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Carbohydrate Polymers 43 (2000) 133–141

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Co-gelation of calcium pectinate with potato maltodextrin. Part 1. Network formation on cooling

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Received 7 June 1999; accepted 26 November 1999

Abstract

Small deformation oscillatory measurements of storage and loss moduli (G' and G'') have been used to explore the effect of segregative interactions in gelling mixtures of calcium pectinate (DE 31.1; stoichiometric Ca^{2+}) and potato maltodextrin. Solutions were prepared at 90°C and gelled by cooling to 5°C at a rate of 1°C/min. Two different methods of sample preparation were used, which gave very different rheology at high temperature, but had little effect on the networks formed on cooling. In most of the experiments, the pectin concentration was held constant at 2.0 wt% and the concentration of maltodextrin was varied between 0 and 25 wt%. The moduli at 30°C, before the onset of gelation of maltodextrin, decreased steeply with increasing maltodextrin concentration, consistent with a collapse of the calcium pectinate network structure by formation of large aggregates in response to segregative interactions between the two polymers. At high concentrations of maltodextrin, network collapse could be seen directly as sharp drops in modulus during cooling. The final moduli at 5°C showed a similar reduction at maltodextrin concentrations up to ~12.5 wt%, but increased steeply at higher concentrations, due to gelation of maltodextrin. In a converse series of experiments, where maltodextrin concentration was held fixed at 20 wt% and the concentration of calcium pectinate was varied between 0 and 3.0 wt%, the observed moduli of the calcium pectinate networks immediately before gelation of the maltodextrin component were virtually independent of pectin concentration, consistent with the concept of a solubility product for unaggregated pectin chains proposed in the preceding study of gelation of calcium pectinate in the presence of oxidised starch. These qualitative interpretations are consolidated by quantitative analyses reported in the following paper.

Keywords: Co-gelation; Potato maltodextrin; Calcium pectinate

1. Introduction

Interactions between two different biopolymers can be classified as "associative" or "segregative", depending on whether they are enthalpically more favourable or less favourable than homotypic interactions between like chains of each type (Piculell et al., 1994). Electrostatic attraction between polyanions (e.g. sulphated or carboxylated polysaccharides) and polycations (e.g. chitosan, or proteins below their isoelectric point) is the most common mechanism of association, and often leads to formation of an insoluble precipitate (see, for example, Argüelles-Monal, Gárciga & Peniche-Covas, 1990; Chilvers & Morris, 1987; Hember et al., 2000; Hugerth, Caram-Lelham & Sundelöf, 1997; Imeson, Ledward & Mitchell, 1977; Michon, Cuvelier, Launay, Parker & Takerkart, 1995; Stainsby, 1980; Tolstoguzov, 1986, 1991; Tolstoguzow & Wajnermann, 1975).

Precipitation in mixed biopolymer systems can, however, also arise from segregative interactions ("thermodynamic incompatibility") between the constituent polymers. This phenomenon has been observed in two previous investigations. Both involved potato maltodextrin. In the first study (Kasapis, Morris, Norton & Gidley, 1993) the other polymer was gelatin, and the precipitates consisted almost entirely of maltodextrin (with only small, erratic, amounts of protein, attributable to the practical difficulties of ensuring complete separation of the precipitate from the overlying supernatant). In the second investigation (Manoj, Kasapis, Hember, Richardson & Morris, 2000), the maltodextrin remained in solution, and the precipitates consisted almost entirely of the other component, which was whey protein. Both systems, however, showed two common features: (i) the precipitates were formed from monophasic solutions (i.e. with both polymers competing for space-occupancy and solvent within a single phase); (ii) the extent of precipitation was

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0144-8617/00/$ - see front matter
PII: S0144-8617(99)00201-5

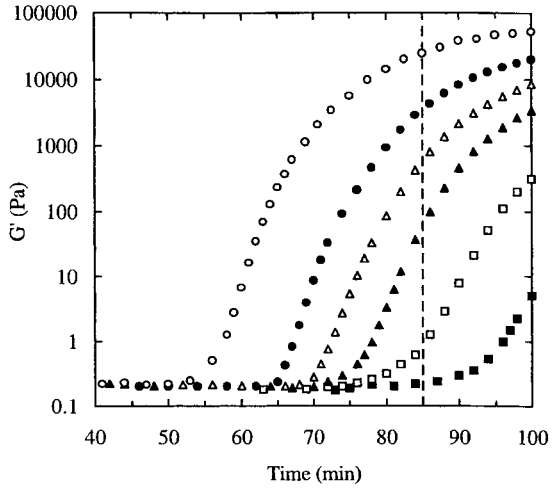

Fig. 1. Variation of G' (10 rad s^{-1}; 0.5% strain) on cooling from 90°C to 5°C at 1°C/min and holding for a further 15 min at 5°C for maltodextrin at concentrations (wt%) of 15.0 (■), 17.5 (□), 20.0 (▲), 22.5 (△), 25.0 (●) and 30.0 (○). The vertical dashed line shows the end of the cooling stage.

directly proportional to the concentration of the non-precipitating component.

