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Effect of polymeric cosolutes on calcium pectinate gelation. Part 2. Dextrans and inulin

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Abstract

In a continuation of the work reported in the preceding paper, the effect of chicory root inulin ($M_r \approx 4.5$ kD) and branched dextrans of M_r 67, 464 and 2000 kD on gelation of low methoxy pectin (DE 31; 2.0 wt%; pH ≈ 2.9–3.0) on cooling from 90 to 5 °C in the presence of stoichiometric Ca^{2+} has been characterised by low amplitude oscillatory measurements of G' and G''. As found for other polymeric cosolutes studied previously (oxidised starch, potato maltodextrin, guar gum and locust bean gum), increasing concentrations of dextran or inulin caused a progressive increase of G' and G'' in the solution state at 90 °C (attributed to segregative interactions promoting formation of calcium-mediated 'egg-box' junctions between pectin chains) and a progressive reduction in final moduli at 5 °C (attributed to excessive association of calcium pectinate into large aggregated bundles), with cooling curves crossing those for calcium pectinate alone at ~55 °C. For the dextran samples, the ability to promote initial association of pectin chains at high temperature decreased with increasing molecular weight (i.e. with the smallest molecules having the greatest effect, as was also found for guar gum), but the reduction in final modulus on completion of cooling to 5 °C became more pronounced. By the criterion of the decrease in the change in log G' during cooling, the three dextran samples studied seem roughly comparable in their overall effectiveness in promoting self-association of pectin, with inulin having a substantially smaller effect. Both materials, however, are less effective than the partially depolymerised starches and galactomannans studied previously. It is tentatively suggested that this may be associated with the flexibility introduced by the presence of three single bonds in the predominant glycosidic linkages of both dextran and inulin.

Keywords: Pectin; Dextran; Inulin; Gelation; Rheology; Segregation

1. Introduction

In the preceding paper (Giannouli, Richardson, & Morris, 2004a) it was shown that addition of guar gum or locust bean gum to mixtures of low methoxy pectin (DE 30; 2.0 wt%; pH ~ 2.9–3.0) with $CaCl_2$ at stoichiometric equivalence to the unesterified carboxyl groups of the pectin caused large increases in G' and G'' at high temperature (90 °C), but reduced the moduli attained on cooling to 5 °C. The proposed interpretation was that segregative interactions between the pectin and the galactomannan promote formation of Ca^{2+}-mediated 'egg-box' junctions (Grant, Morris, Rees, Smith, & Thom, 1973) between pectin chains in solution at high temperature, but at lower temperatures cause excessive association of pectin into large aggregated bundles which make little contribution to network crosslinking. The changes observed were comparable to those reported previously for oxidised starch (Picout, Richardson, Rolin, Abeysekera, & Morris, 2000b) and substantially greater than for potato maltodextrin (Picout, Richardson, & Morris, 2000a).

It was also found that the effectiveness of different samples of guar gum in promoting self-association of pectin chains was inversely proportional to hydrodynamic volume, as characterised by intrinsic viscosity, [η], with the smallest molecules having the greatest effect. The purpose of the work reported here was to determine whether dextrans and inulin, which also have low hydrodynamic volume, are equally effective in driving Ca^{2+}-mediated association of low methoxy pectin.

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Dextran is a bacterial exopolysaccharide with extensive biomedical applications, notably as a blood plasma extender (De Belder, 1992), and is available commercially in a range of well-characterised molecular weights. Most commercial dextrans are produced by fermentation of sucrose with *Leuconostoc mesenteroides* NRRL B-512. They consist of α-D-glucose residues (in the pyranose ring form), connected predominantly by 1 → 6 linkages, but with ~5% of 1 → 3 linkages which introduce branching. The solution properties of dextran at molecular weights greater than ~10 kD are characteristic of a highly branched polymer.

After starch, inulin is the most abundant storage polysaccharide in nature, occurring widely in cereals, vegetables and fruit. Although there is evidence (De Leenheer & Hoebregs, 1994) of some limited (1–2%) branching, inulin consists essentially of linear chains of (2 → 1)-linked β-D-fructofuranosyl residues, terminating in a 2 → 1 linkage to α-D-glucopyranose (the same linkage as in sucrose). The degree of polymerisation (DP) in native inulin ranges from small oligomers (DP 3 or 4) up to DP ≈ 70. The main commercial source of inulin is chicory (*Cichorium intybus*) root, and the oligomeric fraction is often removed by physical processing, giving material with an average DP of ~27–29 (De Leenheer & Hoebregs, 1994). The sample used in the present work was of this type.

2. Materials and methods

The experimental procedures used were identical to those described in the preceding paper (Giannouli et al., 2004a). Solutions of calcium chloride (AnalaR grade from BDH), low methoxy pectin (DE 31%) and the polymeric cosolute (dextran or inulin) were prepared separately, and mixed (at 90 °C) in the proportions necessary to give the required final concentrations of cosolute, pectin and Ca^{2+}. The concentration of pectin in the mixtures was held fixed at 2.0 wt%, and the concentration of Ca^{2+} was also held fixed at stoichiometric equivalence to the unesterified carboxyl groups of the pectin. Samples were loaded (at 90 °C) onto an oscillatory rheometer (with 50 mm cone-and-plate geometry), coated around their periphery with light silicone oil, and cooled to 5 °C at 1 °C/min, with measurement of G' and G'' at 10 rad s^{-1} and 0.5% strain. A mechanical spectrum (frequency-dependence of G', G'' and η^*) was then recorded (at 0.5% strain).

Three dextran samples were purchased from Sigma. According to information provided by the Supplier, their average molecular weights (relative molecular mass, M_r) are 77, 464 and 2000 kD, and they are identified here as, respectively, dextran L (low molecular weight), dextran M (medium) and dextran H (high). The inulin sample used was Frutafit EXL from Sensus Operations C.V., Roosendaal, The Netherlands (a prototype of a current commercial product, Frutafit TEX). The Suppliers specify a minimum average DP of 23; based on the analysis by De Leenheer and Hoebregs (1994) of inulins fractionated in the same way, we have assumed an average DP of 28, giving $M_r \approx 4.5$ kD. The intrinsic viscosity, $[\eta]$, of each of these polymeric cosolutes was derived from measurements of dilute solution viscosity (at 20 °C), made using cup-and-bob geometry on a Contraves Low Shear 30 rotational viscometer.

