Carbohydrate Polymers 43 (2000) 143–153

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Co-gelation of calcium pectinate with potato maltodextrin. Part 2. Analysis of co-gel moduli

D.R. Picout[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 7 June 1999; accepted 26 November 1999

Abstract

The experimental moduli reported in the preceding paper for co-gels of calcium pectinate (DE 31.1; stoichiometric Ca^{2+}) with potato maltodextrin have been analysed using the procedures and assumptions developed for mixtures of calcium pectinate with oxidised starch. In outline, part of the calcium pectinate was assumed to be "precipitated" into a dispersed phase in response to segregative interactions between the two polymers, with the residual concentration of unprecipitated ("free") pectin being controlled by a solubility product K, defined as the maltodextrin concentration multiplied by the square of the concentration of free pectin, and with the phase volume of dispersed particles being directly proportional to the amount precipitated (constant of proportionality, k). The modulus of the continuous matrix was estimated by simple addition of the individual contributions from maltodextrin and free pectin, derived from standard calibration curves, and calculated values of co-gel moduli were obtained using the Takayanagi isostress blending law in the limiting form for an infinitely hard filler. Best-fitting values of $K = 2.8$ and $k = 0.059$ were identified by least-squares minimisation of the overall difference between observed and calculated values of log G' at 5°C for mixtures incorporating 2.0 wt% calcium pectinate prepared by two different procedures and measured 100 and 400 min after the start of cooling from 90°C at 1°C/min, with maltodextrin concentrations in the range 0–25 wt% (100 min values) or 0–17.5 wt% (400 min), and for 20 wt% maltodextrin with 0–3.0 wt% calcium pectinate (100 min values for one method of preparation). The fits to all five data sets were virtually within experimental error. The best-fitting value of k is almost identical to the value obtained for mixtures of calcium pectinate with oxidised starch (0.059 in comparison with 0.061), consistent with collapse of calcium pectinate network structure to a fixed concentration of ~17 wt% in both systems. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Biopolymer co-gels; Potato maltodextrin; Takayanagi blending laws; Pectin

1. Introduction

This is the last paper in a series of four related publications on the effect of partially depolymerised starch products (oxidised starch and gelling maltodextrin) on the gels formed by low-methoxy pectin on cooling in the presence of Ca^{2+}. The first paper (Picout, Richardson, Rolin, Abeysekera & Morris, 2000a) showed that the strength (storage modulus, G') of the calcium pectinate network could be increased, decreased, or remain unaffected by the presence of oxidised starch, depending on the concentration of Ca^{2+} used. Decrease in gel strength at high concentrations of Ca^{2+} was found to arise from sharp reductions in G' during cooling, and was accompanied by development of a grossly heterogeneous network structure (as visualised by light microscopy). It was tentatively suggested that: (i) segregative interactions between the two polymers promote conversion of pectin to a progressively more compact structure as the starch concentration is increased; (ii) at low concentrations of Ca^{2+}, the network is enhanced by formation of additional intermolecular junctions; and (iii) at higher Ca^{2+} concentrations, where there is already extensive intermolecular association in the absence of starch, gel strength is reduced by further association of pectin chains into large aggregated bundles that make little contribution to the overall connectivity of the network (effectively precipitation of ordered pectin in response to thermodynamic incompatibility with starch).

In the second paper (Picout, Richardson & Morris, 2000b), the concept of reduction in gel strength by a precipitation mechanism was explored further by quantitative analysis of G' values for 2.0 wt% pectin with stoichiometric Ca^{2+} after cooling to 5°C in the presence of increasing concentrations of oxidised starch (0–40 wt%). The central assumption in the analysis was that the pectin component could be regarded as comprising two fractions: precipitated

---

* Corresponding author. Tel.: + 353-21-490-3625; fax: + 353-21-427-0001.

E-mail address: ed.morris@ucc.ie (E.R. Morris).

0144-8617/00/$ - see front matter
PII: S0144-8617(99)00202-7

("missing") pectin and unprecipitated ("free") pectin. The precipitated material was treated as a dispersed phase surrounded by a continuous matrix of free pectin and oxidised starch. The extent of precipitation was characterised (Eq. (1)) by a solubility product:

$$K = [\text{starch}][\text{free}]^2 \tag{1}$$

and the phase volume of the dispersed particles (ϕ_Y) was assumed (Eq. (2)) to be directly proportional to the amount precipitated.

$$(\phi_Y) = k[\text{missing}] \tag{2}$$

The local concentrations (c_X) of free pectin and starch in the continuous matrix were then calculated (Eq. (3)) from the phase volume ($\phi_X = 1 - \phi_Y$) and the overall concentrations (c) across the whole system:

$$c_X = c/\phi_X \tag{3}$$

and the corresponding moduli were obtained from standard calibration curves of G' versus concentration for calcium pectinate and oxidised starch alone. The overall modulus of the continuous phase (G'_X) was then estimated by simple addition of the individual values of G'. The modulus of the dispersed particles (G'_Y) was calculated in two ways: (i) by using the calibration curve for calcium pectinate; and (ii) by regarding them as "deswollen" gel, and applying the modulus–concentration relationship anticipated for a permanent network by classic swelling/deswelling theory (Flory, 1953). In practice, the values of (ϕ_Y/G'_Y) obtained by either method were insignificant in comparison with the corresponding ratio for the continuous phase (ϕ_X/G'_X), allowing calculated values of the overall co-gel modulus to be determined using a limiting form (Eq. (5)) of the isostress blending law (Eq. (4)) of Takayanagi, Harima and Iwata (1963).

$$\frac{1}{G} = \frac{\phi_X}{G_X} + \frac{\phi_Y}{G_Y} \tag{4}$$

$$\frac{1}{G} = \frac{\phi_X}{G_X} \qquad \text{if } \frac{\phi_Y}{G_Y} \ll \frac{\phi_X}{G_X} \tag{5}$$

Finally, the values of the two adjustable parameters (K and k) required to give best agreement with experiment were obtained by least-squares minimisation of the difference between observed and calculated values of $\log G'$. The discrepancies between observed and fitted values were virtually within the experimental scatter of the results, suggesting that the assumptions made in the analysis may be physically realistic.