The two preceding papers (Picout, Richardson, Rolin, Abeysekera & Morris, 2000a; Picout, Richardson & Morris, 2000b) present evidence that an analogous precipitation process occurs when solutions of calcium pectinate are cooled in the presence of oxidised starch, leading to collapse of the calcium pectinate network as it forms. In contrast to the investigations of maltodextrin–protein mixtures mentioned above, where the experimental conditions were arranged to prevent gelation of either component and precipitation could be observed directly as sedimentation of solid particles, the calcium pectinate preparations already had substantial gel-like character in the fluid state at high temperature, and precipitation of pectin chains within the supporting network was inferred from sharp reductions in gel strength (storage modulus, G') during cooling (Picout et al., 2000a), and from quantitative analysis of final moduli at 5°C (Picout et al., 2000b). As in the maltodextrin–protein systems, however, the initial mixtures were monophasic, and the extent of precipitation (characterised by a calculated solubility product for unprecipitated chains) increased linearly with increasing concentration of oxidised starch.

We now report a parallel study of the gelation of calcium pectinate in combination with potato maltodextrin. As before, the work is presented in two parts. The experimental results are documented here, and their quantitative analysis is described in the following paper (Picout et al., 2000c).

2. Materials and methods

Maltodextrin was kindly supplied by Cerestar (C*deLight MD01970). The pectin sample used was from Hercules (batch number 4907; DE 31.1), and is identical to one of the materials described in Table 1 of Picout et al. (2000a). It should be noted that this sample has slightly lower DE than the pectin used for quantitative analysis (Picout et al., 2000b) of the effect of oxidised starch (batch number 5006; DE 34.2). Both materials were laboratory preparations, and the change was dictated by the amounts available. The two samples, however, give closely similar moduli (Picout et al., 2000a).

The experimental procedure was essentially identical to the method used to obtain the moduli analysed in the preceding paper (Picout et al., 1999b). As before, the calcium source used for gel formation was calcium chloride dihydrate (AnalaR grade from BDH), at stoichiometric equivalence to the carboxyl groups of the pectin. Measurements of G', G'' and tan δ (G''/G') were made at 10 rad s^{-1} and 0.5% strain, using highly truncated cone-and-plate geometry (50 mm diameter; 0.05 rad cone angle; 0.5 mm gap) on a sensitive prototype rheometer designed and constructed by one of us (R.K.R.). Samples were loaded in the solution state at 90°C and cooled at 1°C/min to a final temperature of 5°C. As in the study of gelation in the presence of oxidised starch, moduli for quantitative analysis were recorded after a holding period of 15 min at 5°C (i.e. 100 min from the start of the cooling scan). In the present work, however, a second data set was recorded 5 h later (i.e. 400 min from the start of cooling). For brevity, we will refer to these as "100 min values" and "400 min values", respectively.

Mixed solutions were prepared by two different procedures, which we will call "Method 1" and "Method 2". In Method 1, which follows the approach used in the studies described in the two preceding papers (Picout et al., 2000a,b), the maltodextrin was dispersed in cold water and dissolved by stirring at 90°C. The calcium salt was then dissolved in the maltodextrin solution, and the pectin was slowly added, with continuous stirring until a clear solution was obtained. In Method 2, the individual polymers were dissolved separately, the required amount of calcium chloride was incorporated in the pectin solution by dropwise addition as a dilute solution, and the maltodextrin solution was then added. Both mixing processes were carried out with continuous stirring at 90°C. The volume of the calcium chloride solution was held fixed at 10% of the total volume; the relative volumes of the individual polymer solutions were varied as necessary to allow mixtures of the required final composition to be obtained from starting solutions prepared at experimentally-tractable concentrations. Solutions used for construction of modulus—concentration curves for the individual constituents were prepared in the same way, but omitting the second polymer. As a point of practical detail, the 400 min value of G' for maltodextrin alone at the highest concentration used for calibration (30 wt%) was above the dynamic range of the prototype rheometer (from ~0.05 to ~50 000 Pa), and was obtained using parallel plate geometry (40 mm diameter; 1 mm gap) on a CarriMed CSL 500 rheometer. Agreement between the

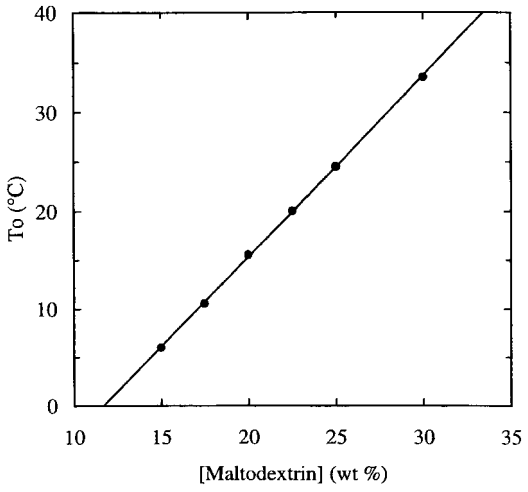

Fig. 2. Concentration-dependence of the onset temperature (T_0) for gelation of maltodextrin on cooling at 1°C/min.

two instruments was confirmed by measurements at lower concentrations of maltodextrin (15 and 20 wt%).

In most of the experiments, the pectin concentration was held fixed at 2.0 wt% (as in the mixtures with oxidised starch) and the concentration of maltodextrin was varied (between 0 and 25 wt%). In one series of measurements (which was confined to 100 min values for samples prepared by Method 2), the maltodextrin concentration was fixed at 20 wt% and the concentration of calcium pectinate was varied (between 0 and 3.0 wt%).

3. Results and discussion

3.1. Gelation of maltodextrin alone

Fig. 1 shows the changes in G' observed for solutions of maltodextrin at concentrations in the range 15–30 wt% on cooling from 90°C to 5°C at 1°C/min and holding for a further 15 min at 5°C. Development of a continuous network, seen as a sharp increase in modulus, begins at progressively shorter times (i.e. higher temperatures) as the polymer concentration (c) is raised. As shown in Fig. 2, the increase in the onset temperature for gel formation (T_0) with increasing concentration of maltodextrin is essentially linear.

