ELSEVIER

Carbohydrate Polymers 42 (2000) 233–243

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Co-gelation of high methoxy pectin with oxidised starch or potato maltodextrin

V. Evageliou[a], R.K. Richardson[a], E.R. Morris[b,*]

[a]Cranfield University, Silsoe College, Silsoe, Bedford MK45 4DT, UK
[b]Department of Food Science and Technology, University College Cork, Cork, Ireland

Received 18 May 1999; accepted 12 August 1999

Abstract

In a continuation of the work reported in the preceding paper, the effect of oxidised starch on gelation of high methoxy pectin was studied under different experimental conditions. The main changes in procedure were: (i) gelation was induced by slow cooling (1°C $\min^{-1}$) instead of rapid quenching; (ii) the pectin concentration was reduced from 1.0 to 0.5 wt%; and (iii) mixtures were prepared at pH 4 and subsequently acidified to pH 3, rather than being prepared directly at pH 3. The temperature-course of structure formation (increase in G' and G'') during cooling (from 95 to 5°C), and the final moduli at 5°C, are consistent with the conclusions reached for the mixtures gelled by quenching: (i) the effective concentration of both polymers is raised by mutual exclusion; and (ii) the initial reduction in moduli observed on partial replacement of sucrose by oxidised starch is due to the reduction in sucrose content, rather than to the presence of starch. An analogous series of experiments, under identical conditions, was carried out using potato maltodextrin in place of oxidised starch. In contrast to the pectin–oxidised starch systems, there was no evidence of any significant exclusion effects in the pectin–maltodextrin mixtures, but the changes in moduli observed during cooling indicate that maltodextrin, unlike oxidised starch, is almost as effective as sucrose in promoting self-association of high methoxy pectin at acid pH. These differences in behaviour are attributed to a high population of short, linear chains and oligomeric fragments in maltodextrin, facilitating segmental contacts with pectin, in contrast to the densely branched (partially depolymerised amylopectin) structure of oxidised starch, which will limit segmental contacts, but resist penetration by pectin chains, with consequent increase in effective concentrations of pectin and starch. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Co-gelation; Oxidised starch; High-methoxy pectin; Potato maltodextrin

1. Introduction

In the investigation reported in the preceding paper (Evageliou, Richardson & Morris, 2000a), the effect of oxidised starch on gelation of high-methoxy pectin was studied using a rapid reduction in temperature (quenching) to induce gelation, and with pectin concentration held fixed at 1.0 wt%. In the study reported here, we used experimental conditions closer to those typical of normal industrial practice (Christensen, 1986; Rolin, 1993); pectin concentration was reduced to 0.5 wt% and samples were cooled at a fixed rate of 1°C $\min^{-1}$. A further, perhaps more significant, change in procedure was that the pH of the pectin solutions was raised to 4.0 before mixing with starch, and was then reduced to the final value of pH 3.0 by addition of critic acid immediately prior to cooling. As would be expected, these differences in composition, preparation and gelation of the experimental samples caused substantial changes in the absolute values of gel moduli, but the overall pattern of response to progressive replacement of sucrose by oxidised starch remained essentially the same.

We also report an analogous study of the effect of replacement of sucrose by potato maltodextrin. The composition-dependence of final moduli at low temperature was again broadly similar in form to the changes observed with oxidised starch, but the temperature-course of structure formation on cooling suggests some significant differences between the two systems.

2. Materials and methods

The pectin and starch samples used were identical to those described in the preceding paper (Evageliou et al., 2000a): high-methoxy pectin (X-4938) of DE 70.3 from the Copenhagen Pectin Division of Hercules, and oxidised starch (C * Set 06598; batch SH 1338) from Cerestar. The potato maltodextrin used was a commercial sample from

---

* Corresponding author. Tel.: +353-21-903625; fax: +353-21-270001.
E-mail address: ed.morris@ucc.ie (E.R. Morris).

0144-8617/00/$ - see front matter
PII: S0144-8617(99)00174-5

Table 1
Content (%) of oligomeric fragments in maltodextrin (C $*$ deLight MD 01970) and oxidised starch (C $*$ Set 06598)

Degree of polymerisation	Maltodextrin	Oxidised starch
1 (glucose)	0.6	0.2
2	1.9	0.2
3	1.6	0.2
4	1.4	<0.2
5	1.5	<0.2
6	1.7	<0.2
7	1.7	<0.2
8	2.0	<0.2
9	1.7	<0.2
>9	85.9	98.6

Cerestar (C $*$ deLight MD 01970). The percentages of glucose and glucose oligomers (DP 1–9) in the oxidised starch and maltodextrin samples were kindly provided by Cerestar, and are listed in Table 1. Citric acid and trisodium citrate dihydrate were AnalaR grade from BDH. Distilled deionised water was used throughout.

The procedure used for preparation of experimental samples was as follows. First, a stock solution of pectin was prepared at ~5 wt%, and adjusted to pH 4 by addition of trisodium citrate. Oxidised starch or maltodextrin was dispersed in slightly more than the total amount of water required for the mixed system, and dissolved by stirring in a water bath at ~98°C. The required amount of sucrose was then added, with continued stirring, followed by the appropriate volume of the pectin stock solution, and the mixture was brought to the correct total weight by addition of water or continued evaporation. Finally, the sample was adjusted to pH 3.0 by addition of a pre-determined weight of citric acid, and was immediately loaded onto a rheometer pre-heated to 95°C.

In most of the experiments the pectin concentration was held fixed at 0.5 wt%, and the total concentration of cosolute (sucrose plus oxidised starch or sucrose plus maltodextrin) was also held constant at 65 wt% (as in the investigation described in the preceding paper; Evageliou et al., 2000a). Comparative values of gel moduli were obtained for 0.5 wt% pectin in the absence of starch or maltodextrin, at sucrose concentrations between 65 and 47.5 wt%, and for oxidised starch or maltodextrin in the absence of pectin, but with incorporation of the amount of sucrose required to maintain the total solute concentration at 65 wt%. Some further comparisons were made using higher concentrations of pectin (0.75 and 1.0 wt%) in the presence of fixed concentrations of sucrose (50 and 55 wt%), but without incorporation of starch or maltodextrin.

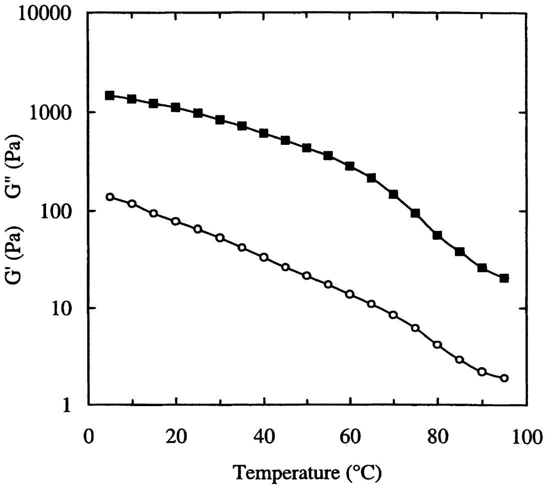

Fig. 1. Changes in G' (■) and G'' (○), measured at 1 rad s^{-1} and 0.5% strain, for 0.5 wt% high-methoxy pectin (DE 70.3; pH 3.0) in 65 wt% sucrose, on cooling from 95 to 5°C at 1°C min^{-1}.

Rheological measurements were made using truncated cone-and-plate geometry (diameter 50 mm; cone angle 0.05 rad; minimum gap 1 mm) on a sensitive prototype rheometer designed and constructed by one of us (R.K.R.). After loading at 95°C, the samples were coated around their periphery with light silicone oil, to minimise evaporation, and were cooled to 5°C at 1°C min^{-1}, with measurement of storage modulus (G') and loss modulus (G'') at a fixed frequency of 1 rad s^{-1} and fixed strain of 0.5%. A full mechanical spectrum (0.5% strain) was then recorded to show the variation of G', G'' and η^* (complex dynamic viscosity) with frequency (ω). Temperature was controlled by a Haake circulated water bath and measured using a thermocouple in contact with the stationary element.