3. Results

3.1. Intrinsic viscosity of dextrans and inulin

As described in the preceding paper (Giannouli et al., 2004a), each sample was prepared at a number of low concentrations (c) chosen to give relative viscosities within the approximate range $\eta_{rel} = 1.0$ to 2.0 (i.e. specific viscosity, $\eta_{sp} = \eta_{rel} - 1 = 0.2$ to 1.0). Intrinsic viscosity, $[\eta]$, was then determined using Huggins and Kraemer plots of, respectively, η_{sp}/c and $(\ln \eta_{rel})/c$ versus c, with the common intercept at zero concentration giving $[\eta]$. The slope of the Huggins plot can be expressed as $k'[\eta]^2$, where k' is the 'Huggins parameter'. The slope of the Kraemer plot can similarly be expressed as $k''[\eta]^2$, with the mathematical constraint that $k'' = k' - 0.5$. Both plots can therefore be fitted jointly by only two parameters, $[\eta]$ and k'. These were varied to minimise the combined root-mean-square deviation between observed and fitted values of η_{sp}/c and $(\ln \eta_{rel})/c$.

Fig. 1 shows the fits obtained for the samples of highest and lowest intrinsic viscosity, dextran H (Fig. 1a) and inulin (Fig. 1b). Similar fits were achieved for the other two polymeric cosolutes used (dextran L and dextran M). The resulting values of $[\eta]$ are reported in Table 1, along with the values of M_r discussed in Section 2.

Fig. 2 shows a Mark–Houwink plot of log $[\eta]$ versus log M_r for the three dextran samples. The corresponding plot for the guar gum samples used by Giannouli et al. (2004a) is included for direct comparison, along with the single point for the inulin sample. It is evident that the intrinsic viscosities for dextran and inulin are around an order of magnitude smaller than for guar gum of equivalent molecular weight. It is also evident that the Mark–Houwink plot for dextran is not linear, but shows a progressive decrease in slope with increasing M_r. This effect has been long known (Senti et al., 1955), and can be attributed to a progressive increase in segment density within the branched structure, which, as seen for synthetic hyperbranched polymers (Prosa, Bauer, Amis, Tomalia, & Schrerrenberg, 1997; Tomalia, 2001), partially offsets the normal increase in hydrodynamic volume with increasing M_r.

3.2. Effect of dextrans on calcium pectinate gelation

Fig. 3 shows the changes in G' (Fig. 3a) and G'' (Fig. 3b) observed for 2.0 wt% low methoxy pectin with stoichiometric Ca^{2+} on cooling (at 1 °C/min) from 90 to 5 °C, alone,

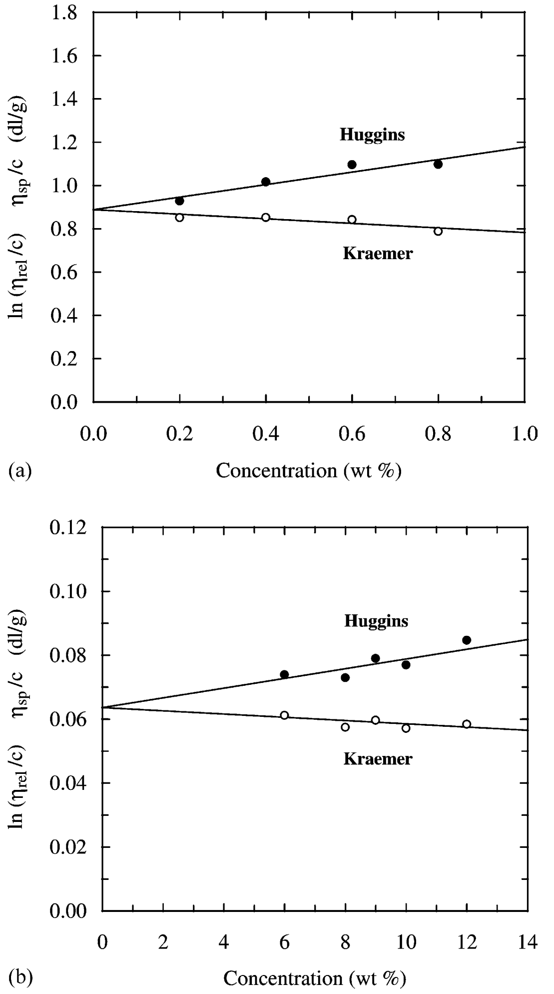

Fig. 1. Determination of intrinsic viscosity (20 °C) from Huggins and Kraemer plots of, respectively, η_{sp}/c (●) and ($\ln \eta_{rel})/c$ (○) against concentration (c) for (a) dextran H and (b) inulin. Only two variable parameters were used to fit both plots for each sample, as described in the preceding paper (Giannouli et al., 2004a).

and in the presence of dextran L at concentrations of 2.5, 5, 10, 15 and 20 wt%. The corresponding plots obtained using the same concentrations of dextran M and dextran H are shown in Figs. 4 and 5, respectively. In each case, increasing concentration of dextran causes a progressive increase in both G' and G'' in the fluid 'weak gel' state at high

Table 1
Molecular weight and intrinsic viscosity of dextrans and inulin

Sample	[η] (dl g^{-1})	M_r (kD)
Dextran H	0.888	2000
Dextran M	0.594	464
Dextran L	0.321	67
Inulin	0.066	4.5

Molecular weight (relative molecular mass, M_r) for inulin was calculated on the assumption of an average degree of polymerisation of 28 (De Leenheer & Hoebregs, 1994); M_r values for the dextran samples were provided by Sigma.