As would be anticipated, the dominant parameter in fitting the initial reduction in moduli at low concentrations of starch was the solubility product K, which determines the calculated concentration of free pectin in the continuous phase, whereas the fit to the increase in moduli at starch concentrations above the minimum required for network formation was dominated by k (which dictates the relative phase volumes and hence the local concentration of starch in the continuous phase).

The third paper (Picout, Richardson & Morris, 2000c) showed a qualitatively similar pattern of response for mixtures of calcium pectinate with potato maltodextrin, with again an initial decrease and subsequent increase in G' at 5°C as the concentration of the starch (maltodextrin) component was raised. Two methods of sample preparation were used. In the first procedure (Method 1) pectin was dissolved in a solution of maltodextrin containing $CaCl_2$ at stoichiometric equivalence to the carboxyl groups of the pectin. This method gave solutions with substantial gel-like character at high temperature, attributed to incomplete dissociation of intermolecular junctions present in the solid state. The high-temperature moduli showed a progressive reduction with increasing concentration of maltodextrin, which can be explained, as before, by aggregation of ordered pectin in response to segregative interactions between the two polymers.

In Method 2, the pectin was dissolved in water and the calcium salt was slowly added as a dilute solution (at 90°C), with subsequent addition of the maltodextrin solution. The moduli at high temperature now increased with increasing concentration of maltodextrin, consistent with segregative interactions promoting conversion from disordered coils to (more compact) ordered junctions. After cooling to 30°C (below the temperature-range of the gelling transition for calcium pectinate alone, but above the onset temperature for gelation of maltodextrin), however, there was a progressive reduction in modulus with increasing concentration of maltodextrin (as was also observed for samples prepared by Method 1), which is again consistent with the concept of precipitation of ordered pectin within a supporting network of calcium pectinate.

In most of the experiments, the concentration of calcium pectinate was held constant at 2.0 wt% (as in the mixtures with oxidised starch), and the maltodextrin concentration was varied between 0 and 25 wt%. Samples were cooled from 90 to 5°C at 1°C/min, and three data sets for quantitative analysis were compiled for each method of preparation: G' at 30°C during cooling, and at 5°C, 100 and 400 min from the start of the experiment (i.e. after 15 min at 5°C, and after a further holding period of 5 h). Because of practical restrictions on the (six decades) range of the rheometer used (from ~0.05 to ~50 000 Pa), the 400 min values were limited to mixtures with maltodextrin concentrations in the range 0–17.5 wt%. In a converse series of experiments, the maltodextrin concentration was held fixed at 20 wt% and the concentration of calcium pectinate was varied between 0 and 3.0 wt%; measurements for quantitative analysis were confined to 100 min values of G' at 5°C for samples prepared by Method 2.

The purpose of the present work was to provide a further test of the validity of the analysis outlined above for the calcium pectinate—oxidised starch system (Picout et al., 2000b), by using the same procedures and assumptions to

Table 1
Variation of G' measured at 5°C 100 and 400 min after the start of cooling from 90°C at 1°C/min, with concentration (c) of maltodextrin

	c (wt%)	G' (Pa)	log c	log G' observed	log G' fitted[a]
100 min values	15.0	4.91	1.176	0.69	0.68
	17.5	311	1.243	2.49	2.52
	18.5	850	1.267	2.93	2.98
	20.0	2972	1.301	3.47	3.47
	22.5	8570	1.352	3.93	3.99
	25.0	19 881	1.398	4.30	4.32
	30.0	52 286	1.477	4.72	4.70
400 min values	9.0	2.62	0.954	0.42	0.57
	10.0	38.5	1.000	1.59	1.41
	12.5	853	1.097	2.93	2.86
	15.0	5100	1.176	3.71	3.76
	20.0	51 900	1.301	4.72	4.74
	30.0	306 000	1.477	5.49	5.45

[a] Using Eq. (6) with polynomial parameters from Table 3.

analyse the experimental data (Picout et al., 2000c) for the co-gels of calcium pectinate with maltodextrin. As before the analysis was carried out using the in-built curve-fitting and minimisation routines on a Microsoft Excel spreadsheet package (Version 5.0).

2. Results

2.1. Calibration curves for individual polymers

Tables 1 and 2 show the values used for calibration of the concentration-dependence of G' for the individual polymers. Six calibration curves were used: 100 and 400 min values for maltodextrin at 5°C; G' at 30°C during cooling for calcium pectinate prepared by Methods 1 and 2; and 100 min values at 5°C for calcium pectinate from both methods of preparation. As mentioned in the preceding paper (Picout et al., 2000c), there were no significant changes in G' for calcium pectinate alone on holding for a further 5 h at 5°C, so the same curves were used in the analysis of 100 and 400 min values of co-gel moduli.

To allow G' to be expressed as a continuous function of polymer concentration (c), each curve was fitted to a polynomial relationship of the general form:

$$B = p(4)A^4 + p(3)A^3 + p(2)A^2 + p(1)A + p(0) \qquad (6)$$

where $A = \log(c/\text{wt\%})$ and $B = \log(G'/\text{Pa})$. The polynomial parameters used are listed in Table 3, and the standard of agreement between observed and fitted values of log G' is shown in Tables 1 and 2. It should be noted that the experimental moduli for the co-gels (Picout et al., 2000c) lie almost entirely within the range of the appropriate calibration curves for the individual components, so that the empirical polynomial fits are used almost exclusively for interpolation (with one slight extrapolation, by ~0.1 in log G', being required for calcium pectinate from Method 1 at 5°C).

