65% of the polymer anionic charge. In preparations therefore, appropriate amounts of sodium chloride were added to balance the difference in terms of monovalent cations, i.e. for the 0·5% gellan sample the molarity of M^+ was about 8 mmol per litre of solution. Proper dissolution of gellan samples required heating of the suspensions at 90°C for 15 min with mechanical stirring. Sucrose and corn syrup were added at the end, reaching a maximum content of 85% in the acidified sample (3 M HCl, pH 3·8). At levels of co-solute higher than 50% in the bulk, sucrose was complimented with corn syrup (dextrose equivalent of 42). This is a common practise in the manufacture of candy, since corn syrup is much cheaper than sucrose and also acts to inhibit or prevent crystallisation (Cramer, 1950).

Dynamic oscillatory measurements were performed at 10 rad/s and 0·5% strain on a controlled stress Carri-Med CSL 500 rheometer using parallel plate geometry of 40 or 20 mm diameter (increase of the available stress given by the formula: stress $= (2/\pi \times \text{radius}^3) \times$ torque) and a 1 mm gap. Gellan samples are notorious for contraction and the development of slippage between their gels and the measuring geometry at high levels of salt, e.g. above 250 mM NaCl in the case of 0·5% sodium gellan (Papageorgiou *et al.*, 1994*a*). Although the amount of monovalent cations present in these gels was roughly equal to the stoichiometric requirement of the polymer, representative samples were checked on a prototype rheometer (Richardson, 1991) using a design of perforated concentric cylinders capable of interlocking the system together (sample and geometry) so that tangential slippage is avoided (Richardson & Goycoolea, 1994). Typical rheological experiments included cooling scans from 90°C to 5°C at 1 deg/min and time sweeps at the lowest temperature for 2 h. At the end, networks were heated back to 95°C, in order to obtain their melting profiles, or subjected to increasing amplitude of oscillation to identify their linear viscoelastic response and failure pattern as a function of the parallel plate edge strain. Throughout this exercise, frequency sweeps were recorded on a regular basis for comparison between samples at different levels of co-solute. Finally intrinsic viscosity $[\eta]$ measurements were made on a Contraves Low Shear 30 rotational viscometer, using concentric cylinder geometry with inner (bob) and outer (cup) radii of 5·5 and 6 mm, respectively. Gellan solutions with the polymer in the disordered conformation were dialysed extensively against a 25 mM NaCl solution at 70°C and analysed at 50°C (Robinson *et al.*, 1991). Experimental values of relative ($\eta_{rel} = \eta/\eta_s$, where η and η_s are the viscosities of solution and solvent respectively) and specific ($\eta_{sp} = \eta_{rel} - 1$) viscosity were determined at gellan concentrations yielding $0{\cdot}2 < \eta_{sp} < 1{\cdot}0$ and extrapolation to zero concentration was made using the single point function $[2(\eta_{sp} - \ln \eta_{rel})]^{1/2}/c$ (Solomon & Ciuta, 1962). Both in solution and gel rheology, the measuring temperature was controlled to within ±0·2°C by a circulating water bath and measured by a thermocouple in direct contact with the sample. Loss of moisture was eliminated either by sealing the measuring geometry in an air-tight compartment or by covering the exposed edge of gels with a low viscosity silicone fluid (50 centistokes).

Table 1. Characteristic viscoelastic parameters of the 0·5% gellan sample at increasing levels of co-solute (0–85%)[a]

Sucrose and corn syrup (%)	Equilibrium modulus (*G′/KPa*)		T_g (°C)	Tan δ	
	90°C[b]	5°C[c]		5°C[c]	95°C[d]
00	—	1·53	31·1	0·020	0·035
10	—	2·29	32·4	0·021	0·051
20	—	6·21	33·6	0·017	0·040
30	—	9·12	37·3	0·013	0·021
50	—	11·05	41·9	0·015	0·024
60	0·04	—	>90	0·689	0·150
50 + 10	0·03	—	>90	0·570	0·114
50 + 20	0·12	—	>90	0·670	0·163
50 + 30	0·68	—	>90	1·354	0·136
50 + 35	6·12	—	>90	2·559	0·333

[a] Experiments were carried out at a frequency of 1·6 Hz (10 rad/s) and 0·5% strain.
[b,c] Beginning and end of a cooling run, respectively.
[d] End of the subsequent heating scan.

