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Development of composite structures in the gellan polysaccharide/sugar system

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A sensitive in-house rheometer and two measuring configurations were employed to examine the structural properties of gellan/sugar preparations at stoichiometric levels of added calcium ions. Perforated cylinders allowed recording of the gelation process in slippery gellan gels (from 0 to 40% sucrose) whereas systems with greater amounts of co-solute could also be analysed with a flat cone-and-plate geometry. The sharp sigmoidal transition of the highly enthalpic aggregated helices in aqueous or low sucrose (up to 30%) gellan gels was observed at temperatures below 60°C upon cooling (1°C/min). This gave way at 60% sucrose and beyond (high solids regime of sucrose plus corn syrup) to a thermally stable structure with a low modulus monotonic temperature profile (from 90 to 5°C). At the intermediate range of co-solute (30 to 60%) a bimodal cooling profile was recorded which was rationalised on the basis of a composite network comprising lightly cross-linked and therefore flexible gellan chains, and rigid aggregates. In the absence of external calcium, at the intermediate level of solids, only the aggregated type of network was formed at the low temperature end, apparently supported by the batch salts. Therefore, the added calcium facilitated stabilisation at the top temperature end of limited intermolecular associations between the thermally vibrant gellan chains in a sugar (>40%) environment. © 1997 Elsevier Science Ltd

INTRODUCTION

The discovery of gellan gum was the result of a drive in the mid 1970s to produce readily available microbial polysaccharides of controlled molecular weight and purity, thus eliminating climatic, geographical and political variations that can affect the physical properties and availability of biopolymers from natural sources (Morris, 1995). Gellan gum is an extracellular exudate secreted during the aerobic fermentation of *Sphingomonas elodea* (formerly known as *Pseudomonas elodea*), and it has been patented by Kelco after preliminary research into its primary structure and physical properties (Kang *et al.*, 1982). The increasingly difficult and costly process of clearing a microbial polysaccharide for food use makes gellan a potentially important functional agent; unrestricted food approval has been granted by the US Food and Drug Administration in 1994 and the European Council in 1995 (Anon, 1995).

Gellan is a linear polysaccharide of a repeating sequence comprising two β-D-glucose and one β-D-glucuronic acid residues which are (1→4) glycosidically linked, with the fourth residue, α-L-rhamnose, being (1→3) linked with the next tetrasaccharide repeat unit (Jansson *et al.*, 1983). In the native form, it also contains glyceryl and acetyl groups, which are removed during commercial production, and it is the deacylated gellan we speak of in the present study. Since the discovery and determination of its primary structure, a flourishing literature has demonstrated conversion from a disordered coil conformation in solution to a coaxial double helix whose aggregation and subsequent network formation is influenced by the concentration and type of counter ions present. Several well written reviews can direct the reader to scientific or technological aspects of particular interest, and there is no need to elaborate further here (Sanderson, 1990; Kang and Pettitt, 1993; Chandrasekaran and Radha, 1995).

In the meantime, a mechanistic understanding of the phase behaviour in gellan/biopolymer mixtures has been accumulated. Complex coacervation with potential applications to pharmaceutical products has been

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reported for acidic gellan/gelatin mixtures in the absence of salt (Chilvers and Morris, 1987). Addition of NaCl eliminates the attractive interactions between the two polymers and creates a phase separated system in which either polymer can form the continuous matrix depending on polymeric composition and ionic strength (Papageorgiou *et al.*, 1994a). Gellan continuous gels are formed without refrigeration, are thermally stable and yet retain a good flavour release upon mastication due to the low polysaccharide to protein ratios ($< 1/50$). Substitution of alginate for gelatin creates composite gels substantially stronger than the corresponding sum of the two components (Papageorgiou *et al.*, 1994c). However, samples remain elastic with gellan forming a strong filler within a weak alginate matrix, an arrangement that can be used in the making of water desserts.

In contrast with the above, there is little information on the structural properties and texture of gellan/co-solute systems. A large-deformation study of gellan/sucrose blends by Willoughby and Kasapis (1994) showed that increasing amounts of calcium chloride result in a reduction of the concentration of sucrose required for maximum network strength. It was suggested that calcium ions and sucrose complement each other in the stabilisation of ordered structures of the gellan network. Sucrose inversion to glucose and fructose produces stronger gellan gels, which might indicate steric hindrance of the aggregation process of the polysaccharide as the molecular size of the co-solute increases (Gibson, 1992). On the other hand, the effect of co-solutes on the structural properties of the industrially important cold-setting polysaccharides, κ-carrageenan and agarose, has been extensively investigated (for a review of the subject see Nishinari *et al.*, 1995). Small deformation experiments were carried out on cylindrical disks of gels containing high concentrations of the polysaccharide, e.g. agarose ranged from 2 to 12%. Networks were quite strong, i.e. the measured shear modulus was in excess of 10^5 Pa at 15°C and its variation was followed with increasing temperature. In the present work, we use a sensitive rheometer to monitor the development of structure during the cooling of gellan/sugar samples and report on a behaviour that might be of general applicability in polysaccharide/sugar systems.