2.2. Space-occupancy by precipitated pectin

Fig. 1 shows the effect of maltodextrin concentration on the 100 and 400 min values of G' at 5°C for mixtures with 2.0 wt% calcium pectinate prepared by Methods 1 and 2,

Table 2
Variation of G', measured at 30°C during cooling from 90°C at 1°C/min and at 5°C 100 min after the start of cooling, with concentration (c) of calcium pectinate (stoichiometric Ca^{2+}) prepared by Methods 1 and 2

			Method 1			Method 2		
	c (wt%)	log c	G' (Pa)	log G'_{obs}[a]	log G'_{calc}[a]	G' (Pa)	log G'_{obs}[a]	log G'_{calc}[a]
30°C	0.5	−0.301	37.2	1.57	1.56	63.0	1.80	1.80
	1.0	0.000	260	2.41	2.46	780	2.89	2.90
	2.0	0.301	1640	3.21	3.24	5500	3.74	3.73
	3.0	0.477	4400	3.64	3.65	11 950	4.08	4.09
5°C	0.5	−0.301	156	2.19	2.20	663	2.82	2.82
	1.0	0.000	1172	3.07	3.05	3779	3.58	3.59
	2.0	0.301	5977	3.78	3.77	15 814	4.20	4.20
	3.0	0.477	13 911	4.14	4.14	32 480	4.51	4.48

[a] G'_{obs} and G'_{calc} denote, respectively, observed values of G' and fitted values calculated using Eq. (6) with parameters from Table 3.

Table 3
Polynomial parameters (Eq. (6)) for calculation of log G' from log c

System	$p(4)$	$p(3)$	$p(2)$	$p(1)$	$p(0)$
Maltodextrin; 100 min values; 5°C	−238.405	1406.411	−3121.64	3093.545	−1151.56
Maltodextrin; 400 min values; 5°C	0.000	12.062	−60.265	101.540	−51.925
Calcium pectinate[a]; Method 1; 5°C	0.000	0.000	−0.7009	2.6193	3.0494
Calcium pectinate[a]; Method 2; 5°C	0.000	0.000	−0.8959	2.3009	3.5900
Calcium pectinate[a]; Method 1; 30°C	0.000	0.000	−0.6056	2.7826	2.4553
Calcium pectinate[a]; Method 2; 30°C	0.000	0.000	−1.5025	3.2070	2.8990

[a] Stoichiometric Ca^{2+}.

and for maltodextrin alone (Table 1). The 100 min values (Table 4) from the two methods of sample preparation become virtually identical (Fig. 1a) at maltodextrin concentrations of ~17.5 wt% and above. The 400 min values (Table 5) show a similar convergence (Fig. 1b) at ~12.5 wt% maltodextrin. At both holding times, the increase in modulus at high concentrations of maltodextrin is similar in form to the concentration-dependence of G' for maltodextrin alone, but the values are systematically higher, indicating that the aggregated particles of calcium pectinate make part of the total volume inaccessible to maltodextrin, and thus raise its effective local concentration.

As mentioned previously, the procedure adopted in analysis of co-gel moduli for mixtures of calcium pectinate with oxidised starch was to assume that the volume occupied by the "precipitated" material is directly proportional to the amount precipitated, which is equivalent to assuming that the concentration of calcium pectinate in the dispersed phase is independent of the concentration of starch/maltodextrin in the surrounding matrix. In systems where segregative interactions lead to conventional phase separation, however, partition of solvent (which dictates the polymer concentration in each phase) can be rationalised convincingly by assuming that the ratio of solvent/polymer in one phase divided by the corresponding ratio for the other phase remains constant at a fixed value (p), which reflects the relative "solvent avidities" of the two materials (Clark, 1987). Although originally entirely empirical, subsequent studies (e.g. Durrani, Prystupa, Donald & Clark, 1993) have shown that "p-factors" can be related directly to Flory–Huggins χ-values, placing the concept on a sound theoretical footing. One aim of the present work was therefore to determine whether the increase in G' values for maltodextrin introduced by the presence of calcium pectinate could be better explained by competition for solvent, determined by a p-factor, than by the assumption of constant polymer concentration in the dispersed phase.

As shown in Fig. 1, the range of compositions in which the overall moduli appear to be dominated by the maltodextrin component in mixtures with 2.0 wt% calcium pectinate is comparatively small (from ~17.5 to 25 wt% for 100 min values, and from ~12.5 to 17.5 wt% at 400 min). Thus the relative concentrations of the two polymers vary by only a factor of ~1.4, which is insufficient to give a reliable test of the changes in concentration that would be expected from competition for solvent. Instead, we have used the results (Table 6) from the series of experiments in which maltodextrin concentration was held fixed at 20 wt% and the concentration of calcium pectinate (prepared by Method 2) was varied from 0 to 3.0 wt%.

Fig. 2 shows the effect of pectin concentration on the 100 min values at 5°C, in direct comparison with the concentration-dependence of G' for calcium pectinate alone (Table 2), and with the moduli recorded for the

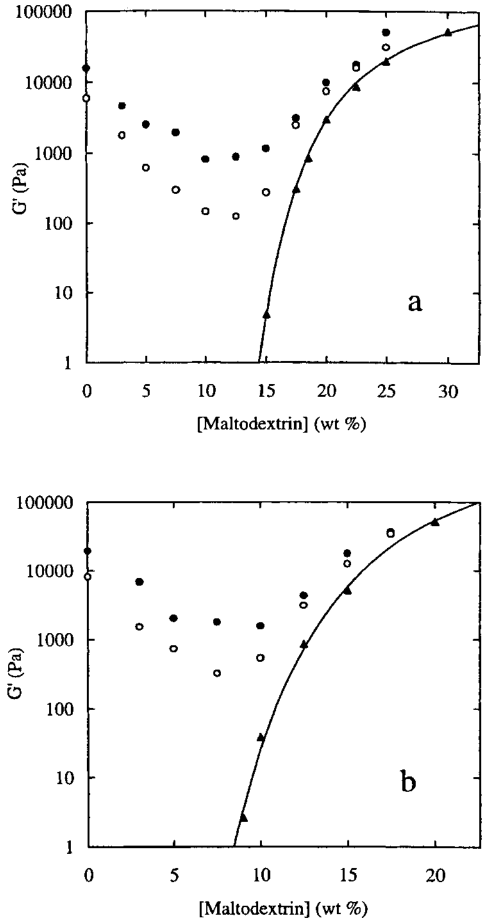

Fig. 1. Variation of G', measured at 5°C (a) 100 min and (b) 400 min, after the start of cooling from 90°C at 1°C/min, for maltodextrin alone (▲) and in co-gels with 2.0 wt% calcium pectinate prepared by Method 1 (○) and Method 2 (●).