3. Results

3.1. Gelation of high-methoxy pectin

Fig. 1 shows the changes in G' and G'' (1 rad s^{-1}; 0.5% strain) observed for 0.5 wt% pectin (DE 70.3; pH 3.0) in the presence of 65 wt% sucrose on cooling from 95 to 5°C at 1°C min^{-1}. Both moduli increase by about two orders of magnitude across this temperature range, with evidence of a co-operative gelling process (sigmoidal increase in G'' and, particularly, G') between 95 and ~60°C. At the initial loading temperature of 95°C, however, G' is about a decade higher than G'', showing that the sample, although fluid, already has substantial gel-like character at high temperature.

Several other biopolymer systems, notably conformationally ordered bacterial polysaccharides such as xanthan (Ross-Murphy, Morris & Morris, 1983), welan and rhamsan (Morris, Gothard, Hember, Manning & Robinson, 1996) also show predominantly elastic (gel-like) response to small deformation, coupled with an ability to flow in response to higher stress, and are commonly known as “weak gels” (Ross-Murphy, 1984). Weak-gel rheology at high temperature, with consolidation into a “true” (self-supporting) network on cooling, has been reported previously for a range of commercial citrus pectins (slow-

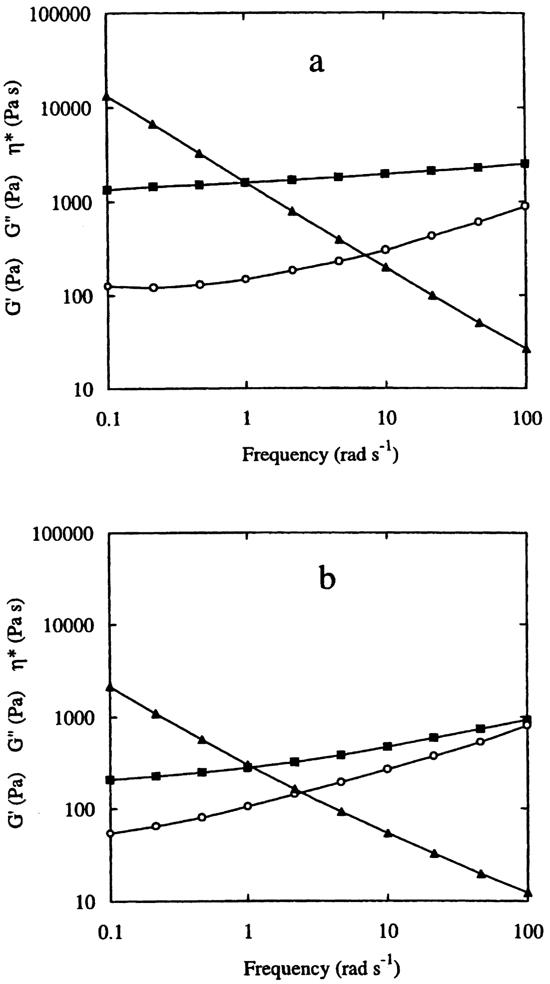

Fig. 2. Mechanical spectra (0.5% strain; 5°C) showing the frequency-dependence of G' (■), G'' (○) and η^* (▲) for (a) 0.5 wt% pectin (pH 3.0) in 65 wt% sucrose at the end of the cooling process shown in Fig. 1; and (b) 1.0 wt% pectin, also in 65 wt% sucrose at pH 3.0, after rapid quenching to 5°C and holding for 1 h (Evageliou et al., 2000a).

set, medium-set and rapid-set) and a novel high-methoxy pectin extracted from pumpkins (Ptitchkina, Danilova, Doxastakis, Kasapis & Morris, 1994). Similar behaviour has also been observed for low-methoxy pectin gelled by cooling in the presence of Ca^{2+} at acid pH (Picout, Richardson, Rolin, Abeysekara & Morris, 2000a; Picout, Richardson & Morris, 2000c).

The mechanical spectrum recorded at the end of the cooling process (Fig. 1) is shown in Fig. 2a. The spectrum has the form typical (Ross-Murphy, 1984) of a biopolymer gel ($G' > G''$; little frequency-dependence of either modulus; linear reduction in log η^* with increasing log ω, with a slope close to -1). For comparison, Fig. 2b shows the corresponding spectrum for 1.0 wt% pectin (DE 70.3; pH 3.0; 65 wt% sucrose, as in Fig. 2a) gelled by rapid quenching to 5°C (Evageliou et al., 1999a). Despite the two-fold reduction in concentration, the slow-cooled sample (Fig. 2a) has substantially higher moduli than the quenched sample (Fig. 2b) and its mechanical spectrum is more gel-like (greater separation of G' and G''; smaller increase in moduli with increasing frequency; steeper slope of log η^* versus log ω) It is evident, therefore, that the procedure used in the present work is more effective in inducing formation of a cohesive gel network than the method adopted in the study reported in the preceding paper (Evageliou et al., 2000a).

In preparation of the mixtures of pectins with oxidised starch or maltodextrin at a total cosolute concentration of 65 wt%, increase in the starch or maltodextrin concentration is, of course, accompanied by a corresponding reduction in the concentration of sucrose. The effect of sucrose concentration on the gelation of pectin in the absence of starch or maltodextrin was therefore investigated, for comparison with the behaviour of the mixed systems. Fig. 3 shows the changes in G' and G''observed for 0.5 wt% pectin (DE 70.3; pH 3.0) on cooling in the presence of sucrose at concentrations ranging from 65 wt% (as in Fig. 1) to 47.5 wt% (the lowest value at which detectable changes occurred). As the concentration of sucrose is lowered, there is a systematic reduction in G' at the loading temperature of 95°C (i.e. progressive loss of initial "weak gel" character), with accompanying displacement of the gelling transition (steep increase in moduli) to progressively lower temperature, and a systematic reduction in the moduli attained on completion of cooling. The variation in the final values of G' and G'' at 5°C with decreasing sucrose concentration is shown in Fig. 4.

3.2. Gelation of oxidised starch and maltodextrin

In the mixed systems with pectin, the total concentration of cosolute (sucrose plus oxidised starch or sucrose plus maltodextrin) was held constant at 65 wt%. Comparative studies of the gelation of oxidised starch and maltodextrin in the absence of pectin were therefore carried out at the same total solute concentration. The starch concentrations used were 10–45 wt% (with 55–20 wt% sucrose). Fig. 5 shows the variation in G' and G''on cooling for representative compositions within this range. The corresponding curves for maltodextrin (at concentrations ranging from 7.5–20 wt%, with 57.5–45 wt% sucrose) are shown in Fig. 6. In both cases there is a progressive reduction in the temperature-course of structure formation (increase in moduli) as the polymer concentrations is decreased, with an accompanying reduction in the moduli reached on completion of cooling.

