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The use of Arrhenius and WLF kinetics to rationalise the mechanical spectrum in high sugar gellan systems

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Abstract

Small deformation measurements were carried out on high sugar gellan mixtures monitoring the combined effect of temperature and time on the changing viscoelasticity. Horizontal superpositions of mechanical spectra produced double logarithmic plots of shear modulus (10^{-1} to 10^7 Pa) versus frequency of oscillation (10^{-1} to 10^7 rad/s) covering the relaxation, rubbery and glass transition regions. Gellan forms lightly cross-linked segments which gradually transform the mixture into a gel with a high "sol-fraction". The transition from the terminal to the rubbery zone is followed by the Arrhenius equation yielding parameters pertinent to the chemical structure of the system. Further cooling sees an exponential development of viscoelasticity which yields a WLF form according to the non-specific function of the free volume theory. Thus the disentanglement of the two processes in the time-temperature continuum is clearly demonstrated. The approach may assist in the purposeful investigation of other sugar/polysaccharide systems. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Gellan gum; Sugar; Relaxation region; Rubbery zone; Glass transition

1. Introduction

Gellan gum, first discovered in 1978, is a new gelling agent which is secreted by the micro-organism *Sphingomonas elodea* during a controlled aerobic fermentation [1]. The primary structure of gellan (deacylated form) comprises a linear, anionic heteropolysaccharide composed of tetrasaccharide repeat units [2]:

$\rightarrow 3)\text{-}\beta\text{-D-}Glcp\text{-}(1 \rightarrow 4)\text{-}\beta\text{-D-GlcpA-}(1 \rightarrow 4)\text{-}\beta\text{-D-Glc}p\text{-}(1 \rightarrow 4)\text{-}\alpha\text{-L-Rha}p\text{-}(1 \rightarrow$

Gellan gum is used for plant tissue culture, microbiological media, and pharmaceutical applications. Since receiving food approval, it has found increasing use in a variety of food applications and is likely to become the second bacterial polysaccharide after xanthan gum to be used widely by the food industry internationally [3].

The structural properties of the polysaccharide have been extensively investigated. Thus, X-ray diffraction studies of gellan fibers documented that the ordered form adopts a left-hand threefold double-helical strand organised in a parallel fashion in an intertwined duplex [4,5]. At high temperatures,

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gellan molecules are in the disordered state while cooling of the aqueous solution results in an ordered and elongated conformation which is thermally reversible [6]. In the presence of gel-promoting cations, firm, brittle gels are formed through cation-mediated helix–helix aggregation which show marked thermal hysteresis [7]. The physical properties of the gel depend on the type and concentration of cations present with divalent ions (calcium and magnesium) giving stronger and more thermally stable gels than monovalents (sodium or potassium) at equivalent concentrations [8]. It is also found that, on increasing the concentration of cations, the network strength rises to a maximum and then decreases again at higher concentrations of salt, a result attributed to the formation of loosely-connected microparticulate structures [9].

In comparison, the literature on gellan/sugar systems is rather limited (albeit this is the case with most polysaccharides). Whittaker et al. reported that in up to 40% co-solute there is a sugar-stabilising effect on the disorder to order transition and the accompanying chain aggregation [10]. Thus, at these levels of co-solute the behaviour of gellan gum can be traced back to the usual ion-dependent and sugar-stabilised properties of enthalpic polysaccharide networks [11]. At concentrated levels of co-solute (e.g., 85%), however, there is a drop in network strength, observed in small deformation dynamic oscillation, although predominantly elastic structures can be formed at 90 °C [12]. On subsequent cooling, another unexpected development is observed, i.e., the viscous component of the network overtakes the elastic modulus with both traces rising sharply with temperature.

The pictorial profile is congruent with the glass transition of amorphous synthetic polymers [13], strongly arguing that the low temperature/high solids regime encourages vitrification of the polysaccharide. This was verified quantitatively when the viscoelasticity of gellan was modelled with the exponential Williams–Landel–Ferry relationship previously used mainly for the glass-transition of synthetic macromolecules [12]. It was proposed that the sugar–water environment allows limited macromolecular cross-linking between flexible polysaccharide chains thus resulting in networks with a dominant entropic viscoelasticity [14]. The reduction in brittleness of networks at high levels of co-solute, seen by large deformation compression testing, also argues for lightly cross-linked chains which stretch further before they relax [15]. In the present investigation, we vary the amount of co-solute between 70 and 80% in an attempt to extend the mechanistic understanding to the rubbery and relaxation regions of the mechanical spectrum of gellan/sugar preparations.