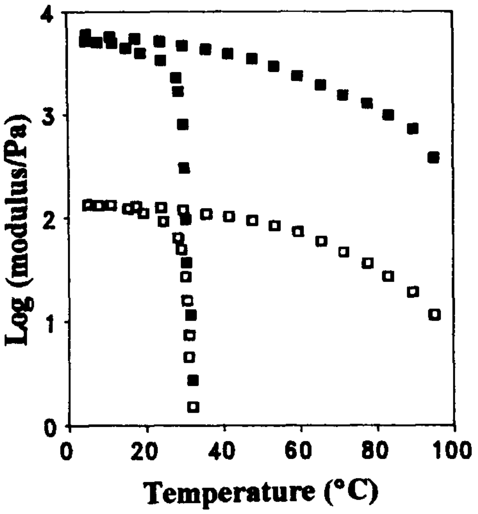

Fig. 1. Cooling and heating profiles of G' (■) and G'' (□) for the 0·5% gellan sample at 20% sucrose (scan rate: 1 deg/min; frequency: 10 rad/s; strain: 0·5%). Samples were set between the cooling and heating runs for 2 h at 5°C.

RESULTS AND DISCUSSION

Effect of sucrose, at levels up to 50% in the system, on the mechanical properties of gellan networks

As monitored by dynamic oscillation and demonstrated in Table 1, the systematic increase of sucrose (0–50%) in the 0·5% gellan series displaces progressively the onset of the disorder–order transition, defined as the temperature (t_g) at which the storage modulus (G') overtakes the loss modulus (G'') on cooling, to higher values (total temperature span of ≈11°C). Figure 1 reproduces a typical cooling scan (20% sucrose) that takes off sharply at T_g and approaches rapidly a constant value at 5°C ('pseudoequilibrium' modulus). Certainly, the effect of a subsequent isothermal period (2 h at 5°C) on the gel strength is negligible as shown by the initial values of the following 'melting' trace. Cooling transitions in combination with the heating profiles reveal a more than 50°C thermal hysteresis (dominant elastic response at 95°C in Table 1), similar to the delay in melting observed for the extensively aggregating agarose (Watase *et al.*, 1989) and κ-carrageenan (Piculell, 1993) polysaccharides. Between the isothermal monitoring and the heating run, a frequency sweep was performed on the gel (Fig. 2), at which time the structuring progress may be regarded as complete. The plot shows the shallow dip in G'' ($\omega \approx 2$ rad/s) observed in this and other gel systems, attributable to rheological processes with relaxation rates longer than the timescale of the frequency sweep (Higgs & Ross-Murphy, 1990). The overall effect of this extended gelling period is a solid-like spectrum with a flat G' trace, a dynamic viscosity (η^*) gradient that approaches the value of −1 and a small tan δ value (0·017) at 10 rad/s (Table 1). Finally, the partial melting of gellan structures with up to 50% sucrose in the system results in a less evident gel-like response at 95°C as indicated by the higher values of tan δ in Fig. 3 and in Table 1. At this stage, the rather limited evidence available on the structure formation of gellan gels argues for double-helical strands stabilised in large aggregates by extensively hydrated, gel-promoting cations (Robinson *et al.*, 1991; Grasdalen & Smidsrød, 1987). Our results, and in particular the substantial increase in gel strength accompanied by an early onset of the gelling process (Table 1), indicate that sucrose has an 'accelerating', stabilising effect on the ordered conformation of gellan gum. Arguing by analogy with the gelation process of κ-carrageenan (Smidsrød & Grasdalen, 1982; Gekko *et al.*, 1987), where water was found to participate in the formation of the polymeric tertiary structure (Gekko *et*