Fig. 7 shows the concentration-dependence of G' and G'' at 5°C for oxidised starch (Fig. 7a) and maltodextrin (Fig. 7b). In both cases the increase in elastic response (G') with increasing polymer concentration is steeper than the associated increase in G'' (viscous response). For maltodextrin, however, G' (at 1 rad s^{-1}) rises above G'' when the polymer concentration reaches ~10 wt% (with 55 wt% sucrose), with the divergence between the two moduli then increasing to around a factor of 10, as found for conventional

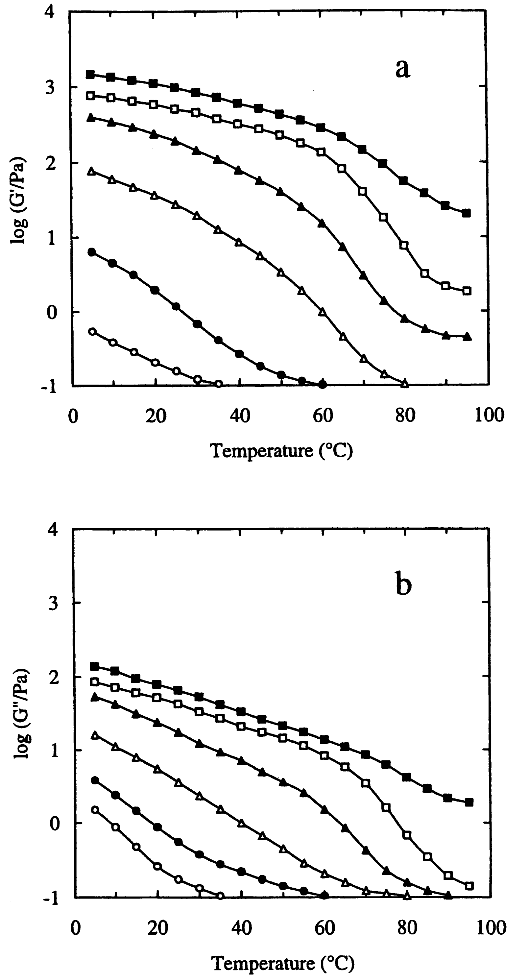

Fig. 3. Variation of (a) G' and (b) G'' (1 rad s^{-1}; 0.5% strain) for 0.5 wt% pectin (DE 70.3; pH 3.0) on cooling (1°C min^{-1}) in the presence of sucrose at concentrations (wt%) of: 47.5 (○); 50 (●); 55 (△); 60 (▲); 62.5 (□); and 65 (■).

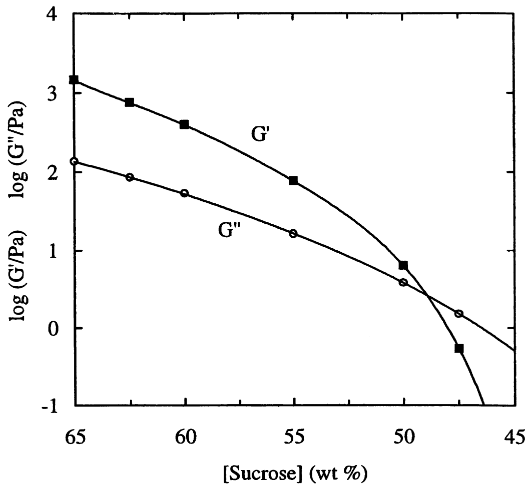

Fig. 4. Effect of sucrose concentration on the observed values of G' (■) and G'' (○) at 5°C for 0.5 wt% pectin (DE 70.3; pH 3.0) at the end of the cooling scans shown in Fig. 3.

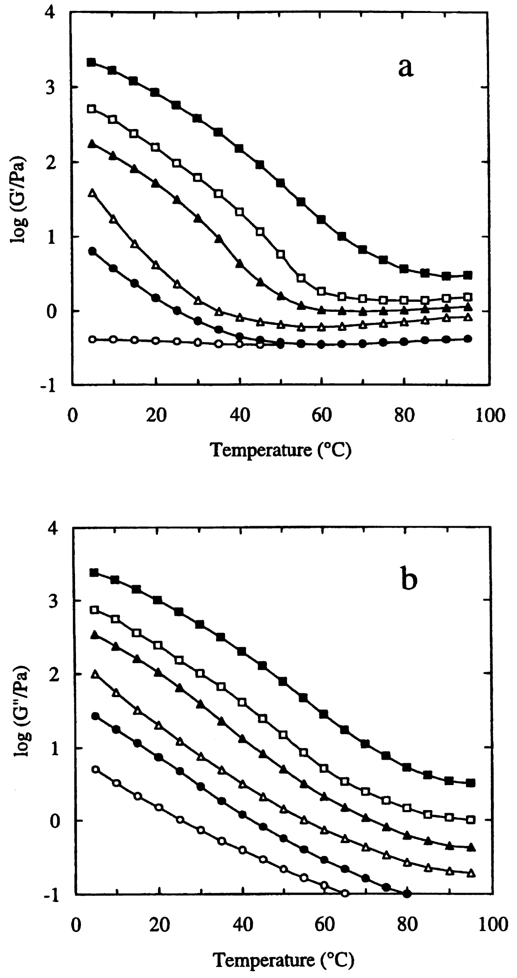

Fig. 5. Variation of (a) G' and (b) G'' (1 rad s^{-1}; 0.5% strain) on cooling from 95 to 5°C at 1°C min^{-1} for mixtures of oxidised starch with sucrose at a combined concentration of 65 wt%, illustrated for starch concentrations (wt%) of: 10 (○); 15 (●); 20 (△); 25 (▲); 30 (□); and 40 (■).

biopolymer gels (Ross-Murphy, 1984), whereas the values of G' recorded for oxidised starch on completion of cooling remain slightly lower than the corresponding values of G'' up to the highest concentration studied (45 wt%, in combination with 20 wt% sucrose). As described in an accompanying paper (Evageliou, Richardson & Morris, 2000c), the time–temperature course of gelation for oxidised starch is complex, and the increases in moduli seen during cooling (Fig. 5) are followed by a second wave of structure formation on holding at 5°C. For the purposes of the present study, however, the metastable values (Fig. 7a) attained at the end of the cooling process are used for comparison with the corresponding values for mixtures with 0.5 wt% high methoxy pectin.

3.3. Mixtures of pectin with oxidised starch

Fig. 8 shows the observed values of G' and G'' at 5°C for the pectin–starch mixtures, in direct comparison with the corresponding moduli for pectin and oxidised starch at the

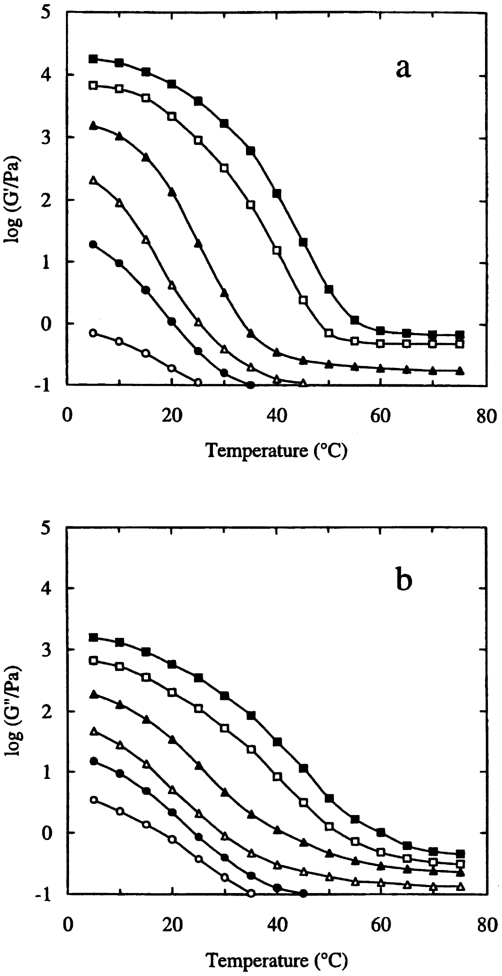

Fig. 6. Variation of (a) G' and (b) G'' (1 rad s^{-1}; 0.5% strain) on cooling from 95 to 5°C at 1°C min^{-1} for mixtures of maltodextrin with sucrose at a combined concentration of 65 wt%, illustrated for maltodextrin concentrations (wt%) of: 7.5 (○); 10 (●); 12.5 (△); 15 (▲); 17.5 (□); and 20 (■).

same sucrose concentrations. As found for samples gelled by rapid quenching (Evageliou et al., 2000a), the initial effect of partial replacement of sucrose by oxidised starch is to cause a sharp decrease in moduli, with the values of G' (Fig. 8a) and G'' (Fig. 8b) for the mixed systems remaining virtually identical for those observed (Fig. 4) for pectin in the presence of the same concentrations of sucrose, but in the absence of starch. It seems evident, therefore, that the initial reduction in moduli arises predominantly from the reduction in sucrose content rather than from the incorporation of oxidised starch.