2. Experimental

Materials.—Deacylated gellan gum (KELCOGEL) was supplied by NutraSweet Kelco and was used without further purification. Atomic absorption analysis produced the following average ionic composition: Na^+: 6330 ppm; K^+: 46800 ppm; Ca^{2+}: 3660 ppm; Mg^{2+}: 1140 ppm. Sucrose was supplied by British Sugar and the corn syrup with a dextrose equivalent (DE) of 42 and a water content of 18% by Gist-Brocades.

Methods.—Samples were prepared by dispersing the gellan gum (1.5 g) in deionised water (60 g) and heating to boiling with gentle agitation. Sucrose (79.5 g) and corn syrup (79.5 g) were added slowly to the hot gum solution whilst maintaining the temperature above 90 °C. The mixture was then boiled until the desired total soluble solids (TSS), measured by refractometer (Atago N-3E), was achieved. Gellan gum concentration at the final TSS was 0.72% w/w at 70% TSS, 0.77% w/w at 75% TSS, and 0.82% w/w at 80% TSS.

Dynamic oscillation measurements were made using a Rheometrics Dynamic Stress Rheometer fitted with parallel plates of either 25 or 40 mm diameter with a gap of 1 or 1.5 mm. Samples were loaded onto the plate of the rheometer whilst hot (90 °C). The sample was cooled from 90 to −5 °C at 2 °C/min, 5% strain and a frequency of 1 rad/s. This was followed by immediate re-heating to 90 °C under the same conditions.

Data for time-temperature superposition were gathered on a second sample by loading onto the rheometer at 90 °C and performing a series of frequency sweeps between 0.1 rad/s and 100 rad/s at discrete temperatures between 90 and −15 °C depending on the system. The sample was allowed to equilibrate for 10 min at each temperature before commencement of the frequency sweep. In agreement with the temperature sweeps, measurements were made within the linear viscoelastic region (< 30% strain), previously determined by a strain sweep performed at a frequency of 1 rad/s. Selected strain values ranged from 0.5 to 10%

depending on the sample and temperature of measurement.

Following the intermittent cooling/frequency sweep routine of the preceding paragraph, similar heating runs were carried out. In doing so, mechanical spectra were obtained at discrete temperatures as the sample was heated implementing a 10 min equilibrium stage before each frequency sweep. To assess the effect of polysaccharide chains on the vitrification of the mixture with 80% co-solute, frequency sweeps for the concentrated sugar solution were obtained at regular temperature intervals during cooling to −30 °C and the estimated glass transition temperature was contrasted with that of the gellan-sugar preparation. Evaporative losses were prevented by covering the exposed surfaces with a silicone oil (BDH DC 200/200). Horizontal shift factors (a_T) for the time–temperature superposition (TTS) of the data were obtained by graphical translation of the data using the Rheometrics Rheocalc software. A vertical shift factor was also applied in order to compensate for changes in sample density with temperature but implementation of the approach and correct sample characterization is independent of this minor adjustment.

3. Results and discussion

Seventy per cent total soluble solids.—Fig. 1(a) shows the temperature profile of the gellan gum in the presence of ≈70% co-solute. The onset of the disorder to order transition appears at 60 °C, as evidenced by the gradual development of G'. Cooling the sample to 50 °C only and reheating to 90 °C shows this transition is thermally reversible [Fig. 1(a) inset]. At about 45 °C a second transition occurs that leads to a rapid development of G' and the establishment of a gel network as the temperature is lowered further. Previously, we have demonstrated that increasing the level of co-solute from 40 to 60% reinforces the thermally stable process at the expense of the second transition which eventually disappears [10]. The former mechanism was attributed to the formation of sparsely cross-linked gellan chains supported by added calcium ions at stoichiometric equivalence of the carboxyl groups. Further drop in temperature, (<45 °C), however, encourages the ordering of new molecules and the development of aggregated helices as seen at the lower range of temperature in