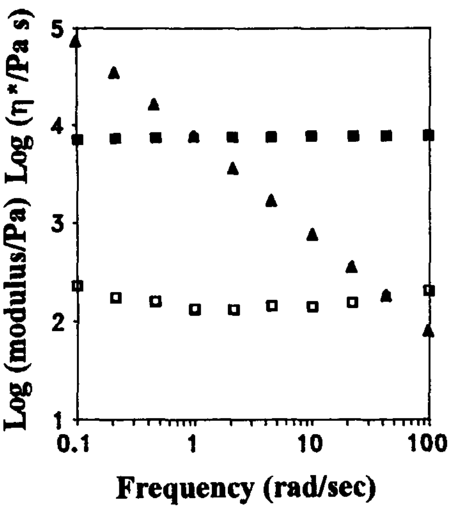

Fig. 2. Frequency sweep of G' (■), G'' (□) and η^* (▲) for the sample in Fig. 1 at the end of a 2 h isothermal period (5°C; 0·5% strain).

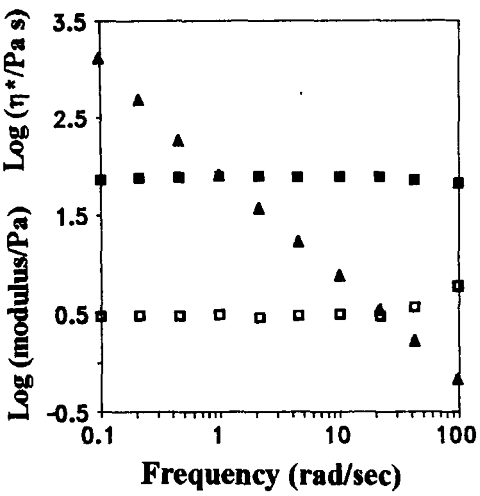

Fig. 3. Frequency sweep of G' (■), G'' (□) and η^* (▲) for the sample in Fig. 1 at the end of a heating scan and a 10 min equilibration time (95°C, 0·5% strain).

al., 1985; Gekko & Kasuya, 1985), one could suggest that the polyhydric sucrose molecules enhance the orientational correlation time of water structure thus replacing to a certain extent the polymer–normal water hydrogen bonds with gel-stabilising, polymer–polymer interactions. However, further detailed investigation is required to elucidate the effect of water, and how it is modified by sugars in the above concentration range and electrolytes, on the conformation and network topology of deacylated gellan chains.

Molecular interpretation of the plateau zone in a high-solids gellan system

Having considered briefly the molecular associations that give rise to structural stability of gellan gels in the sucrose range from 0 to 50%, we now attempt a more detailed investigation of the mechanical properties of gellan networks at amounts of co-solute (50–85%) with practical importance for the confectionery (Poppe, 1992). Solubility limitations preclude incorporation of sucrose at concentrations in excess of 60% and the required levels of co-solute in the product are usually met by adding corn syrup. In this study the problem of sugar crystallisation was avoided by adding corn syrup (10–35%), after it was verified that 60% sucrose and the mixture of 50% sucrose with 10% corn syrup in the 0·5% gellan samples produce the same response upon oscillatory testing (Table 1). In the illustrative evidence that follows, we believe that there is substantial resemblance with the pattern obtained for the transition of poly(*n*-octyl methacrylate) macromolecule from the rubber- to glass-like state, as described by the classic work of Ferry (1980), and thus interpretation of the gellan system transition will be based on the same argument. To open a short parenthesis, the polymer of octyl methacrylate is the stereotype of an uncross-linked (physically interacting) chain of high molecular weight with long, flexible side ester groups which allow only a small volume of the bulk to be occupied by the main backbone. Although the relaxation time of its interactions is much shorter than the viscoelastic character exhibited by the cross-linked polymers (e.g. vulcanised rubbers), they are able to show a pseudo-equilibrium zone with rubber-like consistency at high enough frequencies whereas at longer timescales of measurement they resolve into a dominant viscous component (terminal zone).