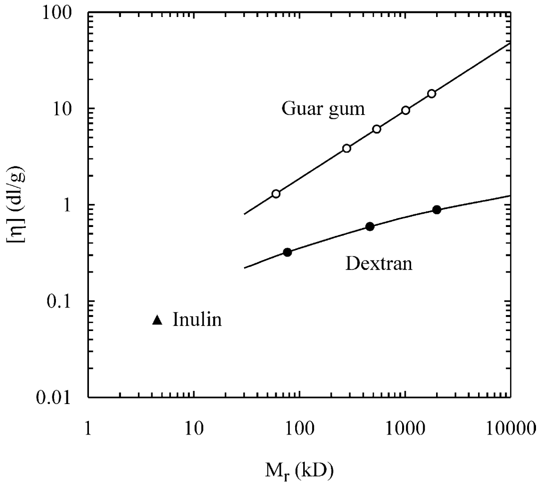

Fig. 2. Relationship between intrinsic viscosity, [η], and molecular weight (relative molecular mass, M_r) for the dextran samples studied (●). The values of [η] and M_r (Table 1) for the single sample of inulin (▲) and the intrinsic viscosities (○) of the guar gum samples used by Giannouli et al. (2004a) are included for direct comparison.

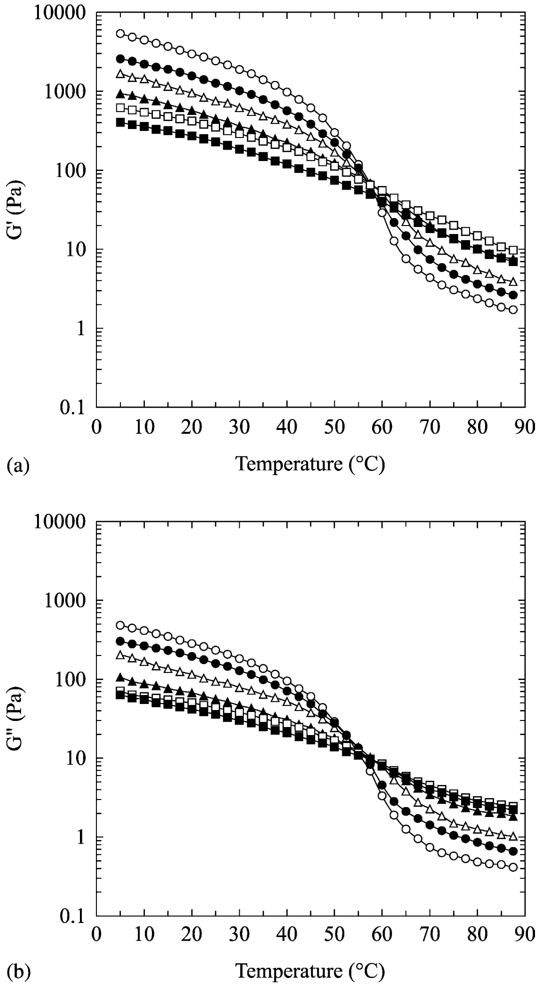

Fig. 3. Changes in (a) G' and (b) G'' (10 rad s^{-1}; 0.5% strain) during cooling from 90 to 5 °C for 2.0 wt% calcium pectinate alone (○) and in the presence of dextran L at concentrations (wt%) of 2.5 (●), 5 (△), 10 (▲), 15 (□) and 20 (■).

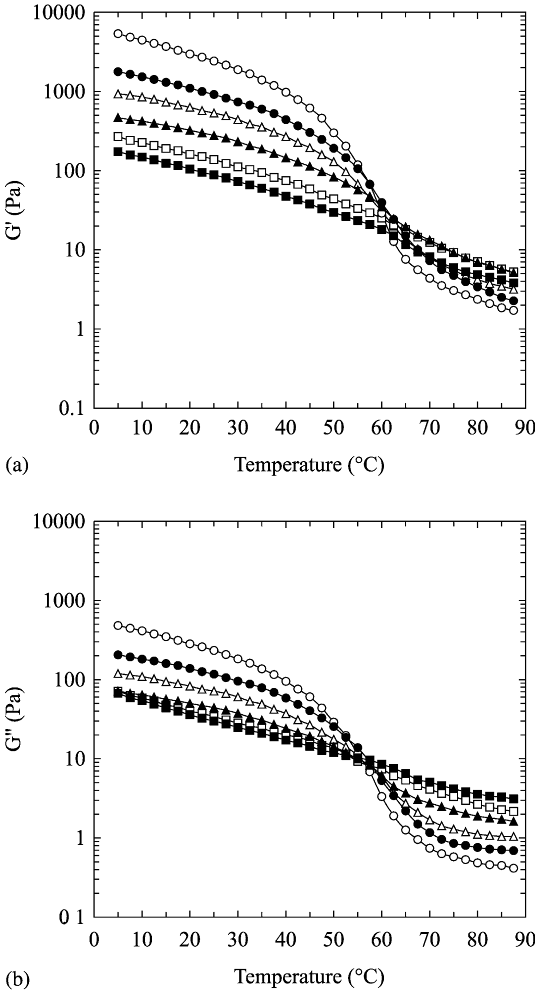

Fig. 4. Changes in (a) G' and (b) G'' (10 rad s^{-1}; 0.5% strain) during cooling from 90 to 5 °C for 2.0 wt% calcium pectinate alone (○) and in the presence of dextran M at concentrations (wt%) of 2.5 (●), 5 (△), 10 (▲), 15 (□) and 20 (■).