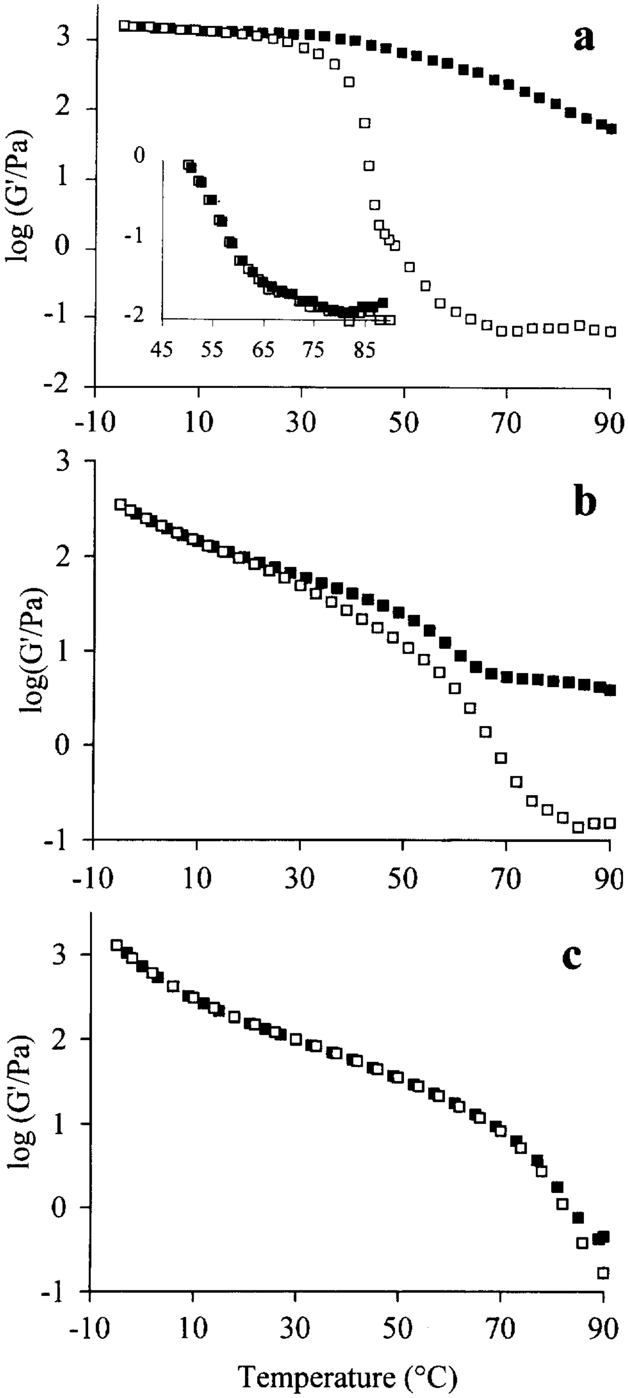

Fig. 1. Cooling (□) and heating (■) profiles of gellan in the presence of (a) 70%, (≡0.72% w/w gellan gum), (b) 75% (≡0.77% w/w gellan gum), and (c) 80% sugar (≡0.82% w/w gellan gum), (scan rate: 2 °C/min; frequency: 1 rad/s).

aqueous gellan preparations. In a recent study, it has been demonstrated that addition of co-solute decreases the calcium required for optimum network strength of 0.5% w/w gellan gum gels, from 9 mM in aqueous gels to 0.5 mM in the presence of 60% w/w sucrose [15]. It appears, therefore, that in the absence of added counterions, the high level of sugar [70% in Fig. 1(a)] is sufficient to stabilise the first mechanism by means of the batch salt. As the sugar level is increased, further aggregate formation is inhibited [Fig. 1(b) and (c)], as has been noted previously [16]. The extensive aggregation in Fig. 1(a) is also reflected in increased thermal stability and thermal hysteresis during heating to 90 °C.

To differentiate mechanistically between the two processes at 70% co-solute, a series of frequency sweeps were recorded at regular temperature intervals and horizontal superpositions were attempted using 70 °C as the reference temperature. As illustrated in Fig. 2(a), a very acceptable overlapping of data was obtained encompassing the temperature range of the thermally stable mechanism in Fig. 1(a) (70 to 50 °C). There appears to be a linear variation of shift factors (a_T) with temperature which can be followed by the Arrhenius equation in the following form:

$$\log a_T = (E_a/2.303R)(1/T - 1/T_0) \qquad (1)$$

where T_0 is the reference temperature and R the gas constant. The energy of activation refers to a barrier to oscillation that allows "permanent" interactions between macromolecules to occur. Thus, E_a can be considered as a measure of the strength of elastic associations within the solution [$G'' > G'$ in Fig. 2(a)] and for the specific features of our sample is calculated to be 20.8 kcal mol^{-1} K^{-1} [Fig. 2(b)]. At this temperature regime, i.e., far above the vitrification or freezing point of a material, the energy quantities are governed by the chemical structure, and for the record, liquid anhydrous glucose produces values of ca. 30 kcal mol^{-1} K^{-1} at 112 °C [17].