In Figure 4(a) the storage and loss moduli are plotted against the frequency of oscillation for the 85% co-solute gellan sample at 90°C, before the onset of a cooling scan. Clearly the viscoelastic properties of 0·5% gellan in the presence of high levels of solids (Table 1) contrast strongly with the temperature profile of shear moduli at amounts of sucrose below 50% (Figs 1 and 2). Thermodynamic studies supplemented by nuclear magnetic resonance measurements have demonstrated that the relaxation rates of hydrogen bonding association between water molecules and solute are enhanced in the case of small and simple carbohydrates (Franks *et al.*, 1972; Tait *et al.*, 1972). As a result water is preferably involved in sucrose–water interactions rather than in water–polymer associations which, of course, are necessary for stabilisation of its tertiary structure and the formation of a continuous network. Increasing amounts of sugar in the system destabilises further the hydrogen bonding structures of polymer–solvent and enhances formation of individual ordered sequences. It is conceivable therefore, that under conditions of extreme solvent deficiency (sucrose concentration ≥ 60%) the lag between conformational ordering and network completion allows only the formation of low functionality macromolecular assemblies, comprised of

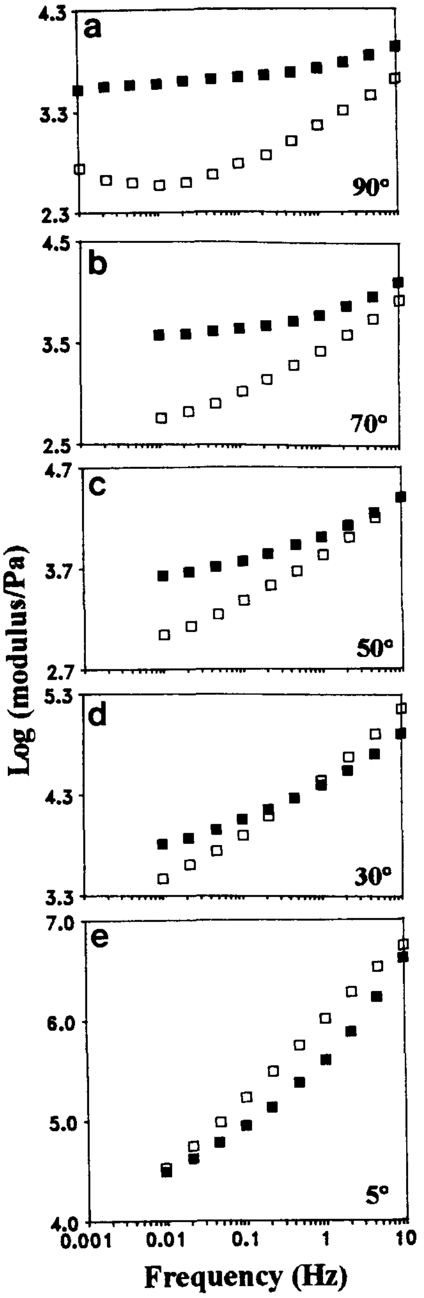

Fig. 4. Storage (■), and loss (□) moduli plotted against frequency of oscillation at different temperatures (a–e) during a cooling scan for a 0·5% gellan sample at 50% sucrose and 35% corn syrup (1 deg/min scan rate; 0·5% strain).

thermally stable, ordered strands. As shown in Fig. 4(a), a solid-like response is noted at temperatures as high as 90°C, giving the superficial appearance of a rubbery structure between the experimental frequencies of 0·001 and 1 Hz. Furthermore the 'equilibrium moduli' of 60–85% co-solute, rubber-like gellan gels at 90°C (i.e. before they undergo a change of state at lower temperatures) disrupt the upward pattern of modulus development in a 'conventional' gellan network at equilibrium (2h isothermal sweep at 5°C for levels of sucrose ≤ 50% in the blend).

The main factors expected to restrain ordering of the gellan network are the high viscosity of sucrose–corn syrup mixture that prevents long chains from disentangling or diffusing in the bulk rapidly and the lack of solvent that confines the polymer in a small proportion of the sample volume and makes the chain segments unable to assume correct positions for the formation of intermolecular bonding sites. Intrinsic viscosity measurements ($[\eta] = 4{\cdot}49$ dl/g) argue for a reduced rigidity in the plateau zone due to a limited number of transient, enthalpic junction zones interconnecting the macromolecular ordered assemblies of the polymer as opposed to the transient, topological hooks of a continuous superentanglement network. Adopting a coil overlap parameter (concentration × $[\eta]$) of 4 for the critical concentration (c^*) at which the expanded coils of linear polysaccharides start to overlap and entangle (Morris *et al.*, 1981), the value of 4·49 dl/g requires a minimum of ≈0·9% polymer for the same process to commence in the case of gellan gum. Furthermore, dilute solutions of purely topological systems (e.g. guar gum) (Richardson & Ross Murphy, 1987) at concentrations well below the c^* create the mechanical spectra of Newtonian liquids instead of the temporary network profile achieved by gellan chains at the experimentally accessed frequency range of Fig. 4(a) ($\omega \geq 0{\cdot}001$ Hz).