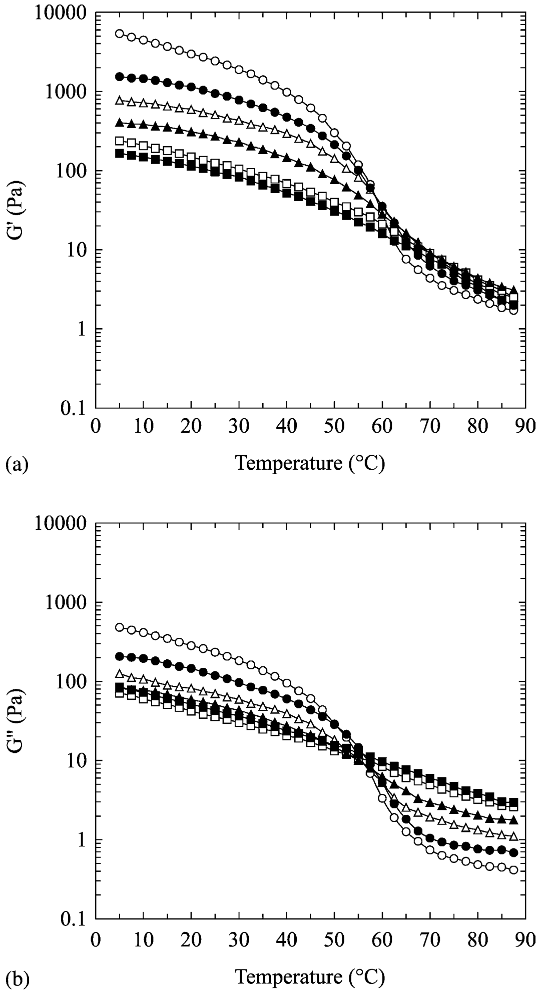

Fig. 5. Changes in (a) G' and (b) G'' (10 rad s^{-1}; 0.5% strain) during cooling from 90 to 5 °C for 2.0 wt% calcium pectinate alone (○) and in the presence of dextran H at concentrations (wt%) of 2.5 (●), 5 (△), 10 (▲), 15 (□) and 20 (■).

temperature, and a progressive reduction in moduli of the gels formed on completion of cooling to 5 °C, with the curves crossing at around 55–60 °C. Similar effects were observed (Giannouli et al., 2004a; Picout et al., 2000a,b) with oxidised starch, potato maltodextrin or galactomannans as polymeric cosolute.

The magnitude of the changes in G' and G'' at high temperature (85 °C) and low temperature (5 °C) is illustrated in Fig. 6 for dextran L (Fig. 6a) and dextran H (Fig. 6b). In both cases, increasing dextran concentration from 0 to 20 wt% reduces G' at 5 °C by over an order of magnitude. For the sample of lower molecular weight (dextran L; Fig. 6a), the increase in G' at 85 °C is again around an order of magnitude, and the separation between G' and G'' at both high and low temperature remains roughly constant across the full range of dextran concentrations studied. For the sample of higher molecular weight (dextran H; Fig. 6b), the increase in G' at 85 °C is smaller, and there is a progressive reduction in the separation between G' and G'' as dextran concentration is raised. Indeed, at the highest concentration studied (20 wt%), G'' in the pre-gel solution state at high temperature is slightly higher than G'. As discussed in the preceding paper (Giannouli et al., 2004a), this can be attributed to a progressive increase in the direct contribution of the polymeric cosolute to overall viscous response (G'') as its concentration and molecular weight increase. The changes in moduli with increasing concentration of dextran M were intermediate between those shown in Fig. 6 for dextrans L and H. A more explicit comparison of the effect of the three dextran samples on gelation of calcium pectinate is presented later in this Section.

The changes in network structure introduced by the presence of high concentrations of dextran are illustrated in Fig. 7, which shows the mechanical spectrum recorded after completion of cooling to 5 °C for 2.0 wt% calcium pectinate alone (Fig. 7a), in comparison with the corresponding spectrum for 2.0 wt% calcium pectinate in combination with 20 wt% dextran H (Fig. 7b). The reduction in gel-like

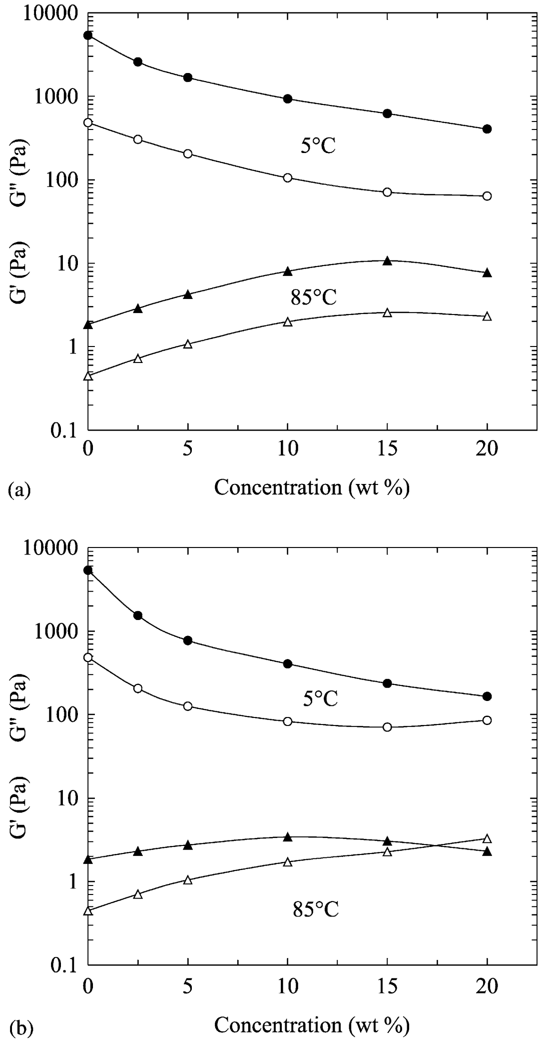

Fig. 6. Measured values (10 rad s^{-1}; 0.5% strain) of G' (filled symbols) and G'' (open symbols) at 85 °C (triangles) and 5 °C (circles) for 2.0 wt% calcium pectinate in the presence of (a) dextran L and (b) dextran H over a range of concentrations of each.

character by incorporation of the polymeric cosolute is clear (lower moduli at all frequencies; smaller separation of G' and G''; greater frequency-dependence of both moduli).

Fig. 8 shows a direct comparison of the changes in G' (Fig. 8a) and G'' (Fig. 8b) at 85 and 5 °C caused by each of the three dextran samples across the full range of concentrations studied. As observed for guar gum (Giannouli et al., 2004a), the increase in G' at high temperature (85 °C) becomes greater as the molecular weight of the polymeric cosolute is decreased, with dextran H having the smallest effect and dextran L the greatest. At low temperature (5 °C), however, this sequence is reversed, with dextran H causing the greatest reduction in G' and dextran L the least. The reduction in G'' at 5 °C also seems slightly smaller than for the dextrans of higher molecular weight, but otherwise the values of G'' for samples incorporating equivalent concentrations of dextrans L, M or H are virtually superimposable.