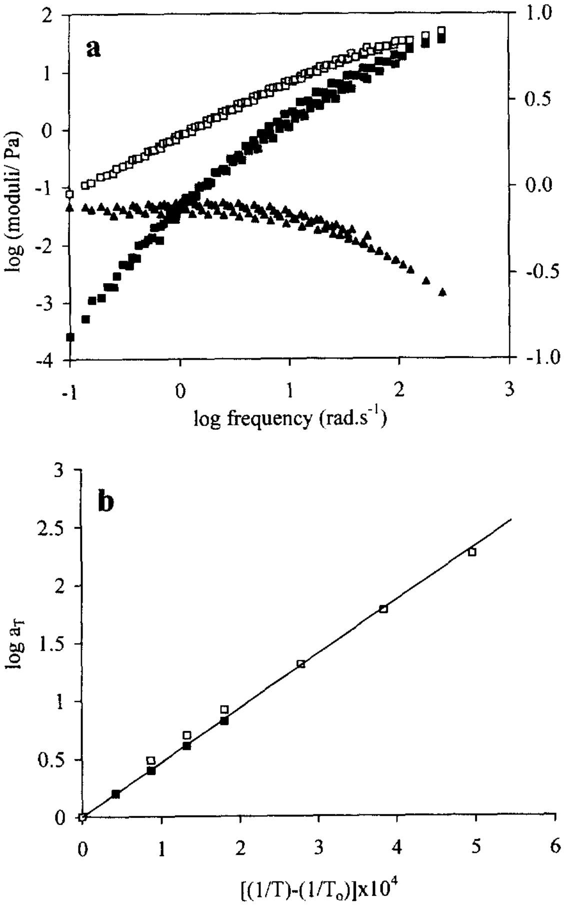

Fig. 2. (a) Horizontal time–temperature superpositions of G' (■), G'' (□) and η^* (▲) for the gellan sample with 70% sugar (≡0.72% w/w gellan gum), and (b) Arrhenius fit of shift factors for viscoelastic data in Fig. 2(a) (■) taken at 70, 65, 60, 55 and 50 °C and Fig. 3 (□) for the gellan sample with 75% TSS (≡0.77% w/w gellan gum) taken at 70, 60, 55, 50, 40, 30, and 20 °C. The reference temperature is 70 °C in both samples.

Further cooling from 50 to 45 °C triggers the sharp transition of Fig. 1(a) which transforms the solution into a firm biopolymer gel network. Thus, mechanical spectra in the form of double logarithmic plots show the elastic modulus being well above the loss modulus ($\tan \delta = G''/G' \approx 0.1$) with little frequency dependence in either trace, and the dynamic viscosity varying linearly with the frequency of oscillation. The ensuing break down of the time-temperature superposition supports further the argument that the second process reflects the ordering and extensive aggregation of new species into the enthalpic arrangement of low solids systems. This behaviour is contrasted with the smooth time-temperature continuum in gellan samples with 75% co-solute.

Seventy-five per cent total soluble solids.—Under this regime, the onset of the conformational transition occurs at approximately 85 °C [Fig. 1(b)], but aggregation should be limited since a clear second transition is not observed as the sample is cooled further. Upon re-heating there is evidence of some aggregate formation (systems remain solid-like at 90 °C) although this is much reduced in comparison with the thermal hysteresis at 70% co-solute. The changing nature of viscoelasticity allows superposition of relaxation processes into a unifying master curve depicted for the temperature range of 70 to 20 °C in Fig. 3. A series of horizontal shift factors are then arranged linearly as a function of temperature via the Arrhenius approach and the energy of activation is estimated from the gradient of Fig. 2(b) (21.3 kcal $\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$). This is in good agreement with the estimate at 70% TSS and argues for the governance of the same process which, at 75% co-solute, is able to engage a greater part of the polymeric "cobweb" thus developing a short rubbery region as indicated in Fig. 3 where G' becomes greater than G''. Besides the rubbery feature, the composite curve depicts the relaxation zone and the onset of the glass transition.

A comparable pictorial response has been noted by Ferry for low-functionality elongated ellipsoids or rodlike molecules (e.g., 2% poly(γ-benzyl-L-glutamate)) which struggle to support the excessive levels of solvent in the system (*m*-methoxyphenol in this case) [13]. We do not envisage an ordered gellan molecule due to the reduction in network strength and brittleness of the system at high levels of sugar. Indeed, Ferry reported short rubbery regions for low-functionality entanglements as opposed to the permanent network of vulcanised rubbers. The critical concept, therefore, is that of reduced polymer functionality, and in the case of gellan this is the result of diminishing order assisted by the absence of added counterions. Further, the organic solvent dictates both the extent of the rubbery region allowed to the synthetic polymer and the subsequent vitrification of the mixture. In our case, increasing the level of co-solute prevents the development of aggregate-dominating structures which break up the time-temperature continuum between 50 and 45 °C at 70% co-solute. However, modelling of the relaxation characteristics of the same process is feasible. Thus, we are able to follow the development of lightly cross-linked vestiges within the gellan solution at 70% sugar [Fig. 2(a)]. At 75% co-solute, these entities progress eventually into a three-dimensional structure with a high sol-fraction (Fig. 3), but again this corresponds to the gradual build up of one process that can be followed by the horizontal superposition.