Table 4
Variation of G', measured at 5°C 100 min after the start of cooling from 90°C at 1°C/min, with concentration (c) of maltodextrin in mixtures with 2.0 wt% calcium pectinate (stoichiometric Ca^{2+}) prepared by Methods 1 and 2

		Method 1			Method 2		
c (wt%)	log c	G' (Pa)	log G'_{obs} [a]	log G'_{calc} [a]	G' (Pa)	log G'_{obs} [a]	log G'_{calc} [a]
0.0		5954	3.78	3.77	15 766	4.20	4.20
3.0	0.477	1773	3.25	3.11	4611	3.66	3.65
5.0	0.699	620	2.79	2.83	2509	3.40	3.40
7.5	0.875	298	2.47	2.60	1942	3.29	3.19
10.0	1.000	145	2.16	2.43	807	2.91	3.03
12.5	1.097	124	2.09	2.29	871	2.94	2.91
15.0	1.176	272	2.43	2.40	1145	3.06	2.86
17.5	1.243	2459	3.39	3.34	3068	3.49	3.41
20.0	1.301	7352	3.87	3.98	9748	3.99	3.99
22.5	1.352	15 776	4.20	4.35	17 565	4.24	4.36
25.0	1.398	30 900	4.49	4.60	50 075	4.70	4.60

[a] G'_{obs} and G'_{calc} denote, respectively, observed values of G' and values calculated by the analysis described in the text.

Table 5
Variation of G', measured at 5°C 400 min after the start of cooling from 90°C at 1°C/min, with concentration (c) of maltodextrin in mixtures with 2.0 wt% calcium pectinate (stoichiometric Ca^{2+}) prepared by Methods 1 and 2

		Method 1			Method 2		
c (wt%)	log c	G' (Pa)	log G'_{obs} [a]	log G'_{calc} [a]	G' (Pa)	log G'_{obs} [a]	log G'_{calc} [a]
0.0		8017	3.90	3.77	19 234	4.28	4.20
3.0	0.477	1510	3.18	3.11	6720	3.83	3.65
5.0	0.699	726	2.86	2.83	1995	3.30	3.40
7.5	0.875	318	2.50	2.60	1750	3.24	3.19
10.0	1.000	530	2.72	2.59	1584	3.19	3.08
12.5	1.097	3074	3.49	3.43	4236	3.63	3.52
15.0	1.176	12 287	4.09	4.19	17 380	4.24	4.20
17.5	1.243	33 880	4.53	4.69	36 300	4.56	4.69

[a] G'_{obs} and G'_{calc} denote, respectively, observed values of G' and values calculated by the analysis described in the text.

mixtures at 22.5°C during cooling. At the lowest concentration of calcium pectinate used (0.4 wt%), the 100 min value of G' for the mixed system is about an order of magnitude higher than the corresponding value for calcium pectinate alone, but at higher concentrations the separation between the two curves is much smaller, and both have approximately the same slope. It might therefore seem reasonable to attribute the increase in modulus of the mixed systems with increasing concentration of pectin to a progressive increase in strength of the calcium pectinate network. However, the moduli recorded at 22.5°C, where gelation of calcium pectinate alone is almost complete but the maltodextrin component is ungelled (Picout et al., 2000c), are about two orders of magnitude lower than the 100 min values at 5°C. We therefore conclude that the direct contribution of calcium pectinate to the overall moduli at 5°C is negligible, and that the increase in G' with increasing pectin concentration comes almost entirely from reduction in the space available to the maltodextrin component (with consequent progressive increase in its effective concentration).

As a working approximation, the final co-gels were regarded as comprising a dispersed phase of calcium pectinate particles surrounded by a continuous matrix containing only gelled maltodextrin. The first step in the analysis was to use the concentration-dependence of G' for maltodextrin

Table 6
Variation of G', measured at 22.5°C during cooling from 90°C at 1°C/min and at 5°C 100 min after the start of cooling, with concentration (c) of calcium pectinate in mixtures with 20 wt% maltodextrin prepared by Method 2

	G' (Pa)		log G' (5°C)	
c (wt%)	22.5°C	5°C	Observed	Calculated[a]
0.0	0.22	2972	3.47	3.47
0.4	76	3681	3.57	3.52
1.0	120	5463	3.74	3.71
1.5	186	6096	3.79	3.85
2.0	216	9748	3.99	3.99
2.5	130	14 440	4.16	4.12
3.0	97	18 248	4.26	4.25

[a] By the analysis described in the text.

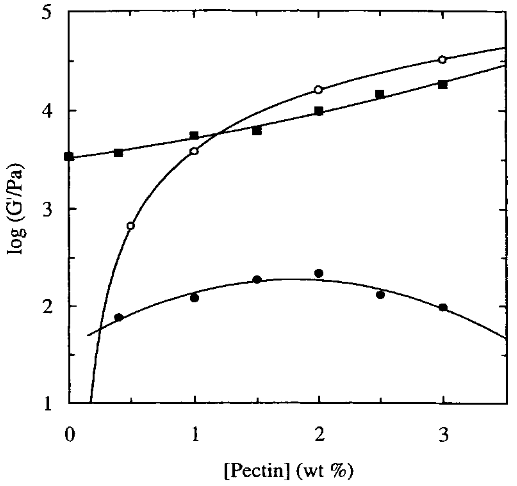

Fig. 2. Variation of G' with pectin concentration in mixtures of calcium pectinate (stoichiometric Ca^{2+}) with 20 wt% maltodextrin, measured at 22.5°C (●) during cooling from 90°C to 5°C at 1°C/min and at 5°C (■) 100 min after the start of cooling, in comparison with the corresponding 100 min values at 5°C for calcium pectinate alone (○).

alone (Table 1) to determine the effective concentrations of maltodextrin ($[MD]_{eff}$) that would be required to give the moduli observed experimentally for the mixed systems at 5°C. As shown in Fig. 3, the calculated values increase smoothly from the starting concentration of 20 wt% in the absence of pectin to ~25 wt% when the pectin concentration is raised to 3.0 wt%. On the assumption of complete segregation, the water content of each phase could then be calculated directly from the relative phase volumes and the total amount of each polymer present, allowing an apparent *p*-factor to be derived for each concentration of pectin.