At higher starch concentrations, the moduli of the mixed systems increase, following essentially the same form of concentration-dependence as found (Fig. 7a) for oxidised starch in the absence of pectin, but displaced to somewhat higher values (by a factor of ~3 for G' and ~2 for G''). The greatest divergence in moduli between the mixtures and the individual polymeric constituents occurs at a starch concentration of ~15 wt% (with 50 wt% sucrose). The preceding paper (Evageliou et al., 2000a) reports a detailed analysis of the rheology of quenched samples prepared at this sucrose concentration, with systematic variation in the concentrations of pectin and oxidised starch. The central finding was that the observed moduli could be explained by an increase in the effective concentration of both polymers due to mutual exclusion. The behaviour of the slow-cooled samples studied in the present work is entirely consistent with that interpretation.

Fig. 9 shows the mechanical spectra obtained on completion of cooling to 5°C for 0.5 wt% pectin with 50 wt% sucrose, in the presence and absence of 15 wt% oxidised starch. The proportion of liquid-like character (G'') is greater in the mixed system (Fig. 9a), and the frequency-dependence of both moduli is steeper, as would be anticipated from the presence of a substantial concentration of predominantly disordered starch. In both spectra, however, G' levels out towards a constant value at low frequency, indicating the presence of a weak, but continuous, pectin network. The absolute value of G' in this plateau region is substantially (~5 ×) higher for the mixed system, consistent with an increase in the effective concentration of pectin in response to space-occupancy by starch.

The temperature-course of structure formation on cooling also indicates an increase in the effective concentration of pectin in the presence of oxidised starch. Fig. 10 shows the increase in gel-like (elastic) response (G') during cooling for the mixed system (0.5 wt% pectin; 15 wt% starch; 50 wt% sucrose), in comparison with the corresponding traces for 15 wt% oxidised starch in 50 wt% sucrose but in the absence of pectin, and for pectin (also in 50 wt% sucrose, but with no added starch) at 0.5 wt% (as in the mixed system) and at higher concentrations (0.75 and 1.0 wt%). At the loading temperature of 95°C, the values of G' for pectin in the absence of starch are too low to be measured, but the starch component gives an initial G' of ~0.5 Pa. The modulus of the mixed system is somewhat higher ($G' \approx 1$ Pa); as discussed above, this small increase can be explained by mutual exclusion of the two polymers, with consequent increase in the effective concentration of starch. On cooling, however, there is a substantial (~10-fold) increase in G' of the mixture before the onset of the increase in modulus for the starch component in the absence of pectin. The onset temperature for the gelation of pectin at its overall concentration in the mixed system (0.5 wt%) is also much lower than the temperature-range of the initial increase in G' for the mixed system. As pectin concentration is raised (to 0.75 and 1.0 wt%), however, the temperature-course of structure formation moves into the range observed for the mixture with oxidised starch and, indeed, the absolute values of G' for 1.0 wt% pectin (with 50 wt% sucrose) at temperature below ~40°C fall into almost exact agreement with those of the mixed system.

We therefore conclude that, as proposed previously for samples cooled by rapid quenching (Evageliou et al., 2000a), the divergence (Fig. 8) between the moduli of the mixed systems and those of the individual constituents can be

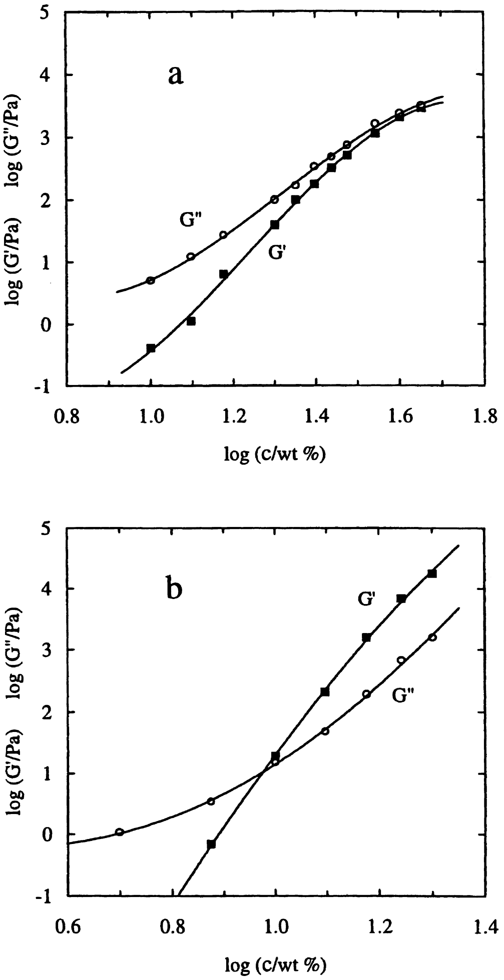

Fig. 7. Variation of G' (■) and G'' (○), measured at 1 rad s^{-1} and 0.5% strain after cooling to 5°C at 1°C min^{-1}, with polymer concentration (c) for (a) oxidised starch and (b) maltodextrin in mixtures with sucrose at a combined concentration of 65 wt%.

explained by mutual exclusion raising the effective concentration of both polymers (and, in particular, promoting association of the pectin component into a continuous network).

3.4. Mixtures of pectin with maltodextrin

Fig. 11 shows the composition-dependence of G' and G'' for the pectin–maltodextrin mixtures (0.5 wt% pectin; 0–20 wt% maltodextrin; 65–45 wt% sucrose), and for the individual polymers at the same sucrose concentrations. As found for the mixtures of pectin with oxidised starch (Fig. 8), progressive replacement of sucrose by maltodextrin causes an initial reduction and subsequent increase in moduli, with the values at the two extremes of the composition range following the behaviour of pectin at low concentrations of maltodextrin and of maltodextrin at high concentrations.

Since the onset of gelation occurs (Fig. 7) at substantially lower concentration for maltodextrin than for oxidised starch, however, the initial decrease in moduli is confined to a much narrower range of composition, before it is overtaken by the increase from gelation of maltodextrin. In particular, the maximum divergence between the moduli of the mixed systems and those of the individual polymers (which, for the mixtures of pectin with oxidised starch, occurs at ~15 wt% starch, 50 wt% sucrose) comes at ~10 wt% maltodextrin (with 55 wt% sucrose).