The gellan sample in the presence of 75% co-solute was kept at 20 °C in order to examine its storage stability. The development of structure, during storage leads to a gradual increase in modulus, the process still consolidating itself after 135 h [Fig. 4(a)]. The slow kinetics of the ageing process however, in relation to the effect of temperature, leave the sample effectively at equilibrium, thus allowing successful prediction of the composite behaviour in Fig. 3. The aged preparation was then cooled to −10 °C and heated back taking frequency sweeps at steps of 10 °C. This allowed data

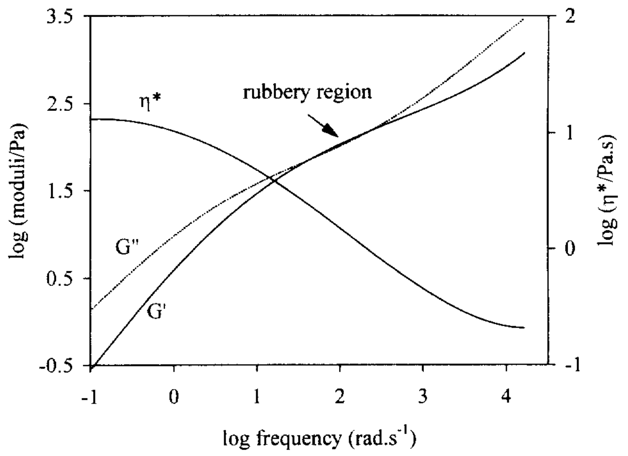

Fig. 3. Horizontal time–temperature superpositions of mechanical spectra of the gellan sample with 75% sugar (≡0.77% w/w gellan gum) taken at 70, 60, 55, 50, 40, 30 and 20 °C. The reference temperature is 70 °C.

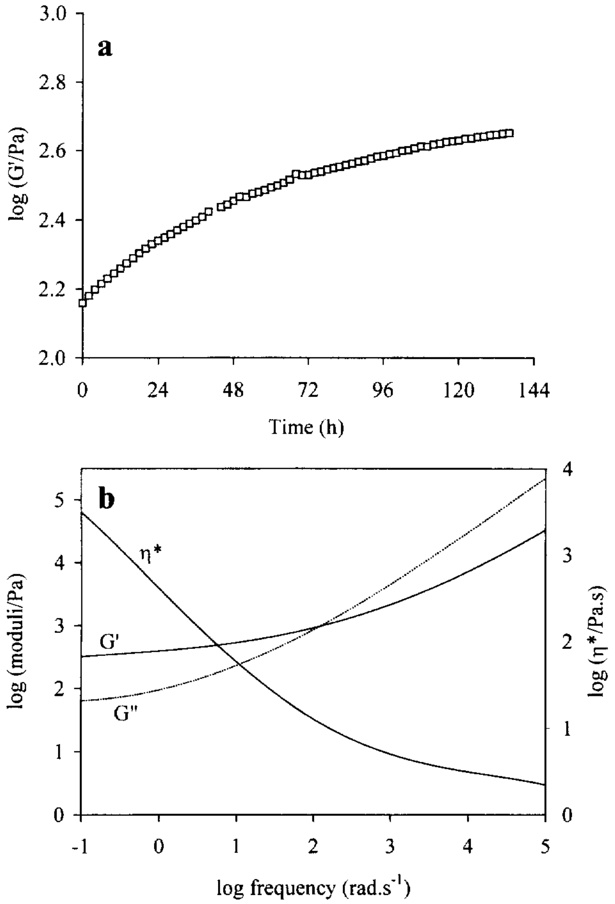

Fig. 4. (a) Structure development with time at 20 °C for the gellan sample in the presence of 75% sugar (≡0.77% w/w gellan gum) and (b) time–temperature superposition of mechanical spectra taken for the aged sample on heating from −10 to 30 °C. The reference temperature is 30 °C.

superposition up to 30 °C since partial melting of the system at higher temperatures introduces a first order thermodynamic transition. Fig. 4(b) reproduces the composite curve which covers a six-decade frequency window. Loss of the terminal zone and development of an extensive plateau zone is seen in the viscoelastic behavior after storage. However, the spectrum does not extend sufficiently deep into the glass transition region thus preventing us from modelling the vitrification of gellan gum at 75% co-solute. Naturally, we extended the work to 80% sugar in an attempt to capture a bigger slice of the glass transition within the experimentally available temperature range.