As shown in Fig. 4b, the calculated values of *p* (defined as water/polymer in the pectin phase divided by the corresponding ratio for the maltodextrin phase) increase steeply with increasing pectin concentration, rather than remaining roughly constant, as would be expected for pro-rata distribution of solvent between the two materials. The calculated phase volumes for the pectin component, however, show an approximately linear increase (Fig. 4a) as the total pectin content is raised, which is consistent with association of most, or all, of the pectin chains into particles with a roughly constant ratio of solvent/polymer. The slope of the line of best fit in Fig. 4a is ~0.06, which would imply that the volume occupied by 1 g of pectin is ~6 ml, giving an effective local concentration of ~16.7 wt%, in almost perfect agreement with the value of ~16.4 wt% obtained from analysis of experimental moduli for mixtures of calcium pectinate with oxidised starch (Picout et al., 2000b).

The concentration of calcium pectinate obtained from the straight line in Fig. 4a cannot, however, be regarded as reliable, since the analysis described above involves several crude approximations. The first is the assumption of complete segregation, in effect setting the concentration of "free" pectin to zero. Next, in equating experimental values of G' to the modulus of the maltodextrin component, we

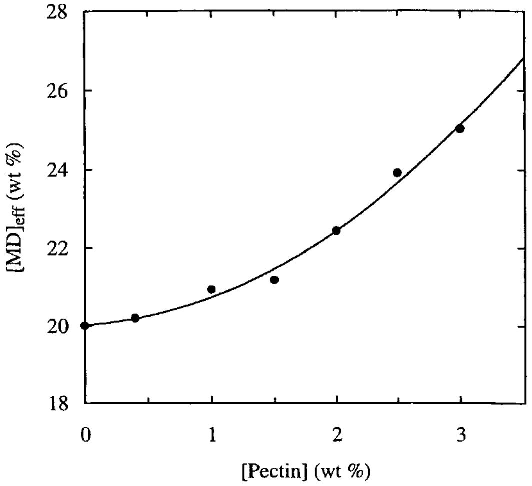

Fig. 3. Variation of the effective local concentration of maltodextrin ($[MD]_{eff}$) with pectin concentration in mixtures of 20 wt% maltodextrin with calcium pectinate (stoichiometric Ca^{2+}).

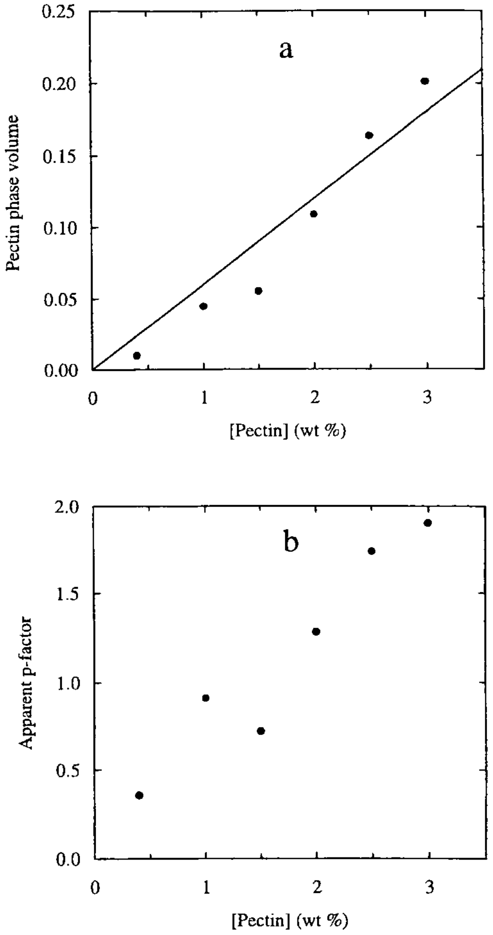

Fig. 4. Effect of pectin concentration in co-gels of 20 wt% maltodextrin with calcium pectinate (stoichiometric Ca^{2+}) on: (a) the calculated phase volume of the pectin (calcium pectinate) component; and (b) the apparent "*p*-factor" for partition of solvent between the two polymers.

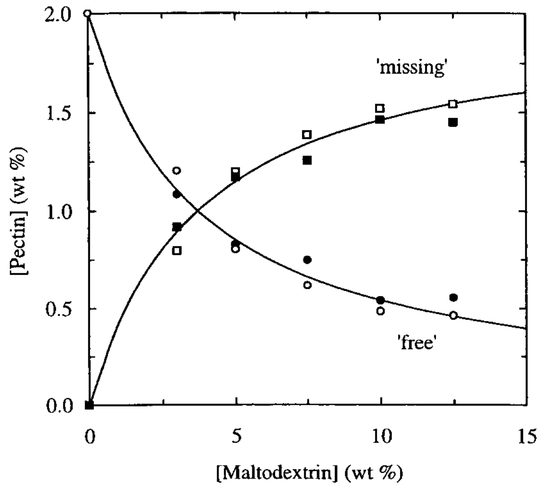

Fig. 5. Effect of maltodextrin concentration in mixtures with 2.0 wt% calcium pectinate prepared by Method 1 (open symbols) and Method 2 (filled symbols) on the concentrations of unprecipitated ("free") pectin (circles) and precipitated ("missing") pectin (squares) calculated from experimental (100 min) values of G' at 5°C.

were ignoring the effect of phase volume in linking overall moduli to those of the constituent phases (Eq. (4)). Finally, the direct contribution of the dispersed particles to the overall moduli was similarly ignored. However, as described later, a virtually identical value for calcium pectinate concentration in the dispersed phase was obtained from the full analysis in which all of these approximations were eliminated. The main conclusion from the simplified treatment presented here is that the polymer concentrations in the two phases do not appear to follow a normal "*p*-factor" relationship.