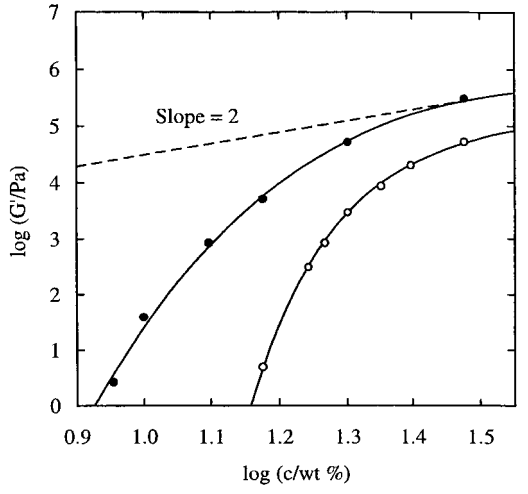

Fig. 3. Concentration-dependence of 100 min (○) and 400 min (●) values of G' for maltodextrin alone at 5°C.

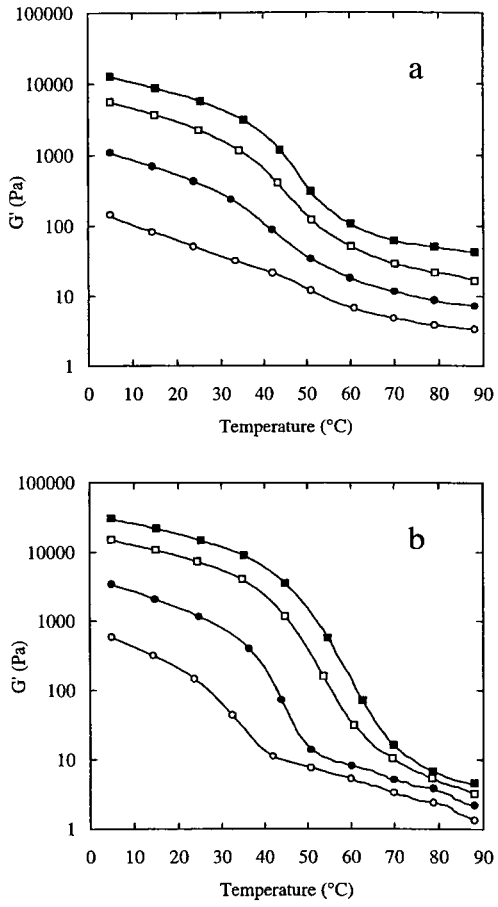

Fig. 4. Temperature-dependence of G' during cooling at 1°C/min for calcium pectinate samples prepared by (a) Method 1 and (b) Method 2, at concentrations (wt%) of 0.5 (○), 1.0 (●), 2.0 (□) and 3.0 (■).

Fig. 3 shows the concentration-dependence of the "100 min values" of G' recorded at the end of the cooling and holding traces in Fig. 1. The second curve in Fig. 3 is the corresponding plot for samples held for a further 5 h at 5°C ("400 min values"). At this longer holding time, the minimum polymer concentration required for significant development of network structure is substantially lower: the 400 min values span the concentration-range 9–30 wt%, in comparison with 15–30 wt% for the 100 min values. In both curves, the slope of log G' versus log c decreases steadily towards a limiting value of ~2 (i.e. c^2-dependence of G') as the polymer concentration is raised, which is typical (Clark & Ross-Murphy, 1985) of a conventional biopolymer gelling system. These plots (Fig. 3) will be used as calibration curves for quantitative analysis (Picout et al., 2000c) of the contribution of maltodextrin to the overall moduli of the

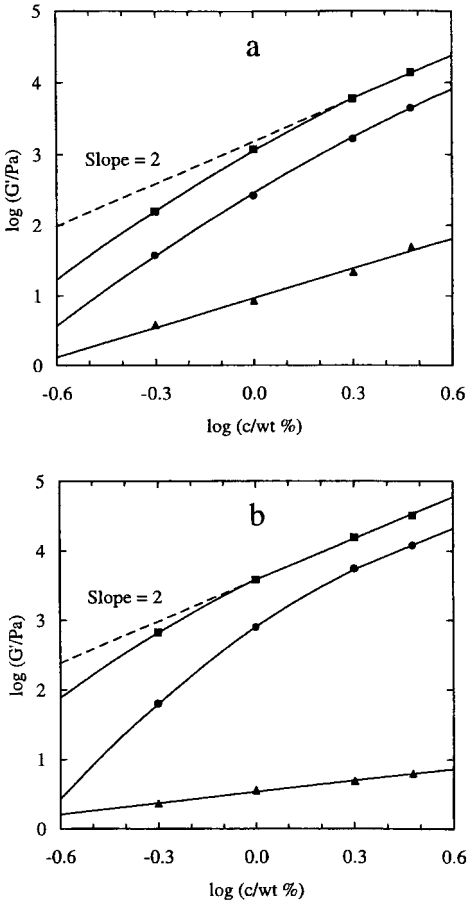

Fig. 5. Concentration-dependence of G' values recorded at 80°C (▲) and 30°C (●) during cooling at 1°C/min, and of 100 min values at 5°C (■), for calcium pectinate samples prepared by (a) Method 1 and (b) Method 2.