Eighty per cent total soluble solids.—At 80% TSS, the conformational transition has already commenced at 90 °C and appears complete by about 70 °C [Fig. 1(c)]. This proceeds smoothly with further cooling until it enters the glass transition region at temperatures below 10 °C where the expected acceleration in modulus development is observed. Overall, the profile appears to be reversible with little thermal hysteresis. The slightly higher G' values above 80 °C when the sample was re-heated suggest the occurrence of limited aggregation of the gellan chains.

We next recorded a series of mechanical spectra at different temperatures (from 70 to −15 °C) and constructed a composite curve along a frequency/time axis of eight orders of magnitude [Fig. 5(a)]. This time, the increase in modulus values does not exhibit a frequency window with a dominant elastic response (tan δ remains above 1). Nevertheless, there is no direct passage from the terminal region to the glass transition observed for concentrated sugar solutions in the absence of the polymeric ingredient [18]. Instead, a separate feature is discernible between the frequency values of 1 to 100 rad/s as gellan tries but fails to form a coherent structure within the time scale of our experimentation.

The temperature dependence of shift factors for the "sugar-saturated" gellan sample is shown in Fig. 5(b). Clearly, the Arrhenius prediction satisfies the development of viscoelastic functions only at the upper range of temperature where the relaxation region is noted. At lower temperatures the process of vitrification can no longer be treated with an expression bearing a linear temperature dependence. To address the exponential progression of viscoelasticity, Williams, Landel and Ferry introduced an empirical relationship [19]:

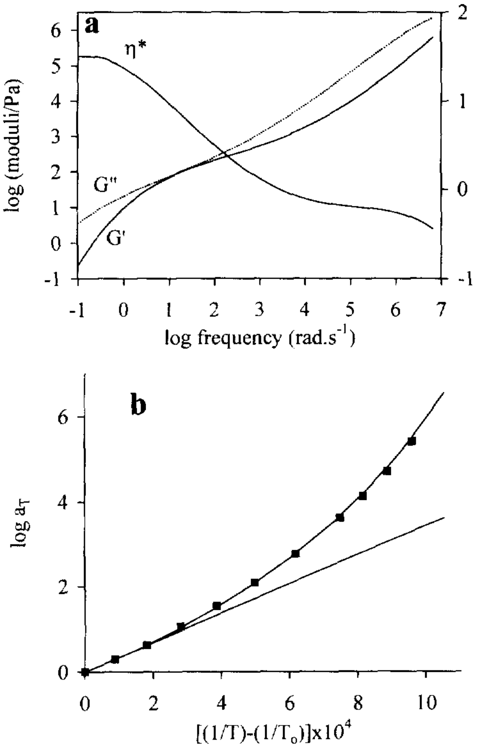

Fig. 5. (a) Horizontal time–temperature superposition of G', G'' and η^* followed by (b) a linear Arrhenius and an exponential WLF fit of the derived shift factors taken at 70, 60, 50, 40, 30, 20, 10, 0, −5, −10 and −15 °C for the gellan sample with 80% sugar (≡0.82% w/w gellan gum). The reference temperature is 70 °C.

$$\mathrm{Log}\, a_\mathrm{T} = -C_1^0(T - T_0)/\left(C_2^0 + T - T_0\right) \qquad (2)$$

where C_1^0 and C_2^0 are constants particular to each preparation. Next, the WLF equation was related to the concept of free volume which now becomes the parameter in linear relationship with temperature (for a detailed discussion of the combined WLF/free volume theoretical framework see [19]). The approach has been applied to the shear modulus/compliance data of a plethora of amorphous synthetic polymers and to the viscosities of anhydrous glucose and fructose predicting the glass transition temperature [13,20]. In this way the viscoelastic behaviour of systems could be explored outside the normal working range (temperature/time) of conventional rheometers. One proviso is that the sample must not undergo a physical alteration such as crystallinity or aggregation with changing temperature which is why the WLF-related TTS has not found utility in the study of aqueous systems of natural biopolymers [21].