2.3. Extent of precipitation

As mentioned previously, a central conclusion from the investigation of calcium pectinate in mixtures with oxidised starch (Picout et al., 2000a,b) was that, at least at high concentrations of co-polymer, the concentration of unprecipitated ("free") pectin is controlled by a solubility product (Eq. (1)). One immediate indication of analogous behaviour in the calcium pectinate–maltodextrin system is that the observed values of G' at 22.5°C for calcium pectinate networks formed in the presence of 20 wt% maltodextrin are virtually independent (Fig. 2) of the total concentration of pectin present. As described below, the reductions in moduli observed (Fig. 1) with increasing concentration of maltodextrin in mixtures with a fixed content of calcium pectinate (2.0 wt%) also seem reasonably consistent with the relationship shown in Eq. (1).

As before (Picout et al., 2000b), the concentration of "free" pectin was calculated from the observed values of G' by using the appropriate calibration curve for calcium pectinate alone (Table 2), and the concentration of precipitated ("missing") pectin was obtained by difference from the starting concentration of 2.0 wt%. As shown in Fig. 5, the values derived from (100 min) measurements at 5°C (Fig. 1a) are closely similar for both methods of sample preparation.

Table 7

Variation of G', measured at 30°C during cooling at 1°C/min, with concentration (c) of maltodextrin in mixtures with 2.0 wt% calcium pectinate prepared by Methods 1 and 2

c (wt%)	G' (Pa)		Equivalent concentration of "free" pectin (wt%)[a]	
	Method 1	Method 2	Method 1	Method 2
0.0	1616	5075	2.00	2.00
3.0	570	3272	1.34	1.67
5.0	389	1840	1.16	1.33
7.5	173	1000	0.86	1.07
10.0	81.0	452	0.65	0.83
12.5	42.0	358	0.52	0.77
15.0	34.3	250	0.49	0.70
17.5	32.6	316	0.48	0.74
20.0	23.2	193	0.43	0.65
22.5	26.9	181	0.45	0.64
25.0	20.5	148	0.41	0.61

[a] From modulus–concentration curves for calcium pectinate alone.

Analysis of moduli at 5°C is restricted (Fig. 5) to the concentration range 0–12.5 wt% maltodextrin, since at higher concentrations the strength of the calcium pectinate network is obscured by gelation of the maltodextrin. The concentration of free pectin can, however, be characterised over the full range of maltodextrin concentrations (0–25 wt%) from moduli recorded at 30°C during cooling (Table 7), before the onset of gelation of maltodextrin (Picout et al., 2000c) at the highest concentration used. As shown in Fig. 6, the values obtained for samples prepared by Method 1 are systematically lower than for Method 2, although both curves are similar in form. The difference is consistent with Method 1 giving a higher initial content of ordered structure, and thus allowing aggregation and precipitation to occur at higher temperatures than in the more fully dissociated solutions obtained by Method 2.

Eq. (1) implies a linear relationship between maltodextrin concentration and $1/[\text{free}]^2$, where [free] denotes the calculated concentration of unprecipitated free pectin. As shown in Fig. 7, the concentrations of free pectin derived (Fig. 6) from measurements at 30°C for samples from both methods of preparation give acceptable linearity when plotted in this way, for maltodextrin concentrations across the full range studied (0–25 wt%). The values obtained from 100 min measurements at 5°C (Fig. 4) also show reasonable linearity across the narrower range of concentrations accessible before the onset of gelation of maltodextrin. Thus the concept of a solubility-product relationship proposed (Picout et al., 2000b) for the concentration of unprecipitated pectin in mixtures with oxidised starch also appears to apply reasonably well to mixtures with maltodextrin.

Again, however, the above analysis is a simplified treatment, which ignores the effect of precipitated pectin on the

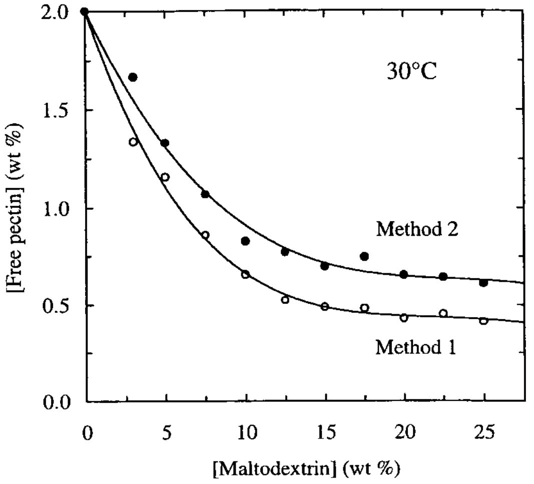

Fig. 6. Effect of maltodextrin concentration in mixtures with 2.0 wt% calcium pectinate prepared by Method 1 (○) and Method 2 (●) on the concentrations of “free” pectin calculated from experimental values of G' recorded at 30°C during cooling from 90°C at 1°C/min.

volume accessible to the free component, and which also ignores the direct contribution of the dispersed phase to the overall moduli. The following section reports the results from the full analysis, which eliminates these approximations.

2.4. Calculation of co-gel moduli

The method used to derive fitted values of G' was identical to the procedure outlined in Section 1 for mixtures of calcium pectinate with oxidised starch. As before (Picout et al., 2000b), preliminary analyses were made using deswelling theory and modulus–concentration curves to calculate G' values for the dispersed phase of precipitated calcium. The moduli derived by both methods were again so much greater than the values calculated for the continuous phase that essentially identical fits were obtained using the limiting form of the isostress blending law shown in Eq. (5).

The final fits, using Eq. (5), were derived by varying the two adjustable parameters, K (Eq. (1)) and k (Eq. (2)), to minimise the overall root-mean-square difference between observed and calculated values of log G' for all five data sets analysed: 100 min values of G' at 5°C for mixtures of maltodextrin (0–25 wt%) with 2.0 wt% calcium pectinate prepared by Methods 1 and 2 (Table 4); 400 min values (Table 5) for the same samples, at maltodextrin concentrations up to 17.5 wt%; and 100 min values for 20 wt% maltodextrin in mixtures with 0–3.0 wt% calcium pectinate, prepared by Method 2 (Table 6). The best overall fit was achieved with $K = 2.8$ and $k = 0.059$. The calculated values of log G' are shown in the appropriate tables, in direct comparison with the experimental values.