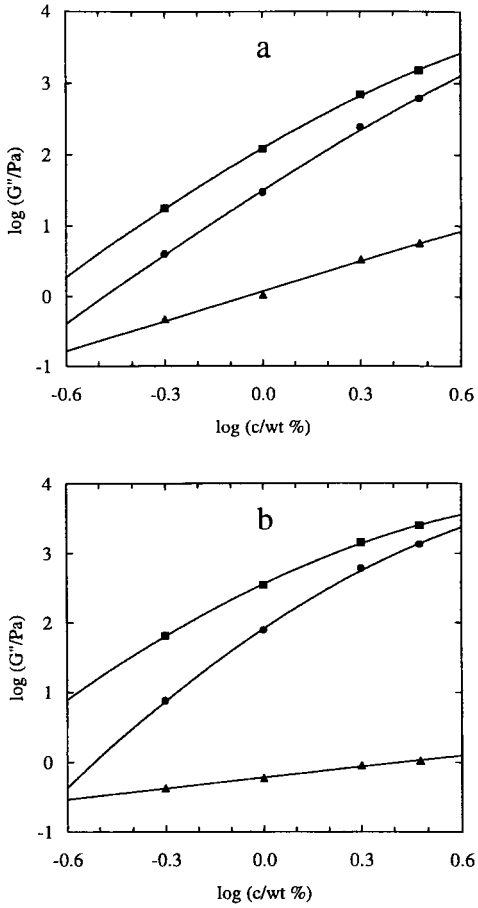

Fig. 6. Concentration-dependence of G'' values recorded at 80°C (▲) and 30°C (●) during cooling at 1°C/min, and of the 100 min values at 5°C (■), for calcium pectinate samples prepared by (a) Method 1 and (b) Method 2.

co-gels formed with calcium pectinate. The main purpose of the work reported in the following section was to obtain corresponding calibration curves for the calcium pectinate component.

3.2. Gelation of calcium pectinate alone

Fig. 4 shows the temperature-dependence of G' during cooling at 1°C/min for calcium pectinate (DE 31.1; stoichiometric Ca^{2+}) prepared by Method 1 (Fig. 4a) and by Method 2 (Fig. 4b) at concentrations of 0.5, 1.0, 2.0 and 3.0 wt%. In all cases there is an obvious sigmoidal transition from the "weak gel" structure present at high temperature (Picout et al., 2000a) to a much stronger "true" gel structure at low temperature. The transition is, however, much larger for the samples prepared by Method 2, and shows a progressive shift to higher temperature with increasing polymer concentration, which is not apparent for the samples prepared by Method 1. The starting values of G' at high temperature are also much lower for Method 2, and show far less variation with concentration, but the final moduli at 5°C are higher.

A possible interpretation is that these differences reflect the relative efficiency of the two procedures in dissociating intermolecular junctions present initially in the pectin powder. In Method 2, where pectin is dissolved in water before incorporation of Ca^{2+}, the extent of dissociation is likely to be far greater than in Method 1, where pectin is dissolved in a solution that already contains Ca^{2+}. This would explain why Method 1 gives higher initial moduli at high temperature, and why these moduli are more dependent on concentration (since it would seem reasonable to expect that the amount of undissociated solid-state structure would increase as the concentration of pectin, and the associated concentration of Ca^{2+} required for stoichiometric equivalence, are raised). Conversely, however, complete, or almost complete, dissociation into individual chains might be expected to give a more perfect (i.e. more homogeneous) final network structure on cooling, which is consistent with the higher values of G' at 5°C for Method 2. Finally, the gelling transition for samples prepared by Method 1, which occurs (Fig. 4a) at virtually the same temperature for different polymer concentrations, may reflect (Picout et al., 2000a) association of pre-existing ordered structures ("egg-box" dimers of unesterified sequences) into larger assemblies incorporating esterified residues. By extension of the same argument, gelation from a solution of isolated

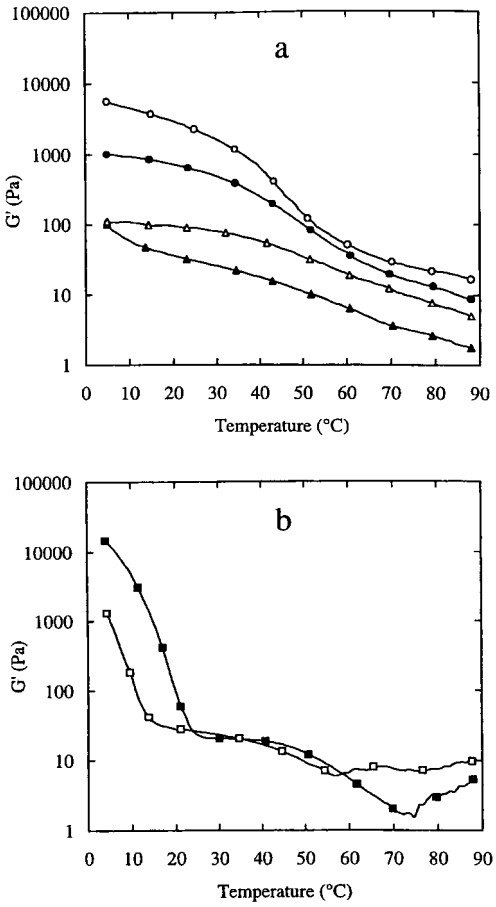

Fig. 7. Temperature-dependence of G' during cooling at 1°C/min for 2.0 wt% calcium pectinate prepared by Method 1, with maltodextrin concentrations (wt%) of 0 (○), 5 (●), 10 (△), 15 (▲), 20 (□) and 25 (■).