As shown in Fig. 5(b), however, the story is rather different in high sugar gellan systems which undergo vitrification according to the WLF principle. This allows calculation of parameters characterising the vitrification of the gellan sample at 80% co-solute, namely: the glass transition temperature ($T_g = -26\ ^\circ C$), the ratio of free to total volume at T_g ($f_g = 0.037$) and the thermal expansion coefficient ($\alpha_f = 7.4 \times 10^{-4}\ \mathrm{deg}^{-1}$). The energy of activation accompanying the vitrification process increases rapidly with decreasing temperature and can be estimated by a modified form of the WLF equation:

$$E_a = 2.303RC_1^0C_2^0T^2/(C_2^0 + T - T_0)^2 = RT_g^2\alpha_f/f_g^2 \tag{3}$$

The first term of eq (3) attains a value of $47.2\,\mathrm{kcal\,mol^{-1}\,K^{-1}}$ for the lowest experimental temperature of Fig. 5 (−15 °C), while at the glass transition temperature the equation transforms into the second term and yields an energy quantity of $65.1\,\mathrm{kcal\,mol^{-1}\,K^{-1}}$. Compared with the E_a estimate in the terminal and rubbery regions which characterises an elementary flow process [$\approx 21\,\mathrm{kcal\,mol^{-1}\,K^{-1}}$ in Fig. 2(b)], the viscoelastic relaxation in the glass transition reflected the additional collapsing of free volume as molecules "fuse" with each other. Our values for the "heat of fusion" and the free volume parameters are congruent with predictions for synthetic polymers, a result which implies that the mechanical properties in the glass transition are independent of chemical structure [13]. Indeed, the acceleration of shift factors in Fig. 5(b) pinpoints the temperature at which non-specific features become dominant.

Once again ageing of the sample results in structure development and leads to an extensive rubbery region and loss of the flow region in the subsequent master curve [Fig. 6(a)]. Therefore, the gellan sample at 80% co-solute phase inverts with ageing from a sugar- to a polysaccharide-continuous system. Further, the plasticizing effect of the extra 5% sugar drives the system deeper into the glass transition region with the values of loss modulus reaching 10^7 Pa at the end of the frequency extrapolation whereas at 75% sugar the values are an order of magnitude lower.

Finally, the WLF equation was recast as a linear relationship between the derived shift factors and the temperature step of two successive frequency sweeps, and the outcome is presented in Fig. 6(b). Alternatively a linear plot of log a_T versus $(T - T_0)/(T - T_\infty)$ can be used to parameterize the glass in question, where $T_\infty = T_0 - C_2^0$ [13], and both approaches have been employed with the same effect in the high sugar κ-carrageenan system [18,22]. In Fig. 6(b), a convincing linear fit predicts the vitrification course of the aged sample which is longer ($T_g = -33\ ^\circ C$) than the corresponding process of the first cooling [$T_g = -26\ ^\circ C$ in Fig. 5(b)]. Yet again the importance of the polysaccharide in the mixture was demonstrated, since the formation of a three-dimensional structure stabilises the rubbery region which requires lower temperatures to convert into a glass. The evident response of the mixture to the time-dependent build-up of macromolecular structure suggested that removal of the polysaccharide could precipitate further changes in the mechanical spectrum of a sugar preparation. To examine this, we implemented a series of frequency sweeps for the concentrated sugar solution

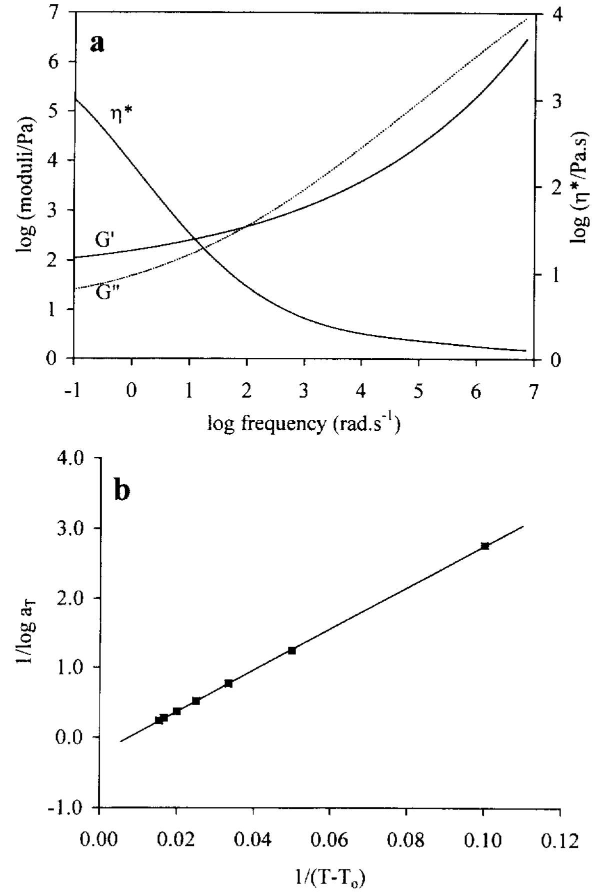

Fig. 6. (a) Horizontal time–temperature superposition of G', G'' and η^* for a gellan sample with 80% sugar (≡0.82% w/w gellan gum) which was aged at 20 °C, cooled to −15 °C and then heated taking mechanical spectra at −15, −10, 0, 10, 20, 30, 40 and 50 °C, and (b) linearised WLF fit for the derived shift factors. The reference temperature is 50 °C.