MATERIALS AND METHODS

The deacylated gellan gum (Kelcogel; batch number 77109A) was supplied by The NutraSweet Kelco Company. Atomic absorption analysis produced the following average ionic composition: Na^+ 6330 ppm; K^+ 46800 ppm; Ca^{2+} 3600 ppm; and Mg^{2+} 1140 ppm. This corresponds to a conversion of 115%, which is typical of the gellan polysaccharide containing a slight excess of ions over and above the amount needed for stoichiometric equivalence. In a previous investigation we used GPC analysis and reported that the average molecular weight of a gellan coil was found to be $1.64 \pm 0.1 \times 10^6$ daltons (Al-Ruqaie *et al.*, in press). The polysaccharide was used as received without further purification.

Gellan samples were prepared in distilled water at 90°C using mechanical stirring for 15 min. Following dissolution, appropriate amounts of sucrose or mixtures of sucrose within corn syrup and calcium chloride were added to produce systems with the required levels of polysaccharide, co-solute and ionic strength. The corn syrup has a dextrose equivalent of 42, the water content is 19%, and its composition in this work refers to dry solids. Samples were loaded on the preheated measuring geometry of the rheometer and covered with silicone fluid to prevent evaporation. Temperature ramps were then implemented from 90 to 5°C at a scan rate of 1°C/min and a frequency of 10 rad/s (0.5% strain). At the end of the cooling runs, mechanical spectra were recorded in the frequency range of 0.1 to 100 rad/s. Frequency sweeps were also taken for selected preparations at 90°C before implementing the cooling run.

As with agarose and κ-carrageenan, aqueous gellan solutions undergo sharp disorder-to-order and aggregation processes which produce contracted brittle gels with a notable degree of syneresis and slippage. Inevitably, breakdown of adhesion between the sample and the flat surface of a plate or a cone results in an artificial drop in the magnitude of the solid-like response. Figure 1 emphasises the nature of the problem recorded some time ago in a preliminary examination of a gellan polysaccharide that was ion exchanged in the sodium form. If a customary smooth cone-and-plate geometry is selected, we record the rapid onset of network formation but then the values of the storage modulus (G') take an unrealistic tumble due to loss of adhesion to the cone and plate as the gel shrinks and undergoes syneresis. At the same time, erratic fluctuations on the trace of the loss modulus (G'') are recorded. However, this slippage can be avoided if a different measuring geometry is employed. This is a three-piece device with a smooth outer cup, a perforated middle cylinder, and a perforated inner cylindrical bob with the first two parts being fastened together as one unit (for more information and a drawing of the device see Richardson and Goycoolea, 1994). Gelation locks the polysaccharide network and the measuring geometry together, thus preventing catastrophic slippage. This is verified in Fig. 1 where the initially rapid increase in the magnitude of storage and loss modulus is maintained in the form of a continuous plateau and a low ratio of G'' to G' ($\tan \delta = 0.03$).

The above measuring system was used, therefore, to obtain reproducible results from the gellan/sucrose preparations of the present study. However, slippage and syneresis effects are eliminated when the co-solute content exceeds 40% since the high levels of sucrose, and as we shall argue, the changing nature of the gellan network contribute to the adhesiveness and pliability of

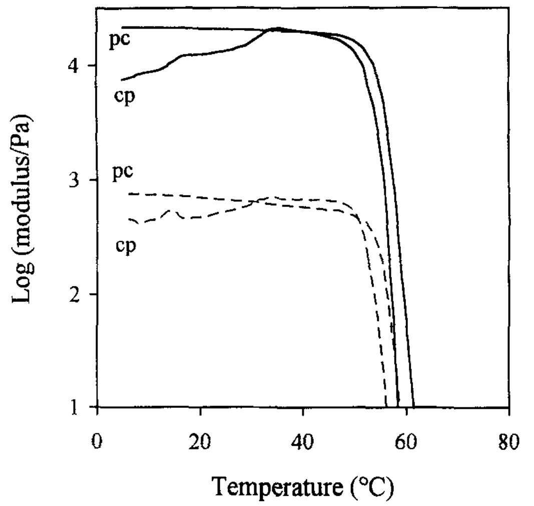

Fig. 1. Variation of G' (———) and G'' (- - -) during controlled cooling (1°C/min) of 0.7% gellan in the sodium form with 0.4 M added NaCl. Perforated cylinders (pc) and cone-and-plate (cp) measuring geometries have been used (0.1% strain; frequency of 10 rad/s).

the system. In the course of this investigation, we observed that beyond this level of co-solute a smooth-surface geometry can be employed with equal validity, in this case, a truncated cone and plate.