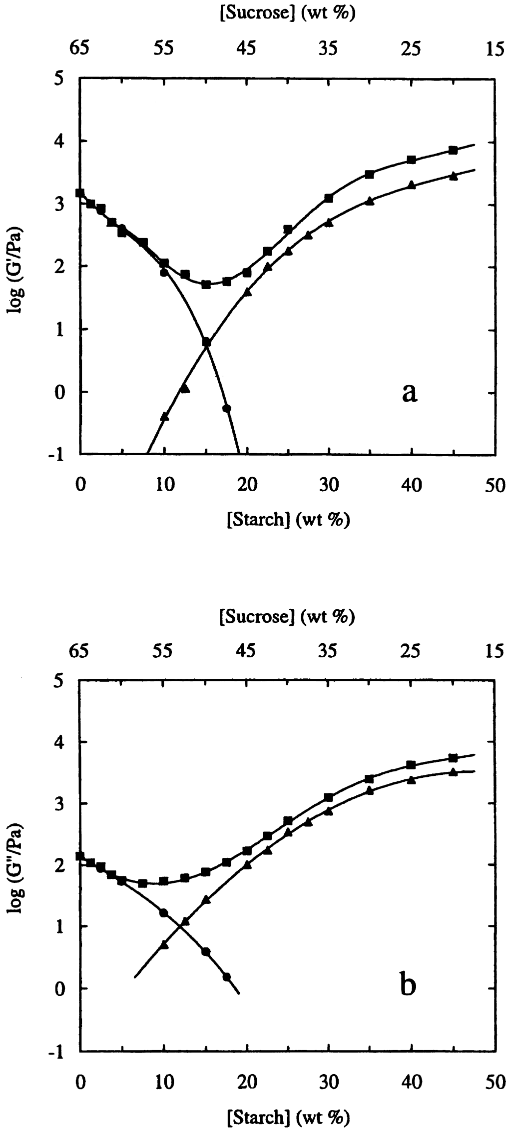

Fig. 8. Composition-dependence of (a) G' and (b) G'' (1 rad s^{-1}; 0.5% strain; 5°C) for: mixtures of 0.5 wt% high methoxy pectin (DE 70.3; pH 3.0) with sucrose and oxidised starch at a combined concentration of 65 wt% (■); 0.5 wt% pectin with varying concentrations of sucrose in the absence of starch (●); and mixtures of oxidised starch with sucrose at a combined concentration of 65 wt% in the absence of pectin (▲).

The mechanical response at this composition (Fig. 12) is close to the form typical of a normal biopolymer gel, but with a progressive upturn in moduli (particularly G'') at high frequency, indicating the presence of a substantial sol fraction of disordered chains. As shown in Fig. 13a, the mechanical spectrum recorded for the pectin component (with 55 wt% sucrose) in the absence of maltodextrin is closely

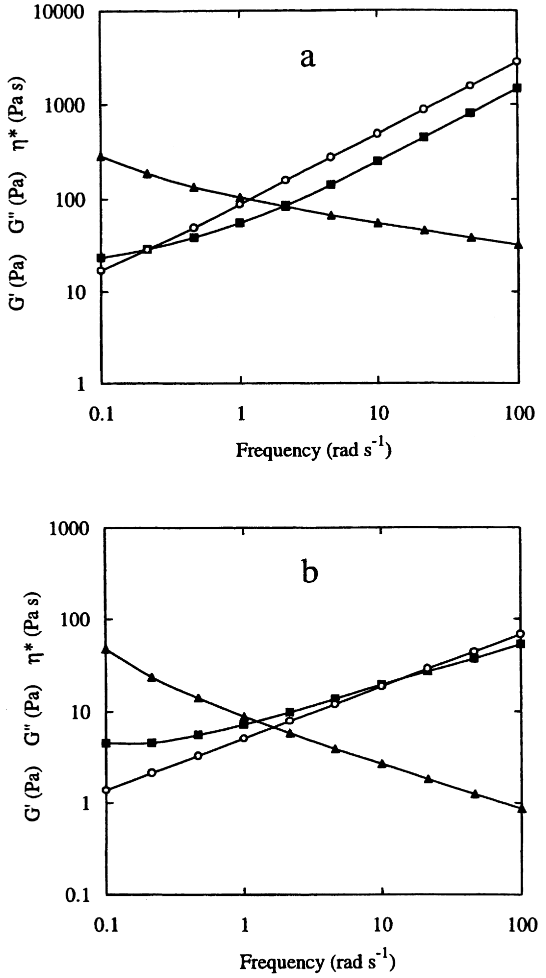

Fig. 9. Mechanical spectra (0.5% strain; 5°C) showing the frequency-dependence of G' (■), G'' (○) and η^* (▲) for 0.5 wt% pectin (DE 70.3; pH 3.0) in 50 wt% sucrose: (a) in combination with 15 wt% oxidised starch; and (b) in the absence of starch.

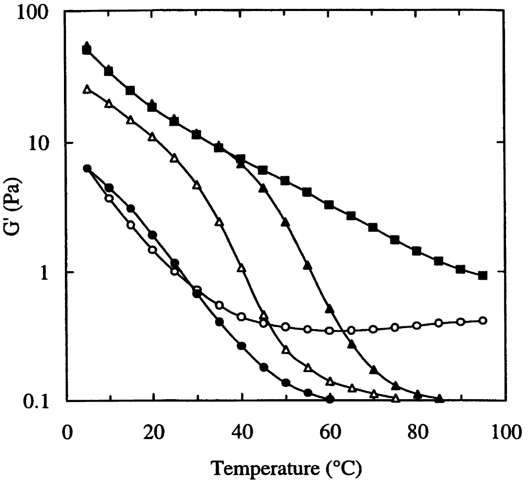

Fig. 10. Variation of G' (1 rad s^{-1}; 0.5% strain) on cooling from 95 to 5°C at 1°C min^{-1} for preparations of pectin (DE 70.3; pH 3.0) and/or oxidised starch in 50 wt% sucrose: 0.5 wt% pectin plus 15 wt% starch (■); 15 wt% starch in the absence of pectin (○); pectin in the absence of starch, at concentrations (wt%) of 0.5 (●), 0.75 (△) and 1.0 (▲).

similar in form to that of the mixture (Fig. 12), although the absolute values of the moduli are much lower. The spectrum obtained for the maltodextrin component at the same sucrose concentration but in the absence of pectin (Fig. 13b), by contrast, has only limited gel-like character. It seems likely, therefore, that the overall response of the mixed system at the point of maximum divergence from the behaviour of the individual constituents is dominated by pectin, but that association of the pectin chains into a continuous network is promoted by the presence of maltodextrin. The mechanism involved, however, appears to be different from the excluded volume effects proposed for the mixtures of pectin with oxidised starch.

Fig. 14 shows the observed changes in moduli during cooling for the maltodextrin–pectin mixture at the point of maximum divergence (Fig. 11) from the individual constituents (i.e. at 10 wt% maltodextrin; 55 wt% sucrose), in comparison with the corresponding curves for the pectin and maltodextrin components at the same sucrose concentration. G' and G'' for the individual constituents reach measurable values only at temperatures well below the initial loading temperature of 95°C. The mixed system, however, already has substantial moduli on loading ($G' \approx 35$ Pa; $G'' \approx 3.5$ Pa), indicating significant association of pectin into a weak gel network. In the absence of maltodextrin, doubling the pectin concentration (to 1.0 wt%) in the presence of the same concentration of sucrose (55 wt%) has little effect on the onset temperature for structure formation on cooling; in particular, the sample has no detectable weak-gel character at 95°C. Raising the sucrose concentration to 65 wt%, with pectin concentration held fixed at 0.5 wt% (as in the mixed systems), however, gives cooling curves close to those observed for the mixture with 10 wt% maltodextrin. It would appear, therefore, that addition of 10 wt% maltodextrin has almost the same effect as addition of a further 10 wt% of sucrose.

After the initial increase in moduli attributable to consolidation of pectin weak-gel structure into a stronger network, the cooling curves for 0.5 wt% pectin with 10 wt% maltodextrin and 55 wt% sucrose (Fig. 14) show only a slight upturn over the temperature range of the increase in G' and G'' for the maltodextrin component in the absence of pectin. When the maltodextrin content is raised to 15 wt% (with 50 wt% sucrose), however, the increase in overall moduli on gelation of the maltodextrin component becomes far more evident (Fig. 15a), and at the highest maltodextrin concentration studied (20wt%) the observed values of G' and G'' for the mixed system and for 20 wt% maltodextrin at the same sucrose concentration but in the absence of pectin fall into almost perfect agreement (Fig. 15b) at temperatures below ~35°C.