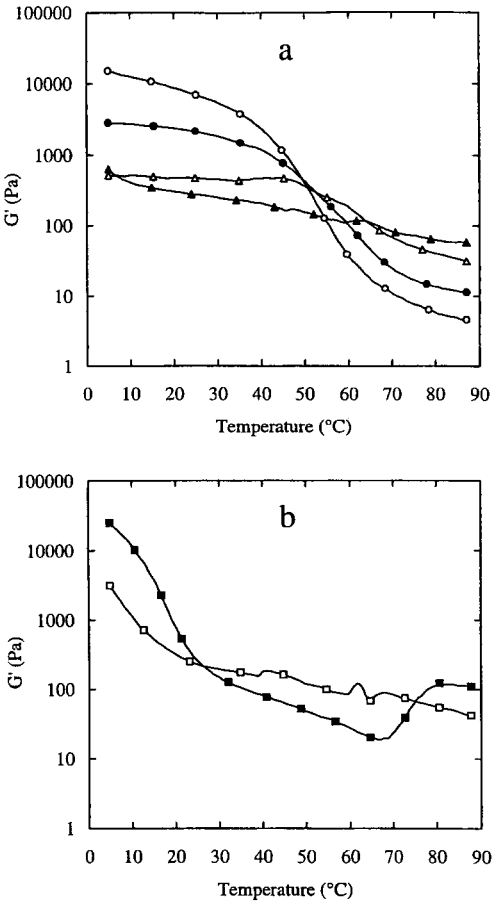

Fig. 8. Temperature-dependence of G' during cooling at 1°C/min for 2.0 wt% calcium pectinate prepared by Method 2, with maltodextrin concentrations (wt%) of 0 (○), 5 (●), 10 (△), 15 (▲), 20 (□) and 25 (■).

chains would require initial nucleation of egg-box junctions, with increasing probability of occurrence as the concentrations of pectin and Ca^{2+} are raised; this could explain the concentration-dependence of transition temperature for samples prepared by Method 2 (Fig. 4b).

Detailed analysis of the structures and processes involved in formation of calcium pectinate gels is, however, beyond the scope of the present work. The essential information from Fig. 4 is the effect of concentration and temperature on the rheology of samples from both methods of preparation, as a baseline for exploring the changes introduced by incorporation of maltodextrin.

The concentration-dependence of the final, 100 min, values of G' at 5°C, and the G' values recorded at 80°C and 30°C during cooling (Fig. 4), are shown in Fig. 5. Fig. 6 shows the corresponding values of G''. As discussed in the following section, the moduli at 30°C provide a useful index of the nature of the calcium pectinate network in the mixed systems, before the onset of gelation of maltodextrin; values at 80°C are included to give an indication of the "weak gel" properties at high temperature (i.e. well above the range of the sigmoidal transitions shown in Fig. 4).

As can be seen by comparison of Figs. 5a and 6a, G' and G'' for samples prepared by Method 1 respond in almost exactly the same way to changes in concentration and temperature, but the values of G' are consistently higher, by about an order of magnitude (i.e. tan δ remains virtually constant at ~0.1 for temperatures ranging from 80 to 5°C and for pectin concentrations varying between 0.5 and 3.0 wt%). This behaviour seems consistent with a substantial proportion of the total crosslinking being carried over from the solid state, and with subsequent increases on cooling coming from reinforcement of the existing network. The samples prepared by Method 2 also have tan $\delta \approx 0.1$ at 30 and 5°C (Figs. 5b and 6b), but the values at 80°C are substantially higher (tan $\delta \approx 0.2$ across the concentration-range studied), which is again consistent with fuller dissociation of solid-state structure when the pectin is dissolved in the absence of Ca^{2+}.

The final (100 min) values of G' at 5°C from both methods of preparation give plots of log G' versus log c (Fig. 5a and b) with a terminal slope of ~2, but this slope is reached at lower concentration for the samples prepared by Method 2. The two curves, however, are virtually identical in form, and can be superimposed by a simple lateral shift along the log c axis. The corresponding curve for G' at 30°C from

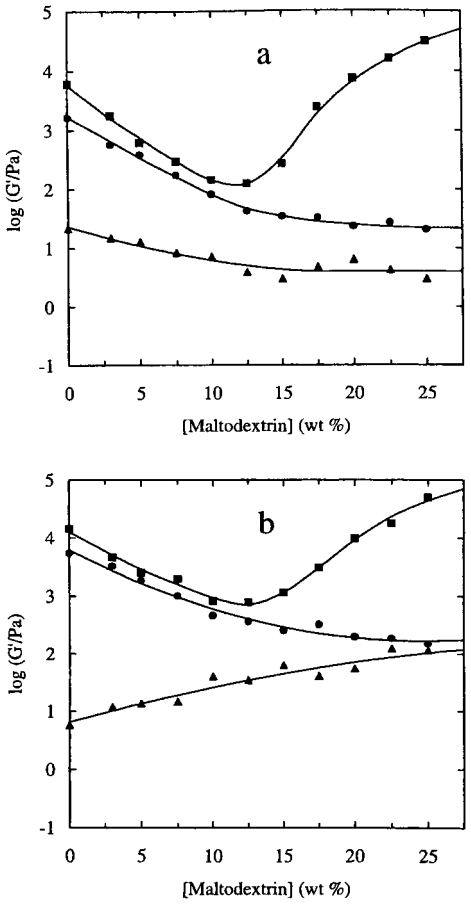

Fig. 9. Effect of maltodextrin concentration in mixtures with 2.0 wt% calcium pectinate prepared by (a) Method 1 and (b) Method 2 on the values of G' recorded at 80°C (▲) and 30°C (●) during cooling at 1°C/min, and on the 100 min values at 5°C (■).