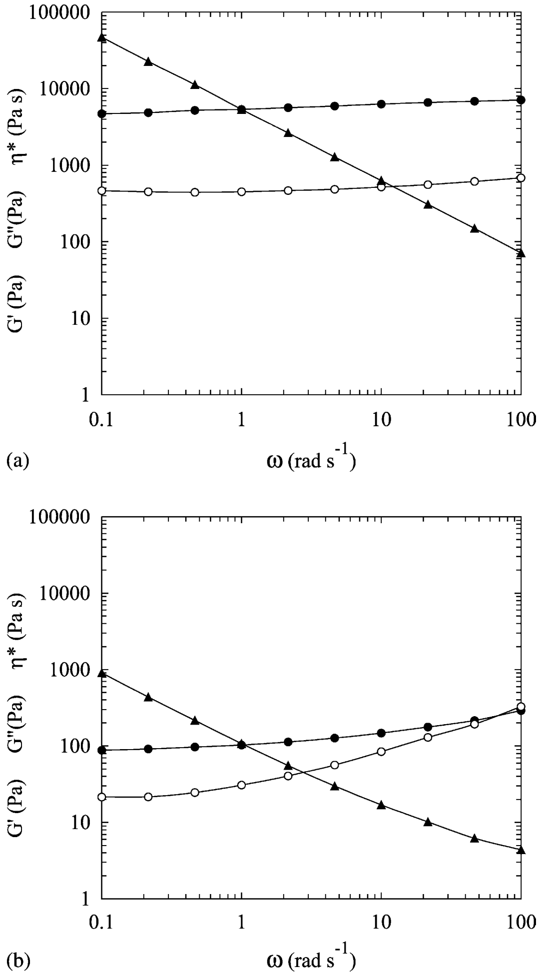

Fig. 7. Mechanical spectra (0.5% strain) showing the variation of G' (●), G'' (○) and η^* (▲) with frequency (ω) for 2.0 wt% calcium pectinate on completion of cooling from 90 to 5 °C (a) alone and (b) in the presence of 20 wt% dextran H.

As discussed in the preceding paper (Giannouli et al., 2004a), it seemed reasonable at the outset of this work to expect that the effectiveness of polymeric cosolutes in promoting self-association of pectin in the presence of Ca^{2+} might be related to their degree of space-occupancy, as characterised by the (dimensionless) product of concentration, c, and intrinsic viscosity, $[\eta]$. Fig. 9 shows the values of G' (Fig. 9a) and G'' (Fig. 9b) from Fig. 8, plotted against $c[\eta]$ rather than against c (as they are in Fig. 8). Although there does appear to be improved superposition of G' at 5 °C for low values of $c[\eta]$, the overall effect of including molecular size (as characterised by $[\eta]$) in the comparison is to pull the curves apart, with equivalent moduli being observed at progressively higher values of $c[\eta]$ as $[\eta]$ increases.

A converse treatment tested for galactomannans of different molecular weights (Giannouli et al., 2004a) was to plot observed moduli against the concentration of cosolute molecules, irrespective of their size. Fig. 10

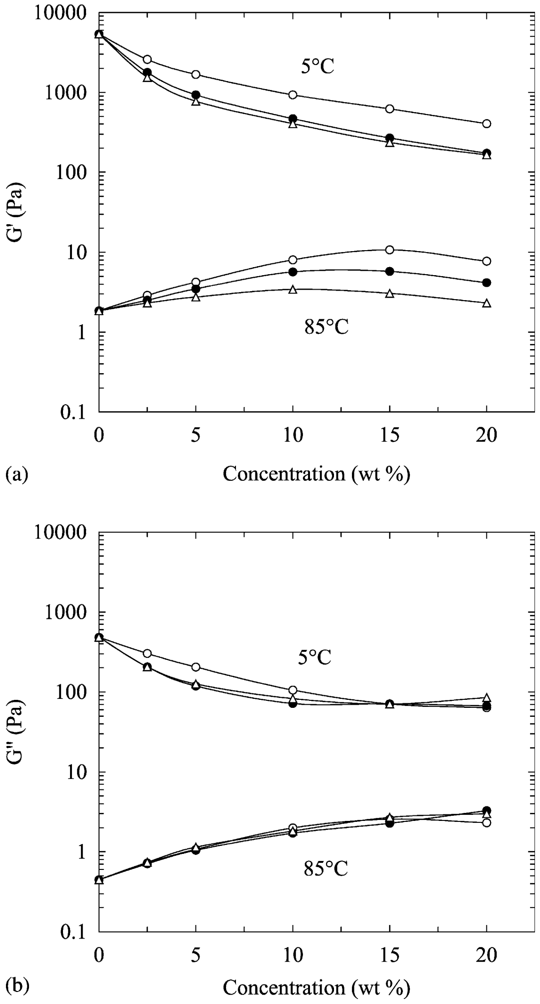

Fig. 8. Measured values of (a) G' and (b) G'' (10 rad s^{-1}; 0.5% strain) at 85 °C (lower curves) and 5 °C (upper curves), plotted against the concentration (wt%) of dextran for mixtures of 2.0 wt% calcium pectinate with dextran samples L (○), M (●) and H (△).

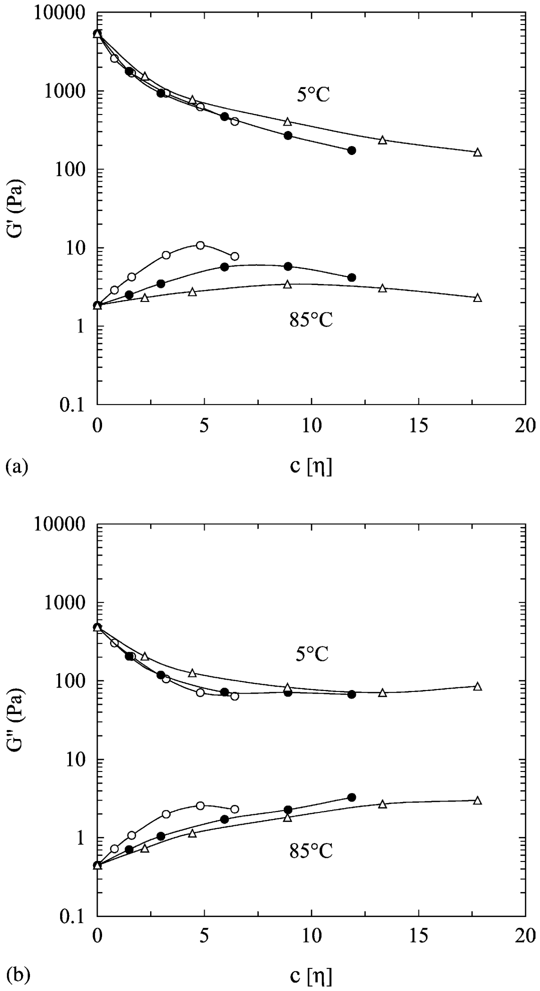

Fig. 9. Measured values of (a) G' and (b) G'' (10 rad s^{-1}; 0.5% strain) at 85 °C (lower curves) and 5 °C (upper curves), plotted against the (dimensionless) product of concentration, c and intrinsic viscosity, $[\eta]$, of the dextran component for mixtures of 2.0 wt% calcium pectinate with dextran samples L (○), M (●) and H (△).