Qualitatively, the characteristic development of viscoelastic functions in the plateau zone corresponds to the blending of long topological changes (chain slippage), mainly contributing to relaxation in the terminal zone, with short configurational vibrations of the network strands, primarily seen in the transition zone from rubber- to glass-like consistency. Consequently, in the intermediate frequency range of the plateau zone the long-lived cross-links between chain segments are effectively permanent, resulting in relatively constant G' values whereas the rapid relaxation time of motions involving configurational changes of strands generates a dip in the G'' trace.

The transition from rubber- to glass-like consistency in sucrose-saturated gellan networks

For many synthetic polymers including the poly(*n*-octyl methacrylate), the effect of temperature on viscoelastic features is quite impressive. An experimental temperature range of about 150°C covers in most of the cases both the glassy and rubbery states with the transition zone unravelling a huge change in the magnitude of measured parameters. In the case of biopolymer dispersions, the accessible temperature range is limited between the melting and boiling points of water and realistic measurements are obtained between 90 and 5°C. However, mechanical spectra of the 85% co-solute gellan sample taken at temperatures (T) of 70, 50, 30 and 5°C during a cooling scan (Fig. 4(b)–(c)), following the frequency sweep at 90°C (Fig. 4(a)), suggest that the transition zone between the two phenomena can be captured in the 0·5% gellan preparations with 85% co-solute. As observed in the transformation of shape for characteristic parameters of synthetic materials, the $G''(T)$ changes very rapidly so that at 5°C the loss modulus has overtaken the values of G' at each measured frequency. Reduction of the long-range configurational motions due to immobilisation (freezing out) of large segments in the gellan network would allow the short relaxation times (freezing in) to develop a viscous rather than an elastic identity in the system, thus offering an interpretation of the above phenomenon. Thermal motions of high molecular weight gellan assemblies about equilibrium positions, freely rotating shorter polymeric components and vibrating dangling ends at the fringes of the network should contribute to the out of phase signal which changes by four orders of magnitude.

The physical state of sucrose–corn syrup mixtures throughout the working temperature range, of course, comes into question. Figure 5 illustrates a representative frequency sweep of such a preparation at 5°C (50% sugar with 35% corn syrup). There is little variation of dynamic viscosity with frequency and G'' dominates over G', although with increasing frequency G' approaches G'' due to storage of energy by contortion of the dimers (number average molecular weight of the blend) into strained conformations (Ross-Murphy, 1984). Additionally, the values of storage and loss moduli remain proportional to ω^2 and ω, respectively (i.e. constant slopes of 2 and 1 on a logarithmic plot), expected from the modulus equations of an infinite Maxwell model: $G' = J_e\eta\omega^2$ and $G'' = \eta\omega$ for Newtonian liquids or viscoelastic solutions at very low frequencies, where J_e is the equilibrium compliance in a viscoelastic solid and η is the steady shear viscosity at zero shear rate (Ferry, 1980). The overriding conclusion from Fig. 5 is that the experimental co-solute combinations remain in an equilibrium state whose solution viscosity is more than two powers of ten below the shear thinning viscosity of the gellan-induced glassy zone transition at 0·01 Hz. The thermal energy of sucrose and corn syrup molecules should force them to execute coordinated movements and hence to augment the viscous component of the network alongside its aforementioned structure defects at the glass transition temperature (T_g). The development of an out-of-phase element as a function of co-solute concentration in the 0·5% gellan system is shown in Fig. 6. Clearly, higher amounts of the syrup act as stronger antiplasticizing agents on the onset of glass transition (point of interception between the G' and G'' traces) which shifts eventually to experimentally accessible temperatures, i.e. about 14 and 38°C for the 80 and 85% samples, respectively. At lower levels of co-solute (below 70%) the plasticizing action of water on the transformation of gellan chains reduces the beginning of the transition zone to temperatures below 5°C. Overall, the sucrose–corn syrup blend behaves as a 'sol-fraction' whose molecular species are not attached to the gellan network, thus being unable to support the imposed stress and subsequently to advance the elasticity of the system. It is well known that the transformation from a rubbery material to a glassy substance and *vice versa* occurs over the same temperature band for synthetic polymers. Similarly, heating runs of the samples in Fig. 6 produce identical values for the onset of glass transition and overlapping traces for the thermally reversible moduli; illustrated for the 80 and 85% preparations in Fig. 7. The relatively broad glass transition and the lack of thermal hysteresis is antithetic to