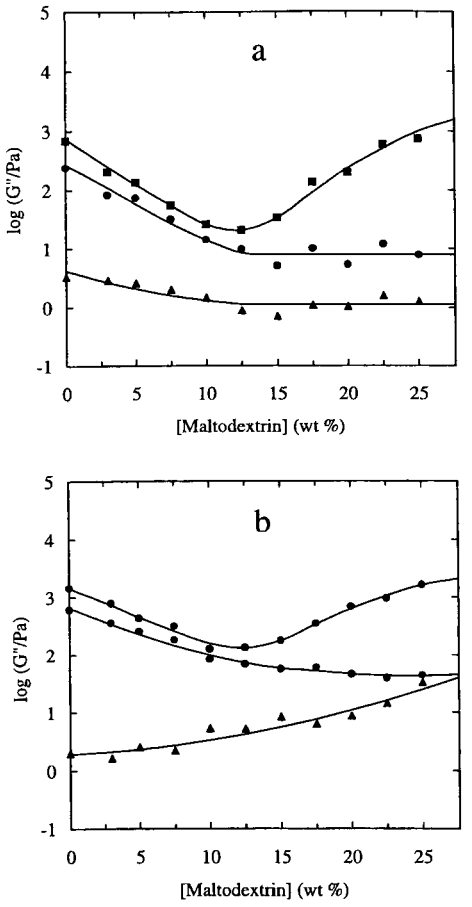

Fig. 10. Effect of maltodextrin concentration in mixtures with 2.0 wt% calcium pectinate prepared by (a) Method 1 and (b) Method 2 on the values of G'' recorded at 80°C (▲) and 30°C (●) during cooling at 1°C/min, and on the 100 min values at 5°C (■).

Method 1 (Fig. 5a) is also virtually identical in form, but the 30°C curve from Method 2 (Fig. 5b) decreases more steeply with decreasing concentration. The origin of this difference can be seen from the cooling traces in Fig. 4. For all four concentrations of calcium pectinate prepared by Method 1 (Fig. 4a), and for the higher concentrations by Method 2 (Fig. 4b), the sigmoidal transition is complete by 30°C, whereas the value of G' at 30°C for the least concentrated sample from Method 2 lies near the centre of the transition.

After the initial 15 min holding period at 5°C, the calcium pectinate gels from both methods of preparation showed no significant changes in moduli at longer times (as was also found in a concurrent investigation of gelation of calcium pectinate in mixture with gelatin; Gilsenan, Richardson & Morris, 2000). The same calibration curves (Fig. 5) were therefore used (Picout et al., 2000c) for analysis of 100 and 400 min values of co-gel moduli.

3.3. Co-gelation at 2.0 wt% calcium pectinate

In the main series of experiments, the concentration of calcium pectinate was held constant at 2.0 wt%, and the maltodextrin concentration was varied between 0 and 25 wt%. Fig. 7 shows the temperature-dependence of G' during cooling at 1°C/min for samples prepared by Method 1 at maltodextrin concentrations of 0, 5, 10, 15, 20 and 25 wt%. The corresponding curves for samples prepared by Method 2 are shown in Fig. 8.

For Method 1, there is a systematic reduction in G' at all temperatures as the maltodextrin concentration is raised from 0 to 15 wt% (Fig. 7a), with the gelling transition becoming progressively less evident. There is no evidence of gelation of the maltodextrin component until its concentration reaches ~15 wt%, when a small upturn in modulus can be seen in the final stages of cooling. At higher concentrations of maltodextrin, this gelation process becomes the dominant feature in the cooling curves (Fig. 7b) and, as found for maltodextrin alone (Figs. 1 and 2), the onset occurs at progressively higher temperatures with increasing concentration. At the highest maltodextrin concentration used (25 wt%) the onset temperature is just below 30°C. Thus, as mentioned previously, we have used

30°C as the lowest single temperature at which the rheology of the calcium pectinate network can be characterised with no contribution from gelled maltodextrin.

In contrast to the monotonic increase in G' seen at lower concentrations (Fig. 7a), the cooling curves for the samples incorporating 20 and 25 wt% maltodextrin (Fig. 7b) show irregularities and drops in moduli, consistent with the collapse in network structure proposed (Picout et al., 2000a) for calcium pectinate gels formed in the presence of oxidised starch. Similar effects are evident (Fig. 8b) for samples prepared by Method 2 at high concentrations of maltodextrin, and are again followed by large increases in modulus from gelation of the maltodextrin component at temperatures below ~30°C. The cooling curves for samples prepared by Method 2 at lower concentrations of maltodextrin (Fig. 8a) show a complex pattern of intersection, which can be understood more readily by examining the effect of maltodextrin concentration on the moduli recorded at selected temperatures.

As before (Figs. 5 and 6), the values chosen for comparison are the moduli at 80 and 30°C during cooling, and the final (100 min) values at 5°C. Fig. 9 shows the variation of G' at these temperatures with increasing concentration of maltodextrin in samples prepared by Method 1 (Fig. 9a) or by Method 2 (Fig. 9b). The corresponding values of G'' are shown in Fig. 10. At all temperatures and compositions, and for both methods of sample preparation, G' is substantially higher than G''. The separation is smallest at 80°C, where G'' will be enhanced by un-gelled maltodextrin, and greatest for the strong networks formed at low temperature by samples with a high content of maltodextrin. For each method of preparation, however, the general pattern of variation is roughly the same for both moduli, and subsequent discussion is therefore confined to G'.