of Fig. 5(a) (40% sucrose plus 40% glucose syrup). Fig. 7(a) reproduces the outcome of an array of superpositions which cover nine decades of shear modulus. Clearly, divergent shapes of viscoelastic functions are obtained with and without the gellan chains with the latter following a smooth transformation from the flow to the glass transition region. Changes were not limited to the absence of the polysaccharide-induced rubbery plateau but also affect the time-temperature course of vitrification. As illustrated in Fig. 7(b), horizontal transposition of mechanical spectra generates a set of shift factors which complies with the temperature dependence of the WLF equation. This generates a T_g value of −45.4 °C which is very close to the glass transition of an 80% sucrose solution (−46.0 °C) obtained with differential scanning calorimetry [23]; the glucose syrup of the present investigation contained a negligible amount of high molecular weight material, with the dextrose equivalent being 42. Therefore, in the absence of stabilising interactions between polymeric chains and the sugar molecules, the high state of entropy is translated into a lower temperature of vitrification.

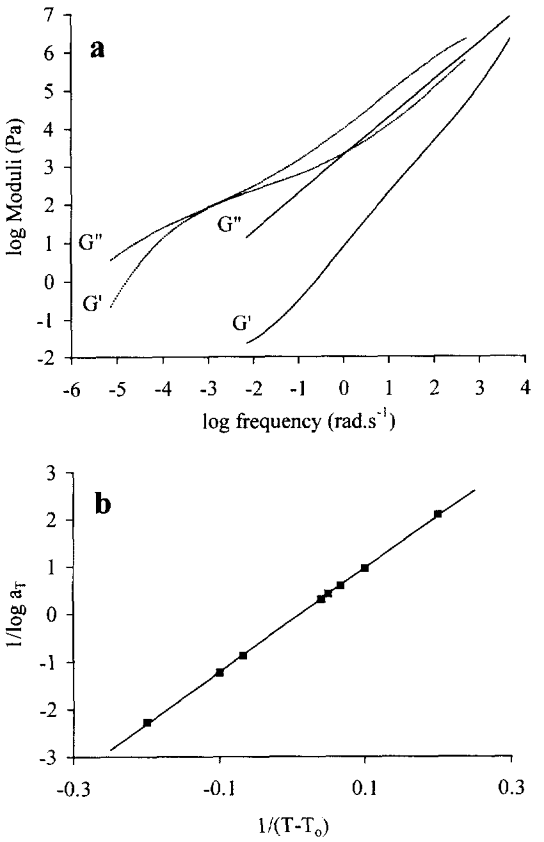

Fig. 7. (a) Horizontal time–temperature superposition of G', and G'' for a concentrated sugar solution of 80%TSS (solid lines), and (b) linearised WLF fit for the derived shift factors taken at 10, 5, 0, −5, −10, −15, −20, −25, and −30 °C. The reference temperature is −5 °C. For comparison the gellan sample with 80% sugar has been replotted from Fig. 5(a) using the same reference temperature of −5 °C (dotted line).

4. Conclusions

The presence of high levels of co-solute had a profound effect on the development of viscoelasticity in gellan gum systems due to the suppression of aggregate formation usually associated with aqueous gellan gum gels. This reduction in aggregate formation enabled time-temperature superposition principals to be applied to small deformation measurements. The data could be successfully modelled using the Arrhenius equation in the terminal to rubbery zone and an activation energy could be calculated that is independent of co-solute concentration. At the highest level of co-solute (80% TSS), viscoelasticity could be modelled using the WLF equation up to approximately 80 °C above the predicted T_g of the system. The limited data above this temperature suggested that Arrhenius kinetics apply once again. Thus for the first time in high sugar polysaccharide systems, the disentanglement of the two kinetic processes in the time-temperature continuum was clearly demonstrated using dynamic oscillatory measurements for the prediction of T_g. In terms of the sugar solution, addition of gellan had a profound effect on the flow properties of the system and also accelerated its vitrification.

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