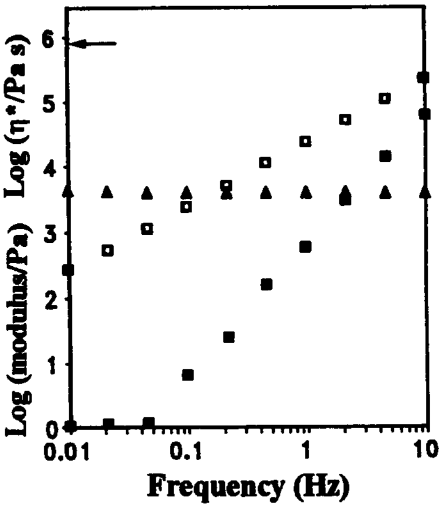

Fig. 5. Mechanical spectra of G' (■), G'' (□) and η^* (▲) for a sucrose–corn syrup blend (50 and 35%, respectively) at 5°C and 0·5% strain. The arrow on the ordinate signifies the viscosity of a 0·5% gellan plus 85% co-solute sample at a frequency of 0·01 Hz (remaining conditions as above).

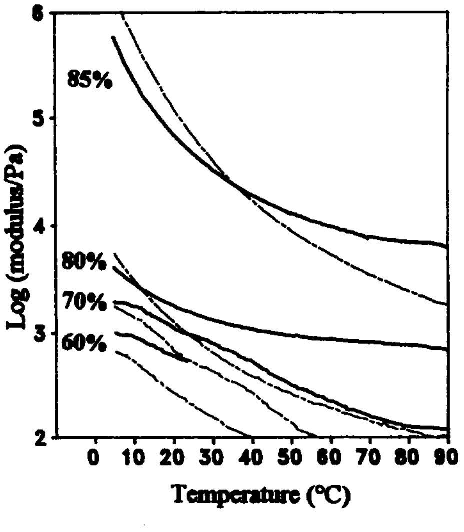

Fig. 6. Cooling traces of G' (——) and G'' (— — —) plotted against temperature for a 0·5% gellan sample at levels of co-solute shown by the individual runs (conditions as in Fig. 1).

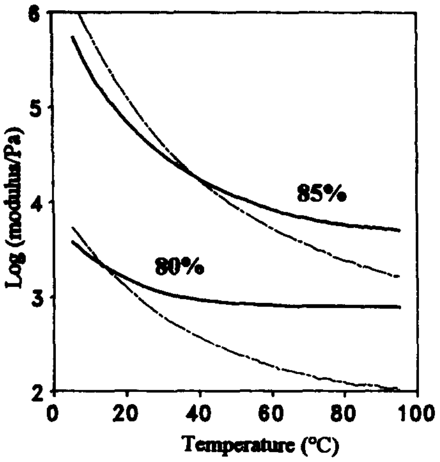

Fig. 7. Glass transition zone shown by the interception of G' (——) and G'' (– – –) traces, obtained during heating of a 0·5% gellan sample at 80 and 85% of co-solute (conditions as in Fig. 1).