As before (Picout et al., 2000b), the effect of the individual parameters on the calculated curves was explored by adjusting them manually and observing the resulting changes. The value of k (which is the reciprocal of the polymer concentration in the dispersed phase of precipitated calcium pectinate) is tightly constrained by the experimental moduli for the mixtures in which maltodextrin concentration was held fixed at 20 wt% and the concentration of pectinate was varied. As shown in Fig. 8, the observed values of G' for these samples agree, to within experimental error, with the fitted curve obtained using the value of $k = 0.059$ required to give the best overall agreement for all five data sets, which corresponds to a calcium pectinate concentration of ~17 wt%. Decreasing k to 0.05 (20 wt% calcium pectinate) or increasing it to 0.07 (~14 wt%) gives curves (Fig. 8) that are, respectively, well below and well above the experimental values, particularly at high concentrations of pectin where the reduction in the fraction of the total volume available to maltodextrin will be greatest.

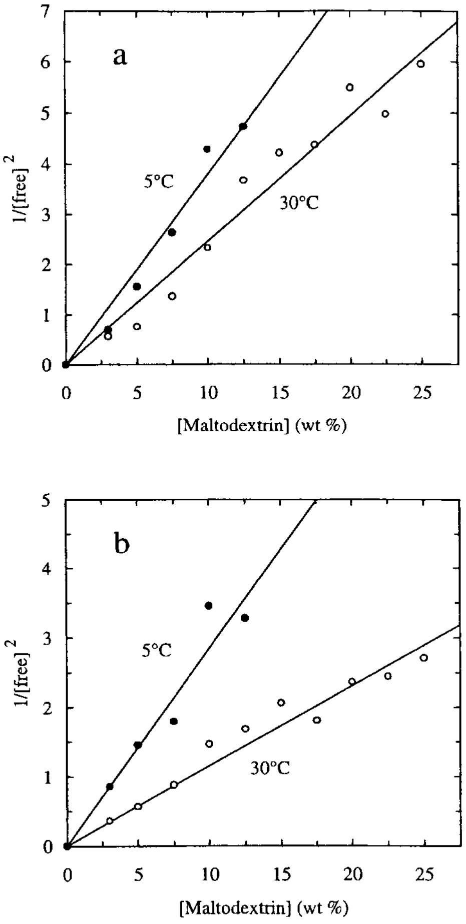

Fig. 7. Solubility-product analysis of the effect of maltodextrin concentration in mixtures with 2.0 wt% calcium pectinate prepared by (a) Method 1 and (b) Method 2 on the concentration of “free” pectin calculated from experimental values of G' recorded at 30°C (○) during cooling from 90°C at 1°C/min and at 5°C (●) 100 min after the start of cooling.

In the systems where pectin concentration was held constant (at 2.0 wt%) and maltodextrin concentration was varied (Fig. 9), the fitted curves at high concentrations of

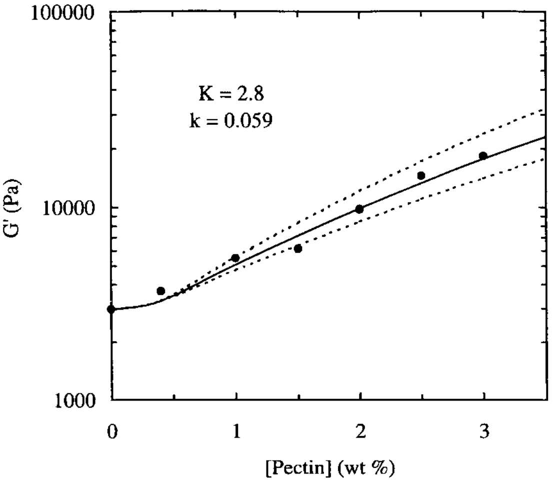

Fig. 8. Effect of pectin concentration in co-gels of calcium pectinate (stoichiometric Ca^{2+}) with 20 wt% maltodextrin on experimental values (●) of G', measured at 5°C 100 min after the start of cooling from 90°C at 1°C/min, and on calculated values (—) from the analysis described in the text (with $K = 2.8$ and $k = 0.059$). The dotted lines show curves obtained with the same value of K, but with k set at 0.07 (upper line) or 0.05 (lower line).

maltodextrin (where the overall moduli are increasing) are again dominated by k (i.e. by the degree of space-occupancy by precipitated pectin). As would be expected, however, the calculated fits to the initial reduction in moduli at lower concentrations of maltodextrin are dominated by the solubility product K, which determines the extent of precipitation, and hence the strength of the network formed by residual free pectin.

The standard of agreement between the observed and fitted moduli for the four data sets shown in Fig. 9 seems reasonably acceptable. The worst discrepancies are for 100 min values of G' in the centre of the experimental range of maltodextrin concentrations. These may be due to inadequacies in the model, or in the procedures used for calculation of co-gel moduli (such as estimation of the modulus of the continuous phase by simple addition of the individual values of G' for maltodextrin and free pectin). It is at least equally likely, however, that they have a more trivial, practical origin.

At low concentrations, the maltodextrin component is non-gelling. At high concentrations, there is a rapid increase in G' during cooling, with a much slower increase on holding at 5°C (Picout et al., 2000c). At intermediate concentrations, however, gelation occurs solely, or predominantly, after the samples have reached 5°C, and the 100 min values are therefore critically sensitive to small variations in the time–temperature regime. In particular, the deviations between observed and fitted moduli for mixtures with maltodextrin concentrations in the range 10–15 wt% (Fig. 9) are closely comparable to the observed differences between 100 min values and moduli recorded 1 min earlier or later, and therefore lie within the likely range of timing errors.