RESULTS AND DISCUSSION

Descriptive account of a structural process recorded for gellan samples with a low sucrose content

The type of behaviour observed here for gellan has also been seen in κ-carrageenan and agarose systems, and relates to the temperature dependence of network formation at relatively low levels of co-solute (up to 30% sucrose in our case). Figure 2 (a) reproduces the cooling profiles of the storage modulus for a range of gellan concentrations (0.1 to 0.9%) at 7 mN added $CaCl_2$. Higher amounts of the polysaccharide result in earlier gelation as monitored by the sharp rise in G' traces over a narrow temperature range. Thus, solutions essentially indistinguishable from water convert into stiff gels with tan $\delta \approx 0.023$, a value that is maintained over the typical range (0.1 to 100 rad/s) of a frequency sweep (not shown here). The systematic increase in the final values of G' as a function of polymer concentration (Fig. 2(a)) was also recorded by Nakamura *et al.* (1993) when gellan solutions were quenched at temperatures well below that of the conformational transition (i.e. 20°C). As the gellan concentration increases in Fig. 2 (a), however, the relative magnitude of network reinforcement decreases with the levelled G' traces approaching a constant value. This phenomenon can be related to the observation of Tang *et al.* (1996) where compression tests of gellan gels at different concentrations indicated a correspondence between maximum yield stress and a calcium ion level of 0.5 per carbohydrate group in the repeat unit. The 7 mN of added Ca^{2+} in our work is approximately the stoichiometric equivalent of 0.5% gellan but it is not quite enough for maximum network strength at higher concentrations of the polysaccharide.

The setting behaviour of gellan with up to 30% co-solute is shown in Fig. 2 (b). The sharp gelling process is again evident but displaced to higher temperatures (by anything from 10 to 20°C). Similarly, the G' traces reach a maximum point and then level off at values higher than for their aqueous counterparts. There is also a rise in the tan δ values to about 0.036 due to the presence of sucrose which usually contributes to the 'sol-fraction' of

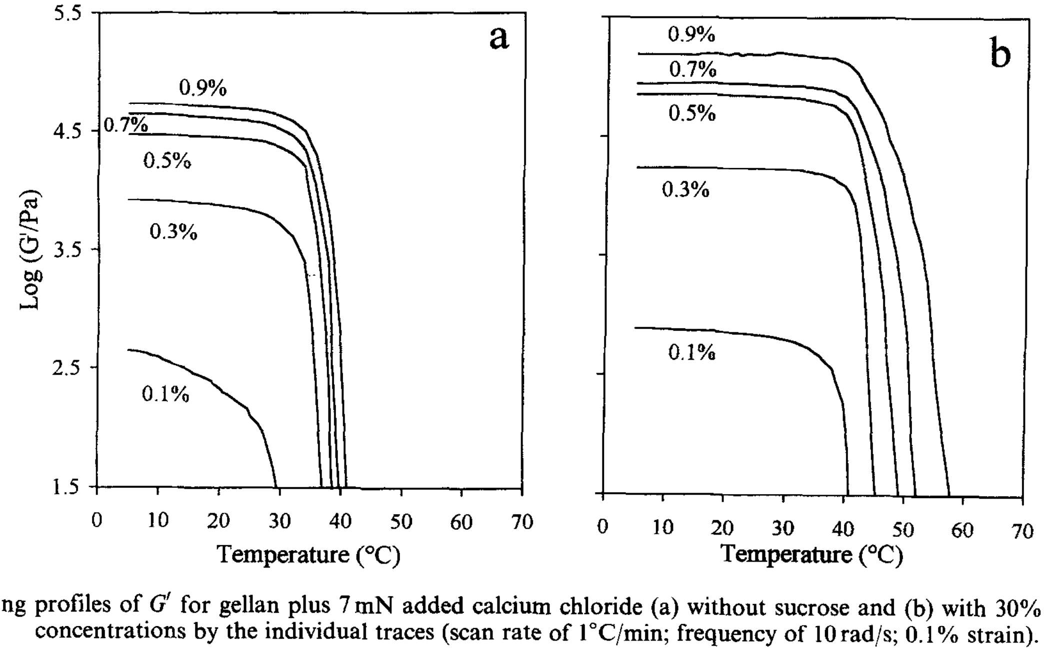

Fig. 2. Cooling profiles of G' for gellan plus 7 mN added calcium chloride (a) without sucrose and (b) with 30% sucrose. Gellan concentrations by the individual traces (scan rate of 1°C/min; frequency of 10 rad/s; 0.1% strain).