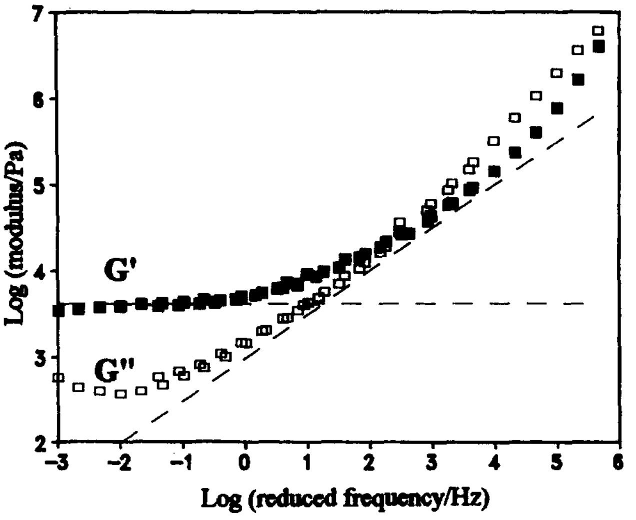

Fig. 8. Time–temperature superposition for the mechanical spectra of Fig. 4 against frequency reduced to 90°C.

the sharp discontinuity of the gellan transition, where exothermic ordering is taking place, and the more gradual melting of Fig. 1. In accordance with the above, changes in the physical state of gellan networks in a high-solids environment reverse the temperature profile of networks produced, with dominant elastic consistencies being developed at 95°C instead of the temperature of 5°C which is now associated with the glass transition region (tan δ values in Table 1).

Application of the method of reduced variables to the viscoelasticity of low solvent gellan–solute systems

Williams *et al.* (1955) demonstrated that the physical parameters of high molecular weight polymer systems, acquired at different temperatures on a logarithmic time scale, can be reduced to a common temperature throughout an extremely long frequency range. The empirical time–temperature superposition of shear moduli into one master curve is implemented by the following expression:

$$\log\{G(T)/G(T_0)\} = -C_1(T - T_0)/(C_2 + T - T_0),$$

where C_1 and C_2 are functions of the fractional free volume at a reference temperature T_0 and of the expansion coefficient of free volume. The term $G(T)/G(T_0)$ from the WLF equation is known as the shift factor (α_T) since it implies that a value of shear modulus measured at temperature T and experimental frequency ω is equivalent to the shear modulus at temperature T_0 and frequency $\omega\alpha_T$. Work on the method of reduced variables indicates that data fitting should be attempted only when the extent of overlapping between experimental shapes at different temperatures is considerable and the temperature dependence of shift factor is identical for long and short relaxation functions or, in other words, both the G' and G'' curves match at the same set of α_T values. Treatment of the data in Fig. 4 according to the time–temperature superposition principle for the reference temperature of 90°C generates a best-fitting set of apparent log a_T values (0, 0·60, 1·51, 2·59 and 4·65 for the 90, 70, 50, 30 and 5°C, respectively) and the logarithmic plots of G' and G'' in Fig. 8. Theoretical postulates of the modified Rouse, bead-spring model predict values around 10^7 Pa for the shear moduli and slopes of 1/2 for their curves in the glass transition zone of individually moving polymer molecules (Ferry, 1980). Similar to the synthetic counterparts, gellan–solute mixtures achieve values of the order of 10^7 Pa in the transformation region but the experimental features of both types of polymers show a progressive increase of slope on a logarithmic display. For practical purposes, the theoretical line with slope of 1/2 is drawn as a tangent to the experimental curve and its intercept with the extrapolation of the relatively frequency independent G' trace at the plateau zone gives the frequency boundary between transition and equilibrium (ω_{tr}). In the case of gellan samples, a value of $\omega_{tr} \approx 17$ Hz is obtained at 90°C that signifies the onset of a frequency regime with a prominent viscous response.