As shown in Fig. 9b, increasing concentration of maltodextrin in samples prepared by Method 2 causes a progressive increase in G' at 80°C, consistent with segregative interactions between the two polymers promoting intermolecular association of pectin. The ability of one component in a monophasic mixture of two thermodynamically-incompatible biopolymers to accelerate conversion of the other component from an expanded coil conformation to a more compact ordered structure has been observed previously for other systems (e.g. Kasapis & Morris, 1994; Tolstoguzov, Belkina, Gulov, Grinberg, Titova & Belavzeva, 1974). At 30°C where 2.0 wt% calcium pectinate alone is almost fully gelled (Fig. 4), however, there is a progressive reduction in modulus with increasing concentration of maltodextrin, suggesting extensive segregation of pectin chains into a large aggregates that make little contribution to the overall connectivity of the calcium pectinate network (as proposed previously for mixtures with oxidised starch; Picout et al., 2000a,b). It is this switch from increasing moduli at 80°C to decreasing values at 30°C that causes crossing of the cooling curves in Fig. 8a. A similar decrease is evident at 5°C for maltodextrin concentrations up to

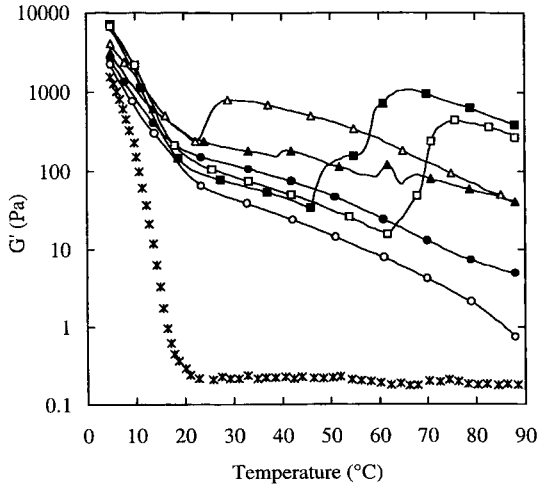

Fig. 11. Temperature-dependence of G' during cooling at 1°C/min for 20 wt% maltodextrin alone (∗), and in mixtures with calcium pectinate, prepared by Method 2, at pectin concentrations (wt%) of 0.4 (○), 1.0 (●), 1.5 (△), 2.0 (▲), 2.5 (□) and 3.0 (■).

~12.5 wt%, but is then obscured by gelation of maltodextrin at higher concentrations.

Samples prepared by Method 1 (Fig. 9a) show a broadly similar pattern of response at low temperatures (30 and 5°C), but at high temperature (80°C) there is a slight, but systematic, decrease in G' with increasing concentration of maltodextrin, in contrast to the substantial increase seen for Method 2 (Fig. 9b). A likely explanation is that, as discussed previously, the samples prepared by Method 1 already have substantial gel-like character at high temperature, and therefore respond to segregative interactions by aggregation of existing ordered structures (as at lower temperatures), whereas the dominant process for Method 2 is conversion from disorder to order.

At maltodextrin concentrations of ~17.5 wt% and above, the 100 min (5°C) values of G' from Method 1 and Method 2 are virtually identical, indicating that when maltodextrin has become the dominant component of the co-gel network the procedure used for dissolving and gelling the pectin component has little effect on overall rheology.

3.4. Co-gelation at 20 wt% maltodextrin

In a subsidiary study, mixtures were prepared at calcium pectinate concentrations of 0.4, 1.0, 1.5, 2.0, 2.5 and 3.0 wt%, holding the maltodextrin concentration fixed at 20 wt%. The main purpose was to use changes in final moduli to explore the volume occupied by pectin, as a further test of the concept of precipitation of pectin chains within a supporting network of calcium pectinate. The analysis used is reported in the following paper (Picout et al., 2000c). Since, as mentioned above, Methods 1 and 2 give virtually identical values of G' at 5°C for samples with a high content of maltodextrin, the investigation was confined to one procedure (Method 2).

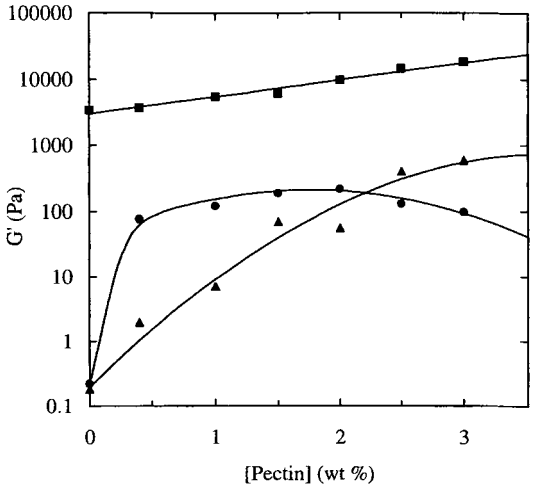

Fig. 12. Effect of pectin (calcium pectinate) concentration in mixtures with 20 wt% maltodextrin on the values of G' recorded at 80°C (▲) and 22.5°C (●) during cooling at 1°C/min, and on the 100 min values at 5°C (■).