the network. All in all, the profile of structure formation at 30% sucrose has obvious parentage to that seen in the aqueous preparations with an increased mechanical and thermal stability. Taking into account that partial replacement of sucrose with calcium chloride did not alter the stability (breaking stress) of compressed gellan gels (Willoughby and Kasapis, 1994), it is suggested that the accelerated gelation properties of gellan/sucrose systems in Fig. 2 (b) is the result of additional ordered associations between the polymer chains. It has been modelled that formation of thermodynamically stable helices in strong gellan gels requires water bridging (Chandrasekaran and Radha, 1995), and it seems that this mode of interaction is sustainable at 30% sucrose. Workers have proceeded along these lines for the κ-carrageenan and agarose co-solute systems (Nishinari *et al.*, 1995).

The second process of transformation from rubber-like to glass-like consistency in high-sucrose gellan samples

This part of the discussion will deal briefly with the second type of rheological behaviour which we encountered at co-solute levels between 60 and 85%. Studies at such low water content have been confined to relatively high biopolymer/co-solute ratios (> 1:1) and recently the state of affairs in this area has been reviewed (Kalichevsky *et al.*, 1993). In our formulations the biopolymer concentration was reduced well below that of the co-solute and the resulting viscoelasticity was first checked on gellan (Papageorgiou and Kasapis, 1995). Fig. 3 (a) reproduces the development of *G′* and *G″* on cooling (1°C/min) for 0.5% gellan with 70% co-solute (50% sucrose plus 20% glucose syrup). Whereas in Fig. 2 systems remain liquid-like at the top temperature end, this time the storage modulus attains greater values than the trace of the loss modulus even at 90°C (highest accessible temperature). Systems were judged to be viscoelastic solids since mechanical spectra yielded *G′* > G″, no frequency dependence on *G′*, and a pronounced minimum on the *G″* trace (not shown here). Cooling of the sample failed to generate the sharp sigmoidal transition of Fig. 2. The two traces converge at the bottom temperature end and hence produce a relatively less solid-like structure than that at 90°C. Clearly this is in direct contrast with the low temperature profile in Fig. 2, thus completing the reversal of behaviour between the two co-solute ranges.

On raising the concentration of co-solute the *G″* trace catches up and then overtakes the course of *G′*. This is illustrated in the frequency sweep of Fig. 3 (b) for 0.5% gellan plus 50% sucrose and 35% corn syrup at 5°C (Papageorgiou *et al.*, 1994b). A rather spectacular dependence of viscoelastic functions with frequency of oscillation is observed with samples behaving like extremely viscous biopolymer 'solutions'. Systematic screening of viscoelastic properties in the concentrated regime (60–85% solids) demonstrated that the transition from solid-like to liquid-like response can equally be accomplished by reducing temperature or increasing frequency, thus implementing the so-called time–temperature superposition principle. The above transformation was fitted using the Williams–Landel–Ferry kinetic scheme in combination with the free volume approach previously largely confined to synthetic polymer work (Ferry, 1980). It was asserted that, similar to its synthetic counterparts, gellan/co-solute blends transform from a rubbery solid to an increasingly vitrified system (glass transition regime). The same approach has also been implemented for high solids gelatin and high methoxy pectin samples, and is therefore a useful avenue for exploring rubber-like and glassy materials of biological origin (Ong *et al.*, in press; Al-Ruqaie *et al.*, in press).