4. Discussion

This investigation was carried out in parallel with studies

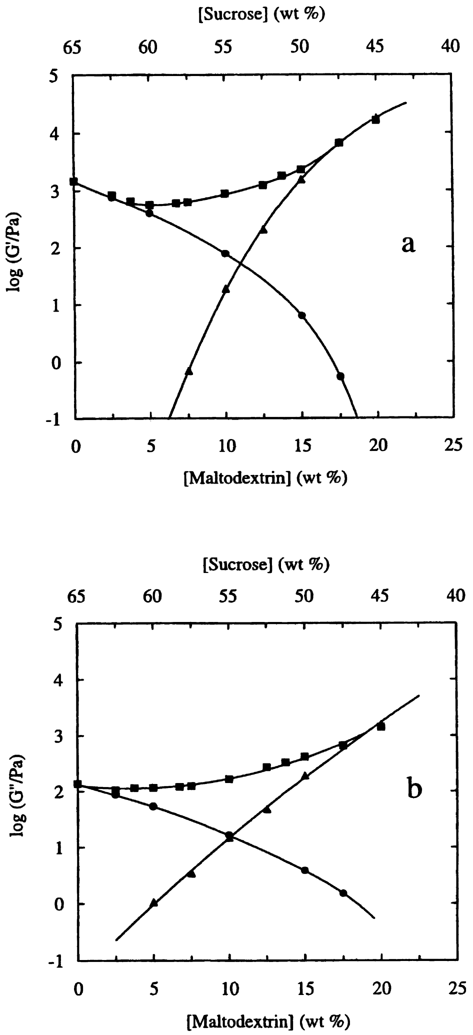

Fig. 11. Composition-dependence of (a) G' and (b) G'' (1 rad s^{-1}; 0.5% strain; 5°C) for: mixtures of 0.5 wt% high-methoxy pectin (DE 70.3; pH 3.0) with sucrose and maltodextrin at a combined concentration of 65 wt% (■); 0.5 wt% pectin with varying concentrations of sucrose in the absence of maltodextrin (●); and mixtures of maltodextrin with sucrose at a combined concentration of 65 wt% in the absence of pectin (▲).

of the effect of the samples of maltodextrin and oxidised starch on the gelation of low-methoxy pectin by cooling in the presence of Ca^{2+} (Picout et al., 2000a–d). At first sight, the results from the two series of experiments appeared similar. As reported here (Figs. 8 and 11) and in the preceding paper (Evageliou et al., 2000a) for mixtures with high methoxy pectin, progressive incorporation of partially depolymerised starch (oxidised starch or maltodextrin) in gelling compositions of low methoxy pectin caused an initial decrease in modulus before the increase associated with gelation of the starch-based polymer. On closer inspection, however, the underlying mechanisms appear to be entirely different.

In the high-methoxy pectin systems, incorporation of large amounts of the starch polysaccharides necessitated a corresponding reduction in sucrose concentration, and it

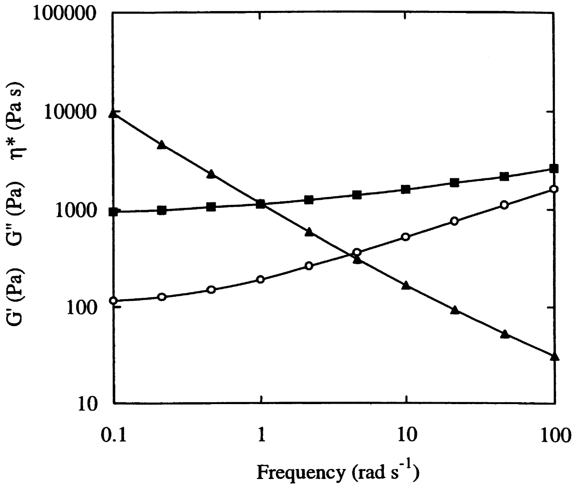

Fig. 12. Mechanical spectrum (0.5% strain; 5°C) showing the frequency-dependence of G' (▲), G'' (○) and η^* (▲) for 0.5 wt% pectin (DE 70.3; pH 3.0) in combination with 55 wt% sucrose and 10 wt% maltodextrin.

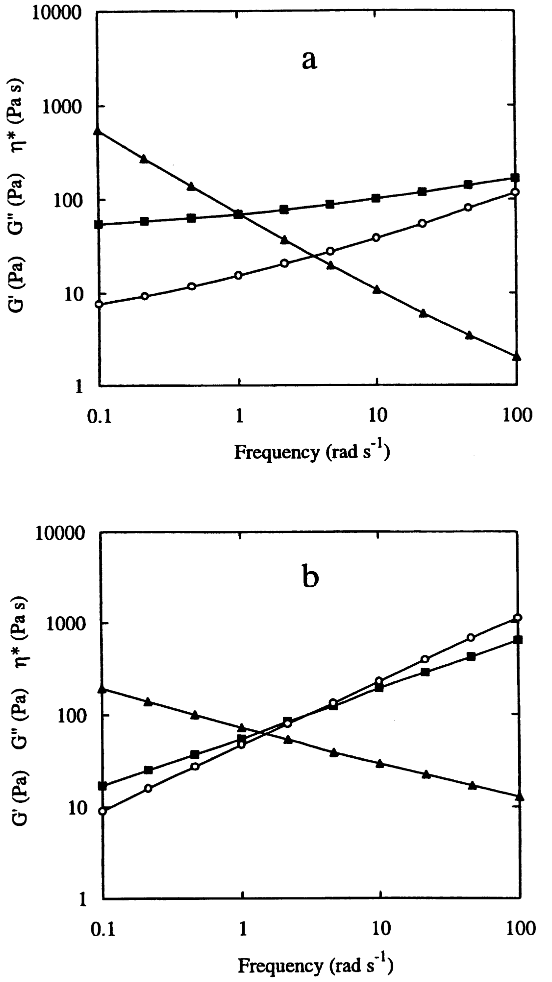

Fig. 13. Mechanical spectra (0.5% strain; 5°C) showing the frequency-dependence of G' (■), G'' (○) and η^* (▲) for (a) 0.5 wt% pectin in 55 wt% sucrose and (b) 10 wt% maltodextrin, also in 55 wt% sucrose.

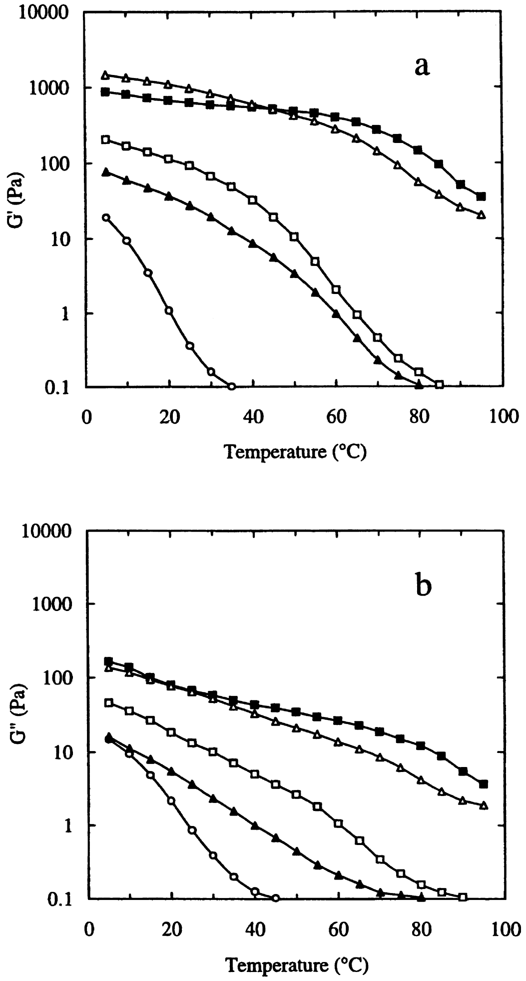

Fig. 14. Variation of (a) G' and (b) G'' (1 rad s^{-1}; 0.5% strain) on cooling from 95 to 5°C at 1°C min^{-1} for: 0.5 wt% pectin (DE 70.3; pH 3.0) in combination with 10 wt% maltodextrin and 55 wt% sucrose (■); 10 wt% maltodextrin with 55 wt% sucrose in the absence of pectin (○); 0.5 wt% (▲) and 1.0 wt% (□) pectin with 55 wt% sucrose in the absence of maltodextrin; and 0.5 wt% pectin in 65 wt% sucrose, also in the absence of maltodextrin (△).