shows corresponding plots of G' (Fig. 10a) and G'' (Fig. 10b) against molar concentration of dextran in mixtures with 2.0 wt% calcium pectinate (as in Figs. 8 and 9). The traces for the three dextran samples are again pulled apart, but in the opposite direction to the displacements seen (Fig. 9) on plotting G' and G'' against $c[\eta]$, with equivalent moduli now coming at progressively lower values of molecular concentration as the size of the individual dextran molecules increases. Thus, neither of the re-scaling procedures shown in Figs. 9 and 10 appears to offer any improvement on the simple comparison of weight concentrations (effectively segment density) presented in Fig. 8.

As a final comparison of the effect of the molecular size of dextran on its ability to promote self-association of pectin, Fig. 11 shows observed values of G' (Fig. 11a) and G'' (Fig. 11b) at 85 and 5 °C for 2.0 wt% calcium pectinate in the presence of a fixed concentration (10 wt%) of each of the dextran samples, plotted against the intrinsic viscosity of the dextran component. As found for guar gum (Giannouli et al., 2004a), the observed values of G' at 85 °C (Fig. 11a) show a progressive increase as the intrinsic viscosity of the dextran decreases, with a smaller accompanying increase in G'' (Fig. 11b). Thus, the effectiveness of dextran, like that of guar gum, in promoting initial association of pectin chains in the pre-gel solution state at high temperature increases as the molecular size of the dextran decreases.

The moduli at 5 °C also show an obvious systematic increase with decreasing intrinsic viscosity of the dextran component, but this now implies that the extent of further, excessive, association of pectin chains into large aggregated bundles is greater for samples incorporating dextran of high molecular weight. A similar reduction in low-temperature moduli with increasing intrinsic viscosity of polymeric cosolute was also observed for guar gum (Giannouli et al., 2004a). However, because of the remarkable effectiveness of the guar gum sample of lowest molecular weight (*M*7) in promoting Ca^{2+}-mediated association of pectin chains at

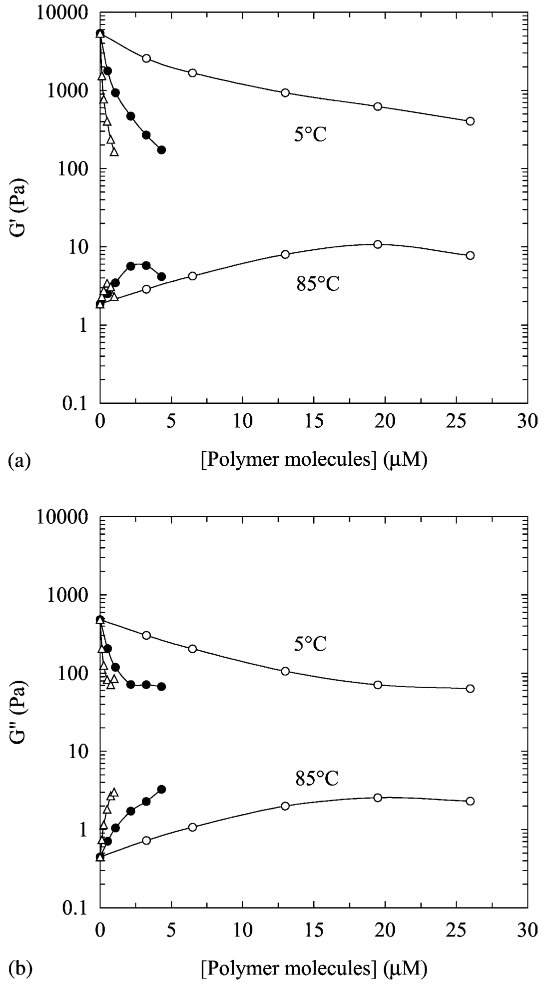

Fig. 10. Measured values of (a) G' and (b) G'' (10 rad s^{-1}; 0.5% strain) at 85 °C (lower curves) and 5 °C (upper curves), plotted against the molar concentration of dextran chains for mixtures of 2.0 wt% calcium pectinate with dextran samples L (○), M (●) and H (△).

high temperature, the maximum concentration of guar gum at which comparison of all samples could be made was 1.0 wt%, and the changes in G' and G'' at 5 °C were much smaller than those shown in Fig. 11 for 10 wt% dextran.

3.3. *Effect of inulin on calcium pectinate gelation*

Fig. 12 shows the changes in G' (Fig. 12a) and G'' (Fig. 12b) observed for 2.0 wt% low methoxy pectin with stoichiometric Ca^{2+} on cooling from 90 to 5 °C, alone, and in the presence of inulin at concentrations of 5, 10, 15, 20, 25, 30 and 35 wt%. As found for the dextran samples (Figs. 3–5) and for oxidised starch, potato maltodextrin and galactomannans (Picout et al., 2000a,b; Giannouli et al., 2004a), increasing concentrations of inulin cause a progressive increase in G' at high temperature (Fig. 12a) and a progressive reduction in G' at low temperature, with the curves again crossing at ~55 °C. The changes in G'' at high temperature are similar (Fig. 12b) to those observed (Fig. 12a) for G', but the values of G'' at 5 °C are virtually unaffected by inulin concentration.