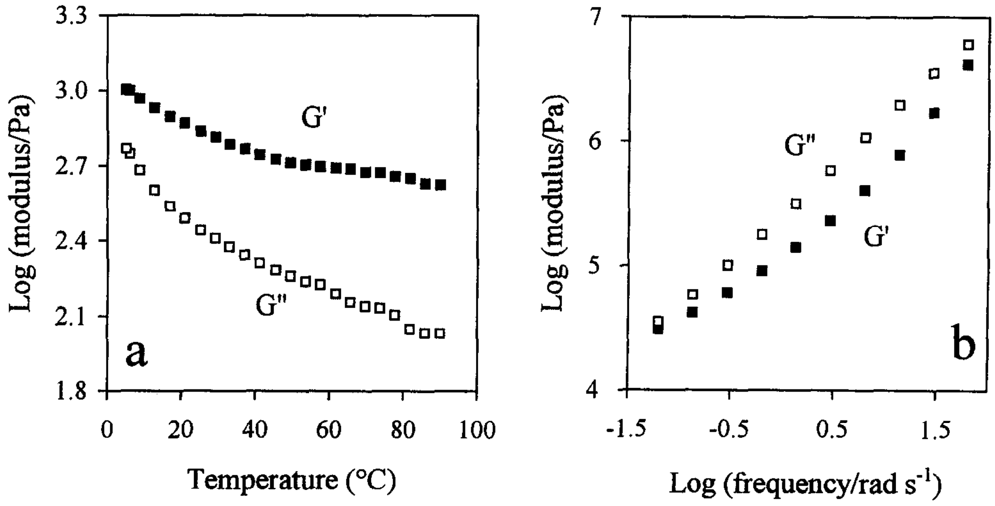

Fig. 3. *G′* and *G″* development during (a) cooling of 0.5% gellan with 50% sucrose and 20% corn syrup (frequency of 10 rad/s; scan rate of 1°C/min), and (b) mechanical spectrum at 5°C of 0.5% gellan with 50% sucrose and 35% corn syrup.

Featuring the gradual shift from the first to the second process at intermediate levels of sucrose

Small deformation measurements of gellan samples with a sucrose content between 30 and 60% unveil the mechanism of transformation between the two foregoing processes (Fig. 2 and Fig. 3, respectively). Figure 4 (a) shows values of *G*′, *G*″ and tan *δ* recorded for 0.5% gellan with 40% sucrose on cooling (1°C/min) from the disordered state at high temperature (7 mN $CaCl_2$ has also been added). Although the abrupt increase and subsequent levelling off of both moduli is congruent with the profiles in Fig. 2, there appears to be an earlier distinctive feature of structure which for *G*′ starts to rise at 62°C and merges with the main signal at about 50°C. This event introduces an unusually prominent spike in the temperature course of the tan *δ* trace. Addition of an extra 5% of sucrose causes a massive change in the cooling behaviour of our sample (Fig. 4 (b)). This time the temperature of structure formation is raised to be in excess of 90°C as, indeed, noted for the high solids gellan sample (70% co-solute) of Fig. 3 (a). The variation of *G*′, *G*″ and complex dynamic viscosity (η^*) as a function of frequency of oscillation at 90°C verifies the predominance of a real structure at the top temperature end (Fig. 4 (c)). The network may be weak but the storage modulus values are constant and remain well above the curved spectrum of loss modulus throughout the accessible frequency range.

Cooling of the sample in Fig. 4b shows a smooth development in viscoelastic response which is interrupted abruptly at about 35°C by another sharper wave of structure formation. The striking switch between processes is also illustrated in the tan *δ* trace which initially increases almost exponentially (i.e. build up of liquid-like character) but then drops rapidly over the second transition, passing through a minimum as the *G*′ and *G*″ traces form the expected plateau at the bottom temperature end. It appears, therefore, that the vestigial and early (62°C) forma-