Fig. 11 shows the temperature-dependence of G' on cooling (1°C/min) for all six samples, in comparison with the corresponding cooling trace for 20 wt% maltodextrin alone. At the two lowest concentrations of calcium pectinate (0.4 and 1.0 wt%) there is a monotonic increase in G', with a sharp upturn at the onset of maltodextrin gelation. At higher concentrations, however, the curves show clear evidence of abrupt collapses in calcium pectinate network structure, seen as sharp drops in modulus. As before (Figs. 5 and 9), the initial "weak gel" structure and the final co-gel network are characterised (Fig. 12) by G' values, at respectively, 80°C and 5°C. However, since the upswing in modulus from gelation of the maltodextrin component starts just above 20°C (Fig. 11), the rheology of the calcium pectinate network is characterised by the values of G' at 22.5°C (rather than the higher temperature of 30°C that was necessary for mixtures where the range of maltodextrin concentrations extended to 25 wt%).

The final (100 min) values of G' at 5°C increase (Fig. 12) by almost an order of magnitude as the concentration of calcium pectinate in increased from 0 to 3.0 wt%. As discussed in greater detail in the following paper (Picout et al., 2000c), however, the increase is almost certainly due to an increase in the degree of space-occupancy by pectin, with consequent increase in the effective concentration of maltodextrin, rather than to any significant direct contribution of calcium pectinate to the overall strength of the co-gel network. Indeed, as shown in Fig. 12, the values of G' for the calcium pectinate network at 22.5°C are about two orders of magnitude lower than the final moduli after gelation of the maltodextrin component (100 min values at 5°C), and show little systematic variation with pectin concentration, which is consistent with the suggestion (Picout et al., 2000b) that the concentration of unprecipitated pectin may be controlled by a solubility product.

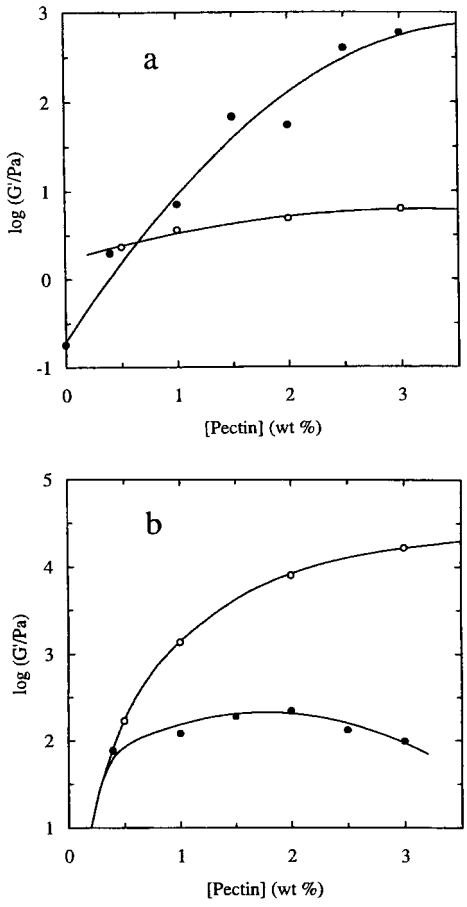

Fig. 13. Effect of pectin concentration on the values of G' recorded at (a) 80°C and (b) 22.5°C during cooling at 1°C/min, for calcium pectinate (stoichiometric Ca^{2+}) alone (○), and in mixtures with 20 wt% maltodextrin (●).

The most striking feature in Fig. 12, however, is the massive (~1000-fold) increase in G' at 80°C as the calcium pectinate concentration is raised from 0.4 to 3.0 wt%. Fig. 13a shows a direct comparison with the concentration-dependence of G' at 80°C for calcium pectinate alone (Fig. 5b); a similar comparison is shown in Fig. 13b for values recorded at 22.5°C. At the lowest pectin concentration (0.4 wt%), the moduli of the mixed system are close to those of calcium pectinate alone at the same temperatures and concentration. As the concentration is raised to 3.0 wt%, however, the values of G' at 80°C and 22.5°C for the mixtures with 20 wt% maltodextrin become, respectively, ~100 times larger and ~200 times smaller than the corresponding values for calcium pectinate in the absence of maltodextrin. As discussed previously, these changes can be explained by segregative interactions between the two polymers driving initial formation (at 80°C) and subsequent aggregation of calcium pectinate junctions, with the magnitude of both processes increasing as the concentration of pectin available for association and aggregation is raised.

3.5. Overview

Although the two procedures used for sample preparation give very different rheology at high temperature, the calcium pectinate networks formed before the onset of maltodextrin gelation show the same pattern of response to maltodextrin concentration and, for compositions where the maltodextrin gels, the final moduli of the co-gels formed at 5°C are virtually identical.

The overall variation of final moduli with increasing concentration of maltodextrin (Fig. 9) is similar in form to the changes observed for co-gels of calcium pectinate with increasing concentrations of oxidised starch (Picout et al., 2000a), suggesting that the properties of both systems are governed by the same general principles. The following paper (Picout et al., 2000c) reports a critical evaluation of this apparent similarity, by using the procedures and assumptions adopted (Picout et al., 2000b) for the calcium pectinate—oxidised starch system to analyse the experimental moduli obtained in the present work.

Acknowledgements

We thank the UK Ministry of Agriculture, Fisheries and Food, and the companies participating in the LINK project "Behaviour of Biopolymer Mixtures in Structuring Food Products" (Unilever, Nestlé, SKW Biosystems, Hercules and Cerestar), for financial support.

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