Moving to temperatures below 5°C at the experimental frequency of 1·6 Hz or to frequencies above 10^6 Hz at the experimental temperature of 90°C the viscoelastic properties of a gellan–solute system should enter the glassy zone. In this region the elastic character is dominant again because the thermal motions are restricted to stretching and bending of chemical bonds. Obviously, a complete picture of glass formation should be associated with the freezing out of the configurational motions of short polymeric sequences and soluble oligomers. Prediction of the glass transition temperature (T_g) for the high-solids gellan sample as a whole is of practical importance as well as of theoretical interest. Therefore the calculation of T was attempted following the empirical procedure applied by Ferry (1980) to the viscoelastic functions of poly(*n*-octyl methacrylate). The values of C_1 and C_2 were estimated for three different reference temperatures, namely 90, 50 and 5°C, using the WLF equation and the following relations:

$$C_{1R} = C_{1R'}C_{2R'}/C_{2R'} + T_R - T_{R'}$$
$$C_{2R} = C_{2R'} + T_R - T_{R'},$$

where the subscripts R and R′ denote different reference temperatures for a particular combination. The last formula allows the introduction of the Vogel temperature:

$$T_\infty \equiv T_R - C_{2R} = T_{R'} - C_{2R'},$$

at which, regardless of the choice of the reference temperature, the log α_T values should approach infinity according to the WLF equation. A useful guide on the quality of time–temperature superposition achieved for a given set of experimental data is to include the T_∞ in the WLF equation and then to draw a graph of log α_T versus $(T - T_R)/(T - T_\infty)$. A valid reduction of viscoelastic functions should produce a straight line that passes through the origin for a single value of T_∞. Processing of the gellan–solute data produces the following values of C_1: 4·62, 6·09, 9·47 and C_2: 165·98, 125·98, 80·98 for the reference temperatures of 90, 50 and 5°C, respectively. Gratifyingly, the value of T_∞ (197°K) derived from this result yields a perfectly linear relationship for the rewritten WLF equation:

$$\log \alpha_T = C_{1R}(T - T_R)/(T - T_\infty),$$

as shown in Fig. 9. The observation that T_∞ is usually about 50°K below the glass transition temperature would indicate that the T of the gellan–solute glass is ≈ −26°C. Roos and Karel (1991*a*,*b*) have studied in detail the plasticizing effect of water on the glass transition temperature of common sugars and demonstrated that highly concentrated sucrose solutions remain unfrozen below 0°C, thus going through the process of vitrification at about −25°C for a water content of 15% in the product. The consistency in T values of sugar solutions with or without polymeric material and the broad temperature range of the glass transition for the 0·5% gellan plus 85% solute sample (onset at 37°C, T at ≈ −26°C) argues for incompatible phenomena in the gellan–solute system and gradual vitrification of the two components in the blend. First that of gellan (high molecular weight species) commencing at temperatures above the freezing point of water (Fig. 7), with the sucrose–corn syrup mixture joining the vitrification process perhaps at sub-zero temperatures (low number average molecular weight species), both components and thus the system as a whole achieving T conditions at about −26°C.

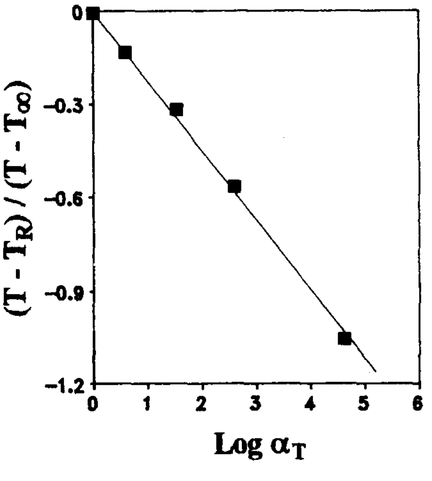

Fig. 9. Linearised form of the WLF equation as a function of T_∞ (197°K) derived from the superposition process of Fig. 8.

This endeavour is part of a bigger exercise on the structural and textural properties of single and mixed gellan–gelatin systems in the presence of high levels of sugars. As mentioned in the introduction, a study on the gellan-gelatin aqueous gels in the absence of co-solute provides a background understanding of the macromolecular organisation in the composite system (Papageorgiou *et al.*, 1994*a*). Currently we are looking at the effect of sugars on single gelatin gels and in combination with gellan gum, thus aiming to familiarise ourselves with the behaviour of food systems in the rubbery and glassy state.

ACKNOWLEDGEMENTS

We thank the Kelco Division of Merck and Co., Inc. (USA) for financial support of this investigation. We also thank Drs G.R. Sanderson and T.A. Talashek (Kelco) and our colleagues, Professor E.R. Morris and Miss L.E. Willoughby, for discussions and practical assistance.

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