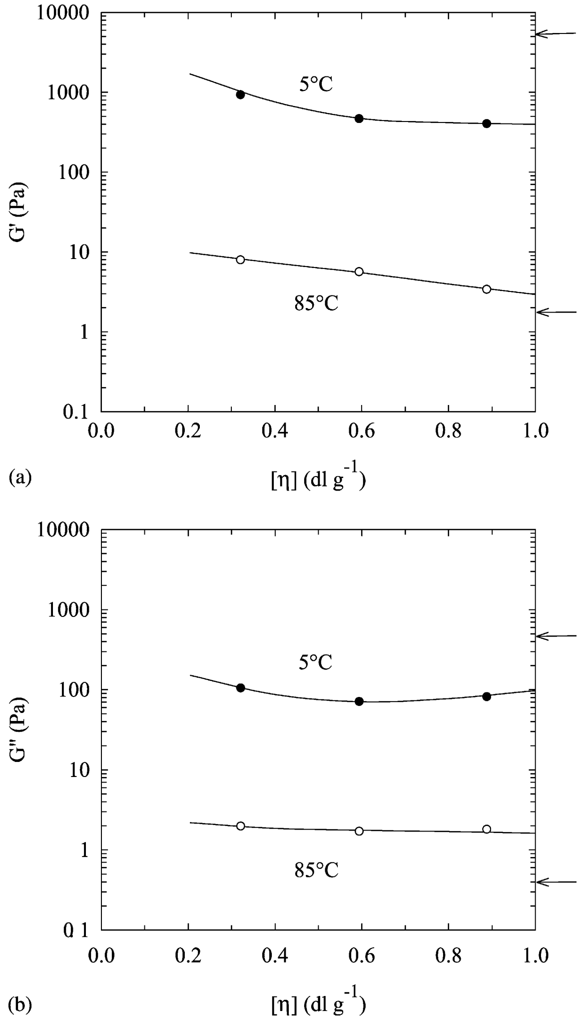

Fig. 11. Variation of (a) G' and (b) G'' (10 rad s^{-1}; 0.5% strain) at 85 °C (○) and 5 °C (●) with intrinsic viscosity, $[\eta]$, of the dextran component for mixtures of 2.0 wt% calcium pectinate with 10.0 wt% of each of the dextrans studied. The arrows on the right-hand axis show the corresponding moduli for 2.0 wt% calcium pectinate alone.

As shown in Fig. 13, the separation of G' and G'' at 85 °C remains essentially constant across the full range of inulin concentrations studied, but at 5 °C there is a progressive convergence, which, as discussed previously, may be caused by a progressive increase in the direct contribution of the polymeric cosolute to overall viscous response (G'') as its concentration in the mixture is increased.

4. Discussion and conclusions

The first conclusion drawn in the preceding paper (Giannouli et al., 2004a) was that the increases in moduli observed for calcium pectinate in the pre-gel solution state at high temperature on incorporation of oxidised starch

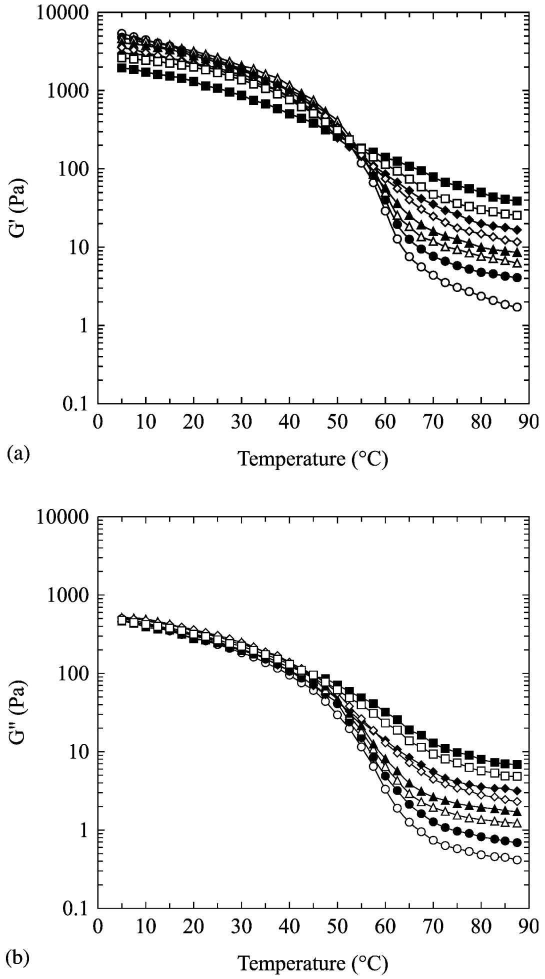

Fig. 12. Changes in (a) G' and (b) G'' (10 rad s^{-1}; 0.5% strain) during cooling from 90 to 5 °C for 2.0 wt% calcium pectinate alone (○) and in the presence of inulin at concentrations (wt%) of 5 (●), 10 (△), 15 (▲), 20 (◇), 25 (◆), 30 (□) and 35 (■).

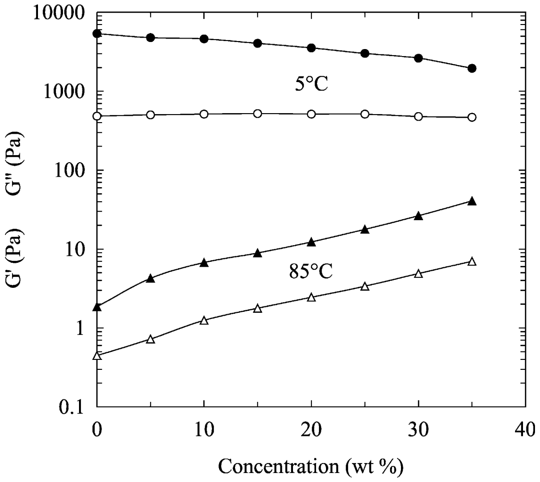

Fig. 13. Measured values (10 rad s^{-1}; 0.5% strain) of G' (filled symbols) and G'' (open symbols) at 85 °C (triangles) and 5 °C (circles) for 2.0 wt% calcium pectinate in the presence of inulin at all concentrations studied.