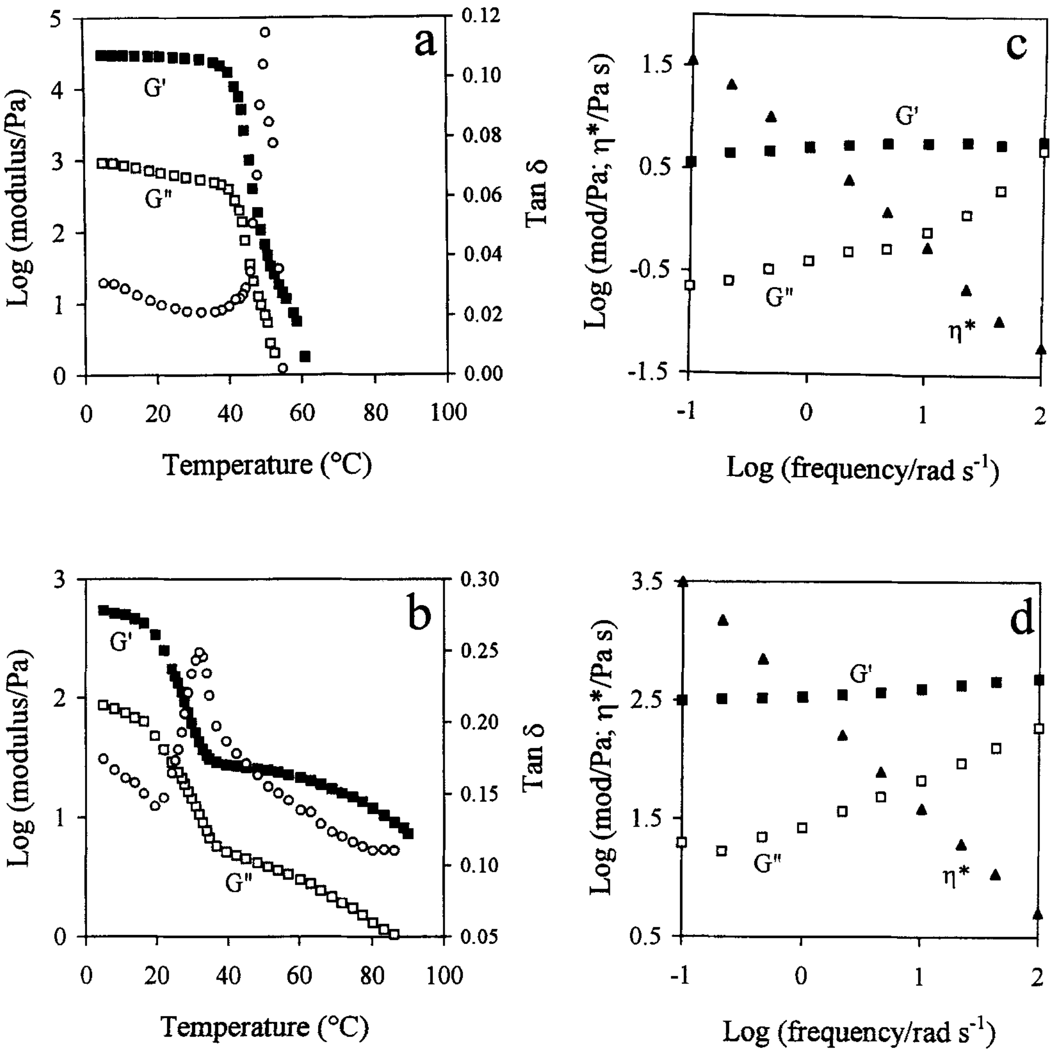

Fig. 4. Variation of *G*′, *G*″, tan *δ*, and η^* during (a) cooling of 0.5% gellan with 40% sucrose, (b) cooling of 0.5% gellan with 45% sucrose, (c) frequency sweep at 90°C for 0.5% gellan with 45% sucrose, and (d) frequency sweep at 5°C for 0.5% gellan with 45% sucrose. All samples contain 7 mN added calcium chloride. The cooling rate is 1°C/min at a frequency of 10 rad/s.