now seems clear that this is the dominant factor in the reduction of gel strength. It is obvious, however, that the same mechanism cannot apply to the low-methoxy pectin systems, where there is no requirement for cosolute to induce gelation. In the illustrative cooling curves shown in Figs. 10, 14 and 15, there is a monotonic increase in G' and G'' for the mixtures of high-methoxy pectin with oxidised starch (Fig. 10) or maltodextrin (Figs. 14 and 15) as temperature is decreased. Under certain conditions of sample preparation, however, the corresponding traces for the low-methoxy pectin–starch systems showed sharp reductions in modulus, indicating collapse of the developing calcium pectinate network in response to thermodynamic incompatibility with the starch polysaccharide (Picout et al., 2000a).

Although the results presented in the preceding paper (Evageliou et al., 2000a) strongly suggested that the initial reduction in modulus for high-methoxy pectin on progressive replacement of sucrose by oxidised starch does not arise in the same way, the quenching procedure used to induce gel formation did not allow the processes leading to the final moduli at 5°C to be characterised. One of the central aims of the present work was to explore the temperature-course of structure formation during controlled cooling (1°C min^{-1}), and in particular to determine whether or not the mixtures of high-methoxy pectin with starch polysaccharides showed any evidence of the collapse in network structure proposed (Picout et al., 2000a–d) for the corresponding low-methoxy pectin systems.

A second aim was to determine the extent to which the changes in moduli reported in the preceding paper (Evageliou et al., 2000a) were dependent on the experimental conditions used. In addition to the change from rapid quenching to controlled cooling, the pectin concentration in the mixtures studied in the present work was halved (from 1.0 to 0.5 wt%). Another significant change was the pH at which the mixtures were prepared. In normal commercial pectins, the carboxyl groups are predominantly in the ionised (salt) form, giving solutions of ~pH 4–4.5 when dissolved. Gelation is then induced by addition of acid to lower the pH to the required final value (typically ~pH 3). The pectin used in the present work, and in the quenching experiments, however, was one of a series of laboratory samples prepared by Hercules as part of collaborative industrial–academic LINK project. The carboxyl groups in these samples are predominantly in the un-ionised (acid) form, giving solutions of pH < 3. In the quenching experiments, the pH was raised to 3.0 (by addition of trisodium citrate), and the mixtures were prepared and used at that pH. One concern in planning the experimental protocol for the present work was that the reductions in moduli observed (Evageliou et al., 2000a) for the quenched samples on partial replacement of sucrose by oxidised starch might have arisen from "pre-gelation" of pectin on addition of starch at low pH. The pH of the pectin solutions was therefore raised to ~4.0 (with trisodium citrate) prior to mixing, and the mixtures were then taken to pH 3.0 (with citric acid) as the final step in sample preparation.

Despite these substantial changes in experimental procedure, however, the final moduli from both studies show the same general pattern of response to progressive replacement of sucrose by oxidised starch, and the central conclusions (Evageliou et al., 2000a) remain unchanged: that there is mutual exclusion between the two polymers, with consequent increase in the effective concentration of both, and that the initial reduction in moduli (Fig. 8) is associated with the decrease in sucrose content of the mixtures, rather than with the accompanying increase in starch content. The initial (slight) decrease in moduli on partial replacement of sucrose by maltodextrin (Fig. 11) also seems likely to arise from the reduction in sucrose concentration, but the effect of higher concentrations of maltodextrin does not appear to follow the excluded volume mechanism proposed for oxidised starch.

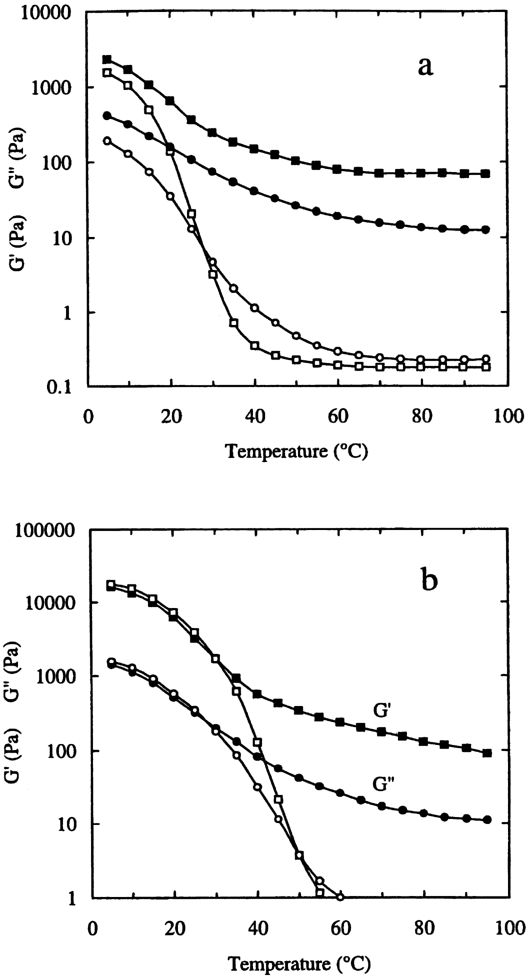

Fig. 15. Variation of G' (squares) and G'' (circles), measured at 1 rad s^{-1} and 0.5% strain during cooling from 95 to 5°C at 1°C min^{-1}, for (a) 15 wt% maltodextrin with 50 wt% sucrose and (b) 20 wt% maltodextrin with 45 wt% sucrose, in the presence (filled symbols) and absence (open symbols) of 0.5 wt% pectin (DE 70.3; pH 3.0).

As shown in Fig. 10, the temperature-course of structure formation for 0.5 wt% high-methoxy pectin in combination with 50 wt% sucrose and 15 wt% oxidised starch (the composition showing the greatest divergence from the behaviour of the individual polymers) can be matched convincingly by a higher concentration of pectin at the same sucrose concentration as in the mixture (consistent with an increase in effective polymer concentration by mutual exclusion). The setting curves (Fig. 14) for the pectin–maltodextrin mixture at the point on maximum divergence from the individual constituents (10 wt% maltodextrin; 55 wt% sucrose), by contrast, show far greater similarity to the temperature-course of structure formation by the same concentration of pectin in the presence of a higher concentration of sucrose than to that of a higher concentration of pectin at the same sucrose concentration.

The difference in the effect of the two types of partially depolymerised starch on the network properties of high-methoxy pectin can be seen directly by comparison of the cooling curves obtained for 0.5 wt% pectin with 50 wt% sucrose in mixtures with 15 wt% of oxidised starch (Fig. 10) or maltodextrin (Fig. 15a). At the loading temperature of 95°C, G' of the pectin–maltodextrin sample is about two orders of magnitude higher than that of the mixtures with oxidised starch. Since the modulus for 15 wt% maltodextrin at the same sucrose concentration but in the absence of pectin (Fig. 15a) is somewhat lower than the corresponding value for oxidised starch (Fig. 10), it seems clear that the gross differences in the initial values for the mixed systems at high temperature must arise from much greater self-association of pectin in mixtures with maltodextrin than in equivalent mixtures with oxidised starch. As shown in Figs 10 and 14, increasing pectin concentration at fixed concentration of sucrose has little effect on the onset temperature for structure formation, whereas comparatively small changes in sucrose concentration have a massive effect on weak gel character at high temperature (Fig. 3). It would therefore appear that the mechanism by which maltodextrin promotes self-association of high-methoxy pectin is more similar to that of sucrose than of oxidised starch.