(Picout et al., 2000b) or potato maltodextrin (Picout et al., 2000a), and the subsequent reductions in moduli of the gels formed on cooling to 5 °C, are not unique to these partially depolymerised starches, but also occur with galactomannans as polymeric cosolute. The results reported here demonstrate that similar changes in the extent of Ca^{2+}-mediated association of low methoxy pectin at high and low temperatures can be induced by incorporation of dextrans or inulin.

A surprising feature of the investigation (Giannouli et al., 2004a) of galactomannans of different molecular weights was the finding that the smallest molecules had the greatest effectiveness in promoting initial self-association of pectin chains in the high-temperature solution state. The results shown in Fig. 11 demonstrate that the same, unexpected, inverse correlation between molecular size and segregative interactions with disordered pectin also occurs for dextrans.

Another surprising feature of the results from the present investigation is that the moduli of the gel networks formed on cooling mixtures of 2.0 wt% calcium pectinate with much higher concentrations of inulin (up to 35 wt%) showed no evidence of any detectable contribution from self-association of the inulin component. Previous studies (Hébette et al., 1998) have shown that when concentrated solutions (30 wt% and above) of chicory root inulin, of the type used here, are cooled at 1 °C/min (as also used in the present investigation), suspensions of semi-crystalline material are formed. The values of G' and G'' observed (Fig. 13) for mixtures of inulin with calcium pectinate on completion of cooling to 5 °C, however, give no indication of an upturn attributable to structuring of inulin at high concentrations. This may imply either that structuring does occur, as in water, but that the associated rheological changes are swamped by gelation of calcium pectinate, or that the presence of the pectin chains inhibits self-association of inulin. The over-riding conclusion from Fig. 13, however, is that inulin, like the other polymeric cosolutes studied (oxidised starch, potato maltodextrin, guar gum, locust bean gum and dextran) is effective in promoting Ca^{2+}-mediated association of low methoxy pectin.

For all of these calcium pectinate–cosolute systems, segregative interactions appear to be manifested in two ways: (i) an increase in moduli in the pre-gel solution state at high temperature, attributed (Picout et al., 2000b) to an increase in the extent of initial association of pectin chains into dimeric egg-box junctions, and (ii) a decrease in moduli on completion of cooling to low temperature (5 °C), attributed to incipient precipitation (wastage) of calcium pectinate in large aggregates.

It was shown in the preceding paper (Giannouli et al., 2004a) that, by the criterion of the overall reduction in the change in log G' on cooling from 85 to 5 °C, oxidised starch and galactomannans of high and intermediate molecular weight are roughly comparable in their segregative interactions with pectin, while guar gum of low molecular weight has a much greater effect, and that of potato

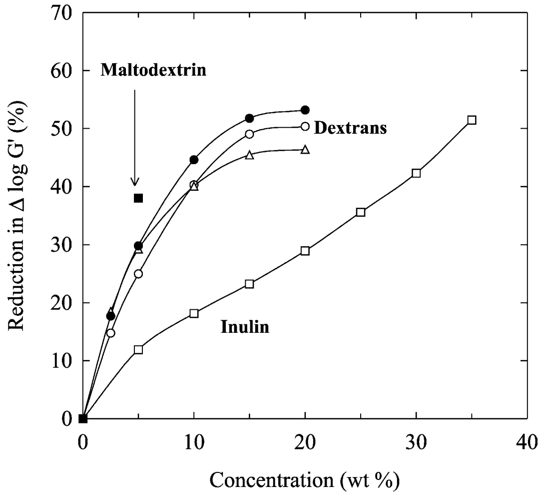

Fig. 14. Percentage reduction of the change in log G' on cooling from 85 to 5 °C for 2.0 wt% calcium pectinate on incorporation of inulin (☐) and dextran samples L (○), M (●) and H (△) at all concentrations studied. The corresponding value for 5.0 wt% potato maltodextrin (Giannouli et al., 2004a) is also shown (■).

maltodextrin is substantially smaller. Fig. 14 extends this comparison to the inulin and dextran samples studied in the present investigation.

For the dextran samples, the overall change in log G' between high and low temperature is virtually independent of molecular size. As shown in Fig. 8, the sample of lowest molecular weight causes the greatest increase in modulus at high temperature, but this is offset by a smaller reduction at low temperature, with the two effects virtually cancelling one another. It would appear, therefore, that the overall effectiveness of the three dextran samples studied in driving self-association of pectin is essentially the same, but that initial association of disordered pectin chains into Ca^{2+}-mediated egg-box junctions at high temperature is promoted preferentially by the smaller dextran molecules, whereas the dextrans of larger hydrodynamic volume are more effective in promoting further, excessive, association of calcium pectinate into large aggregates.

As a point of comparison, Fig. 14 shows the reduction in the change in log G' between 85 and 5 °C caused by potato maltodextrin, which, as summarised above, had less effect on calcium pectinate gelation than the other polymeric cosolutes (oxidised starch and galactomannans) studied by Picout et al. (2000a,b) and Giannouli et al. (2004a). The changes induced by the dextran samples studied in the present work are somewhat smaller than for potato maltodextrin, and inulin has an even smaller effect.

Although inulin consists of short, predominantly linear, chains, whereas the dextran samples studied are branched polymers of much higher molecular weight (Table 1), the two materials have one important structural feature in common. The predominant $1 \longrightarrow 6$ linkage in dextran and the $1 \longrightarrow 2$ linkages in inulin both have three constituent single bonds, in contrast to the normal glycosidic linkages in most other polysaccharides, where adjacent rings are separated by only two single bonds, and have therefore far less conformational freedom than in inulin and dextrans. As shown in Fig. 2, the intrinsic viscosities of dextran and inulin are much lower than those of galactomannans of equivalent molecular weight. For dextrans of high molecular weight, the difference is likely to arise predominantly from branching, but for inulin, and for dextrans of low molecular weight where branching is less extensive, the ability of the molecules to adopt compact conformations of low hydrodynamic volume can be attributed to the enhanced flexibility introduced by the additional bond in the glycosidic linkage. The flexibility of dextrans and inulin may also be relevant to their limited effectiveness in promoting self-association of pectin.

Further discussion of possible relationships between primary structure and segregative interactions with pectin is deferred to the following paper (Giannouli et al., 2004b), where the comparison is extended to the densely branched and conformationally restricted structure of gum arabic.

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