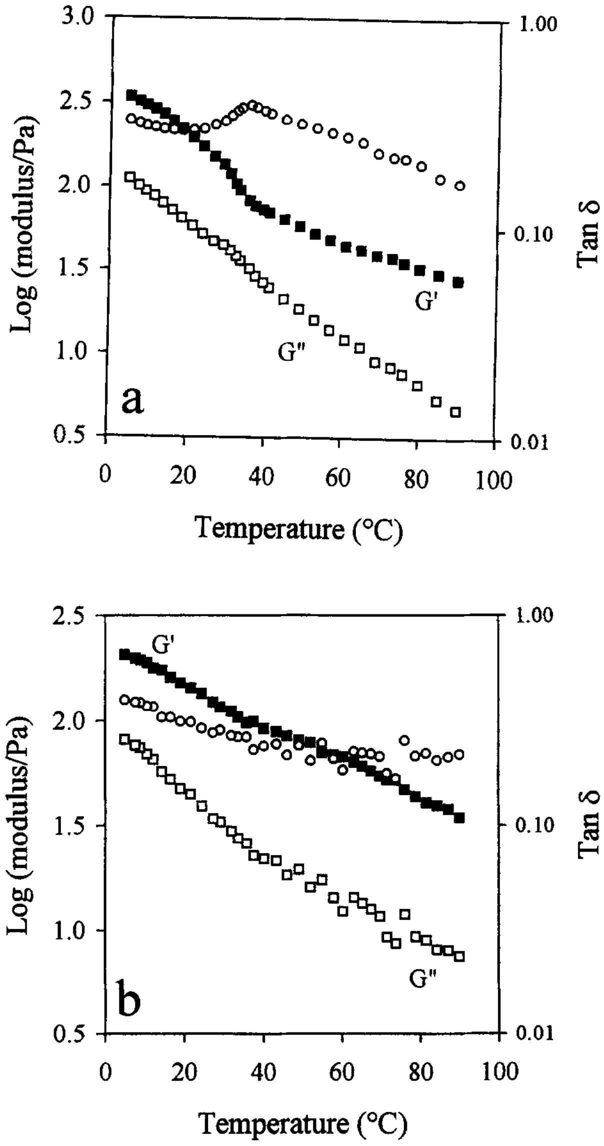

Fig. 5. Development of G', G'' and tan δ during cooling of (a) 0.5% gellan with 50% sucrose, and (b) 0.5% gellan with 60% sucrose (scan rate of 1°C/min; frequency of 10 rad/s; 7 mN added calcium chloride).

tion of structure in Fig. 4 (a) gives rise to a thermally stable network (90°C) on the addition of a further 5% sucrose in Fig. 4 (b). This is achieved at the expense of the second process which only manages a G' value of 0.6 kPa at 5°C in Fig. 4 (b), as compared with the rigid network of Fig. 4 (a) (G' = 30 kPa at 5°C). Finally, the solid-like mechanical spectrum at 5°C (Fig. 4 (d)) shows a pronounced frequency dependence of G'' which strongly contrasts with the flat response of G'' reported for the enthalpically stable highly aggregated helices of aqueous gellan gels (Papageorgiou *et al.*, 1994a).

Further increase in the co-solute content completes the transformation in the mechanical properties of our system. Both trends are still apparent in the gellan sample with 50% sucrose during a cooling run (Fig. 5 (a)). First, the high temperature moduli show a monotonic low gradient ascent followed by a step change in their development at lower temperatures. The rapidly diminishing magnitude of the second process is reflected on a hump in the trail of tan δ. As shown in Fig. 5 (b), this discontinuity becomes non-existent at a sucrose content of 60%. There is an approximately linear development of G' and an accelerating G'' trace at temperatures below ≈40°C which also raises the values of tan δ towards the end of the cooling run. This temperature course is similar to the rheological response in Fig. 3 (a), although there the moduli lines converge even further due to the greater amount of co-solute (70%); tan δ at 5°C is 0.58 and 0.40 for Fig. 3 (a) and Fig. 5 (b), respectively. Therefore, we have safely arrived at the high solids regime (60 to 85% co-solute).

Concluding remarks on the origin of the mechanical behaviour observed in the gellan/co-solute system

To piece together qualitatively the dramatic difference in the development of a gellan network, we have plotted in Fig. 6 the frequency sweeps taken at the end of cooling runs at 5°C as a function of co-solute concentration. As expected from the temperature profiles of 0.5% gellan with and without co-solute in Fig. 2, addition of sucrose up to 30% leads to a systematic increase in G' values with a flat dependence on the experimental frequency of oscillation. This process was discussed earlier on the basis of increasing polymer/polymer

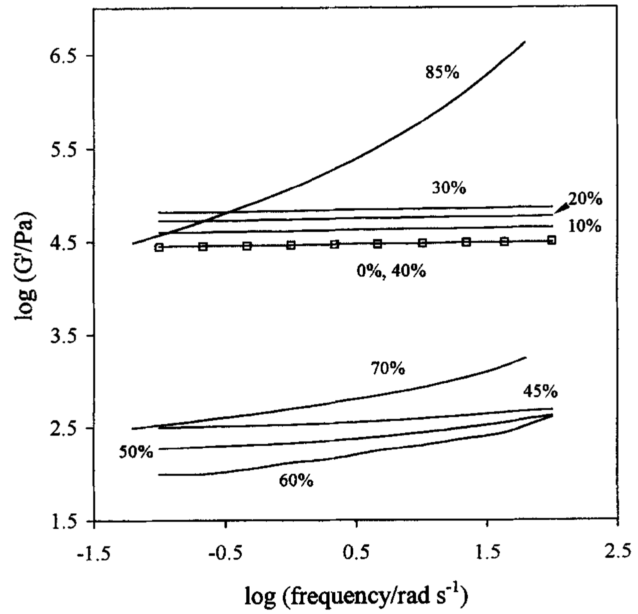

Fig. 6. Frequency sweeps of G' for 0.5% gellan plus 7 mN added calcium chloride at the following levels of co-solute (shown by the individual traces): 0, 10, 20, 30, 40, 45, 50, and 60% sucrose, 50% sucrose + 20% corn syrup, and 50% sucrose + 35% corn syrup. The 40% sugar trace is given with symbols (mechanical spectra were taken at 5°C).