Although the maltodextrin and oxidised starch samples used in this investigation are both prepared by partial depolymerisation of starch, they differ substantially in their method of preparation, composition and properties. The oxidised starch is prepared by chemical modification of intact granules of waxy maize starch (i.e. with essentially no linear amylose), and is washed to remove chemical residues and any low molecular weight products of hydrolysis. On heating in water, the granules gelatinise and disintegrate, giving a solution of partially depolymerised amylopectin (i.e. of densely branched, compact molecules), with a low content of carboxyl groups formed during the oxidation reaction (1 per 30 or 40 residues). The maltodextrin is prepared from potato starch (i.e. with a substantial content of amylose, and with some slight anionic character from phosphate groups) by enzymic digestion at a temperature close to the gelatinisation temperature of the starch granules. This procedure causes extensive debranching of amylopectin, and cleavage of amylose, giving a substantial proportion of short, linear chains in the final product. As shown in Table 1, oxidised starch has ~1.4% of fragments of DP 9 or less; the corresponding value for the maltodextrin is ~14.1%. The molecular-weight distribution at higher DP is less well characterised, but the method of preparation of maltodextrin suggests a much higher proportion of short chains, and a lower content of high molecular weight, branched species.

This difference in composition between the two materials agrees well with the observed differences in their effect on gelation of high-methoxy pectin. As discussed previously (Evageliou et al., 2000a), oxidised starch appears to exclude pectin from its polymer domain, which is consistent with a compact, densely branched structure resistant to penetration by other chains. The consequent increase in effective polymer concentrations can be seen in the differences in moduli for high concentrations of oxidised starch in the presence and absence of pectin, at sucrose concentrations where the pectin component is non-gelling (Fig. 8). The observed moduli for high concentrations of maltodextrin in mixtures with pectin (Fig. 11), by contrast, are virtually identical to those obtained for the same concentrations of maltodextrin in the absence of pectin.

Similar behaviour has been observed (Gilsenan, Richardson & Morris, 2000) for non-gelling compositions of pectin (low-methoxy pectin in the absence of Ca^{2+}) in mixtures with gelatin; the presence of the pectin component had no detectable effect on the moduli of the gelatin gels. It would appear, therefore, that maltodextrin, like gelatin, shows no significant exclusion effects in monophasic mixtures with pectin. The unifying feature may be that the linear chains of gelatin and predominantly linear chains of maltodextrin, which will have fluctuating coil geometry in solution, do not make any part of the total volume permanently inaccessible to pectin, in contrast to the compact amylopectin structure of oxidised starch.

It seems clear from the comparisons shown in Fig. 14, however, that maltodextrin does promote association of high-methoxy pectin at acid pH, but by duplicating (at least partially) the role of sucrose, rather than by raising the effective concentration of pectin. The effect of cosolutes on gelation of biopolymers is complex. At the simplest level of interpretation, however, association of polymer chains into gel junctions will occur only if the polymer–polymer interactions are thermodynamically more favourable than the competing interactions between polymer and solvent. Introduction of a cosolute will cause partial replacement of polymer–solvent interactions by interactions between the polymer and the cosolute. For aqueous solutions of polysaccharides, the polymer–cosolute interactions will normally be less favourable than interactions between polymer and solvent, because of the ability of water to participate in extensive hydrogen bonding to the hydroxyl groups of the polysaccharide chains. Thus, in general, the effect of partial replacement of water by other materials will be to promote self-association of the polysaccharide.

For polymeric cosolutes, however, the extent of interaction with the other polymer will be limited by geometric constraints, and by loss of conformational entropy in forming (transient) contacts. Both restrictions will be progressively eliminated as the degree of polymerisation is decreased. Conversely, densely branched cosolutes will have less scope for segmental interactions, due to physical inaccessibility.

These simple considerations may explain, at least to a first level of approximation, why maltodextrin, with composition skewed towards short, linear chains, is very much more effective than partially depolymerised amylopectin (oxidised starch) in promoting association of high-methoxy pectin into a weak gel network at high temperature, but less effective than sucrose. The role of cosolutes in inducing gelation of high-methoxy pectin at acid pH is discussed further in the following paper (Evageliou, Richardson & Morris, 2000b).

Acknowledgements

This work was carried out as part of an industrial–academic LINK project, “Behaviour of Biopolymer Mixtures in Structuring Food Products”. We thank the participating companies (Unilever, Nestlé, Cerestar, Hercules and SKW Biosystems), and the UK Ministry of Agriculture, Fisheries and Food, for financial support. We also thank Dr B. Kettlitz (Cerestar, Vilvoorde, Belgium) for kindly providing the analytical results presented in Table 1, and Dr A.H. Clark (Unilever Research, Bedford) for helpful discussions.

References

Christensen, S. H. (1986). Pectins. In M. Glicksman. *Food Hydrocolloids*, vol. 3 (pp. 205–230). Boca Raton, FL: CRC Press.

Evageliou, V., Richardson, R. K., & Morris, E. R. (2000a). Effect of oxidised starch on high methoxy pectin–sucrose gels formed by rapid quenching. *Carbohydrate Polymers, 42*, 219–232.

Evageliou, V., Richardson, R. K., & Morris, E. R. (2000b). Effect of pH, sugar type and thermal annealing on high-methoxy pectin gels. *Carbohydrate Polymers, 42*, 245–259.

Evageliou, V., Richardson, R. K., & Morris, E. R. (2000c). Effect of sucrose, glucose and fructose on gelation of oxidised starch. *Carbohydrate Polymers, 42*, 261–272.

Gilsenan, P. M., Richardson, R. K., & Morris, E. R. (2000). Associative and segregative interactions between gelatin and low-methoxy pectin. Part 2. Co-gelation in the presence of Ca^{2+}. *Biopolymers,* submitted for publication.

Morris, E. R., Gothard, M. G. E., Hember, M. W. N., Manning, C. E., & Robinson, G. (1996). Conformational and rheological transitions of welan, rhamsan and acylated gellan. *Carbohydrate Polymers*, *30*, 165–175.

Picout, D. R., Richardson, R. K., Rolin, C., Abeysekera, R. M., & Morris, E. R. (2000a). Ca^{2+}-induced gelation of low methoxy pectin in the presence of oxidised starch. Part 1. Collapse of network structure. *Carbohydrate Polymers,* in press.

Picout, D. R., Richardson, R. K., & Morris, E. R. (2000b). Ca^{2+}-induced gelation of low methoxy pectin in the presence of oxidised starch. Part 2. Quantitative analysis of moduli. *Carbohydrate Polymers,* in press.

Picout, D. R., Richardson, R. K., & Morris, E. R. (2000c). Co-gelation of calcium pectinate with potato maltodextrin. Part 1. Network formation on cooling. *Carbohydrate Polymers,* in press.

Picout, D. R., Richardson, R. K., & Morris, E. R. (2000d). Co-gelation of calcium pectinate with potato maltodextrin. Part 2. Analysis of co-gel moduli. *Carbohydrate Polymers,* in press.

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

Rolin, C. (1993). Pectin. In R. L. Whistler & J. N. BeMiller (Eds.), *Industrial Gums: Polysaccharides and their Derivatives* (3rd Ed.) (pp. 257–293) San Diego, CA: Academic Press.

Ross-Murphy, S. B. (1984). Rheological methods. In H. W.-S. Chan (Ed.), *Biophysical Methods in Food Research* (pp. 195–290). London: Critical Reports on Applied Chemistry, SCI.

Ross-Murphy, S. B., Morris, V. J., & Morris, E. R. (1983). Molecular viscoelasticity of xanthan polysaccharide. *Faraday Symposia of the Chemical Society*, *18*, 115–129.