interactions supported by hydrogen bonding with water molecules. Then we observe the intermediate region of a continuously weakening gellan network as a result of raising the sucrose content of preparations from 40% to 60%, a trend that is also associated with a bimodal cooling profile (Figs 4 and 5). It appears, therefore, that the water shortage and the enhanced hydrogen bonding between the polyhydric sucrose and the remaining water molecules destabilise the rigid aggregated helices of an aqueous gellan gel. These are taken over by a limited step of intermolecular associations which decreases the maximum network strength from about 60 kPa at 30% sucrose to a magnitude in the order of hundreds in the case of 60% sucrose. Through the intermediate range of sucrose concentration, both types of macromolecular arrangement coexist thus effectively creating a composite system with a single structuring agent.

Suppression of the enthalpic ordering in the gellan/co-solute network should create flexible chains with a high degree of local configurational freedom. Differential calorimetry work on κ-carrageenan and agarose documented an increase and then a reduction in the enthalpy of gelation upon increasing the sucrose concentration from 0 to 60%, a result that renders important the entropic contribution to the stabilisation of a high solids network (Nishinari *et al.*, 1990; Watase *et al.*, 1990). A lightly cross-linked, highly entropic gellan network should undergo a glass transition in the way reported by Ferry and coworkers (1980) for the mechanical properties of amorphous synthetic polymers. In Fig. 6 the trace of storage modulus at 60% sucrose develops a characteristic frequency dependence which defines the end of the plateau region. At 70% co-solute the values of G' rise more steeply with increasing frequency, and at 85% co-solute they show an exponential frequency dependence that reinforces the gellan network by two orders of magnitude. The molecular mobility of the high solids gellan system was followed by the kinetic scheme of the WLF formalism thus documenting its transition from a rubber-like to a glass-like response with decreasing time or temperature of measurement (Papageorgiou *et al.*, 1994b). By contrast, attempts to apply the same principle to aqueous gellan gels are unsuccessful because changes in free volume are swamped by other temperature-dependent effects such as the dominating enthalpic interactions between the aggregated helical chains.

In Fig. 4 (b) and (c) we have shown that, however low the G' values at 90°C, the intermolecular associations are permanent within the experimental constraint, as opposed to the sharp increase in the frequency dependence of G' and G'' for transient mechanical interactions between biopolymer chains (Morris, 1984). In Fig. 7 a brief study was made on the thermal stability of gellan/sucrose blends in the absence of added $CaCl_2$ (7 mN). The chosen level of sucrose was 50%, which, with added calcium ions, produces on cooling a composite gellan network (Fig. 5 (a)). However, with no added calcium chloride, the high temperature network of Fig. 5 (a) does not survive and the sample in Fig. 7 is a solution. Nevertheless, further cooling induces a gelation process which in terms of temperature band and overall form is similar to the second step of structure in Fig. 5 (a). This result strongly suggests that the lack of external calcium prevents the formation of stable associations between the flexible thermally moving gellan coils at high temperatures. Reduction in the configurational freedom of polymeric chains on cooling allows the batch salts (see Materials section) to induce a gelation process, although in the absence of CaCl the firmness of the network generated is well below that in Fig. 5 (a) ($G' = 0.15$ kPa and 0.31 kPa at 5°C, respectively). Therefore, it appears that the extra amount of calcium ions facilitates formation of thermally stable calcium mediated associations between the sparsely cross-linked gellan chains whose increased entropic character (reduced ordering) allows development of rubbery and glassy phenomena.

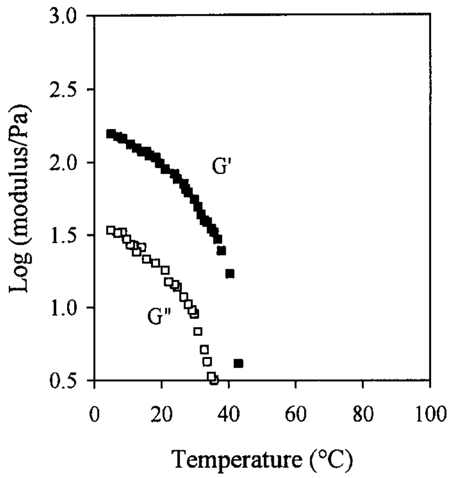

Fig. 7. Cooling spectra of G' and G'' for 0.5% gellan with 50% sucrose (no added calcium chloride: scan rate of 1°C/min; frequency of 10 rad/s).

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