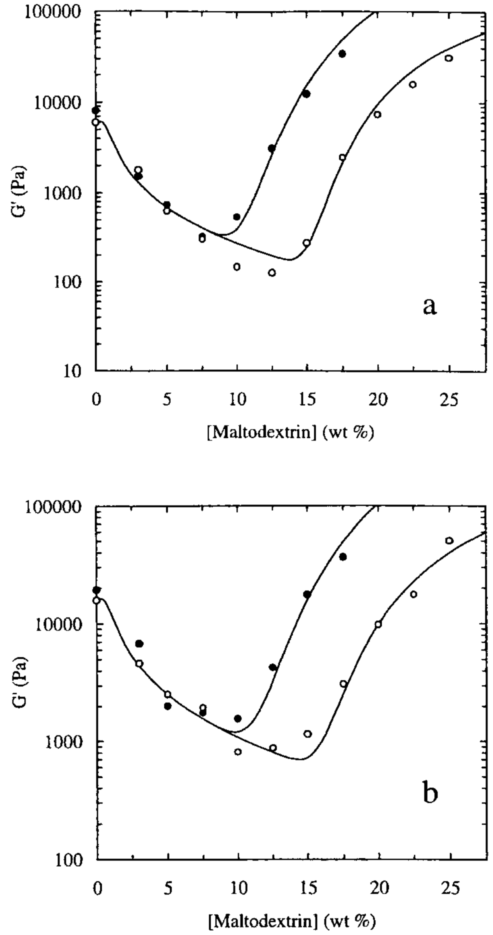

Fig. 9. Effect of maltodextrin concentration in co-gels with 2.0 wt% calcium pectinate prepared by (a) Method 1 and (b) Method 2 on the experimental values of G' recorded at 5°C 100 min (○) and 400 min (●) after the start of cooling from 90°C at 1°C/min, and on calculated values (—) from the analysis described in the text.

3. Discussion

As might be anticipated from their structural similarity, oxidised starch and potato maltodextrin appear to influence the network properties of calcium pectinate in very much the same way, both qualitatively and quantitatively. Qualitatively, both materials cause an initial reduction and subsequent increase in modulus as their concentration in mixtures with a fixed content of calcium pectinate is raised. Quantitatively, the procedures and assumptions used to fit a single data set of G' values for mixtures of calcium pectinate with oxidised starch (Picout et al., 2000b) give calculated moduli that agree, almost to within experimental error, with the five data sets analysed here for mixtures with maltodextrin.

Although encouraging, this standard of agreement does not, of course, necessarily imply that the underlying model is correct. An obvious alternative possibility is that the mixtures undergo phase separation during cooling, into a maltodextrin-rich continuous phase and pectin-rich dispersed phase. The networks formed below the onset of gelation of maltodextrin would then come from the minor pectin component in the continuous phase and, as in any conventional phase relationship (e.g. Tolstoguzov, 1995), the concentration of the minor component would decrease progressively with increasing concentration of the major, maltodextrin, constituent, giving a progressive reduction in modulus, as observed. Our reasons for favouring a precipitation mechanism are summarised as follows:

1. As discussed previously (Picout et al., 2000a), the response to changes in degree of esterification of the pectin component in mixtures with oxidised starch seems more consistent with extensive aggregation than with phase separation.
2. The concentrations of "free" pectin calculated from G' values for mixtures prepared by two different procedures and measured at two different temperatures show good linearity (Fig. 7) when plotted according to the solubility-product relationship in Eq. (1), as was also found for the single data set of G' values for mixtures of calcium pectinate with oxidised starch.
3. The effect of increasing concentrations of pectin on the moduli of co-gels incorporating a fixed (gelling) concentration of maltodextrin seems more consistent (Fig. 4) with collapse of the calcium pectinate networks to a constant local concentration than with solvent partition according to a p-factor (as found in phase-separating systems).
4. The best-fitting value of k (the reciprocal of the local concentration in the dispersed phase) obtained in the present work (0.059) is in close agreement with the value derived (Picout et al., 2000b) for mixtures with oxidised starch ($k = 0.061$), again indicating that the extent of collapse is determined by some inherent property of the calcium pectinate network, rather than by pro-rata distribution of water between the constituent polymers.

Nonetheless, we certainly do not rule out the possibility of a phase-separation mechanism. Indeed, the purpose of presenting the experimental values of co-gel moduli, and the calibration data, in tabular form is to allow alternative interpretations to be tested.

The concept of network collapse to a condensed form by extensive aggregation (effectively precipitation) of ordered sequences does, however, have some parallels in the behaviour of other systems. In a previous investigation Kasapis, Morris, Norton and Gidley (1993), concentrated mixtures of gelatin and potato maltodextrin (Paselli SA6), at a temperature above the onset of gelation of either component, were found to give classic phase separation into clear solutions with compositions lying along a well-defined binodal. Mixtures prepared at concentrations in the single-phase region below the binodal, however, gave dense precipitates of maltodextrin, demonstrating that phase separation, and precipitation of one component, can occur as separate, distinct responses to segregative interactions between two different polymers. In a later study of mixtures of maltodextrin with whey proteins (Manoj, Kasapis, Hember, Richardson & Morris, 2000), there were again indications of phase separation and incipient precipitation (network collapse) occurring as separate processes, although, as in the present work, the evidence came from interpretation of co-gel moduli, rather than from direct observation of macroscopic precipitation.

Formation of biphasic composites in which the relative phase volumes are dictated by the inherent properties of one component rather than by a p-factor relationship also has a precedent in the co-gels obtained when starch granules are gelatinised in solutions of gelling biopolymers (Abdulmola, Hember, Richardson & Morris, 1996; Mohammed, Hember, Richardson & Morris, 1998). On gelatinisation, the individual granules swell to a fixed volume (i.e. a fixed local concentration of starch), which is unaffected by the polymer concentration in the surrounding matrix. Network collapse to a fixed local concentration is not, of course, directly analogous to disordering and swelling of highly-branched amylopectin, but there may be some parallels between the response of calcium pectinate to the presence of a polymeric co-solute and the sharp transitions from swollen to contracted states observed for covalent networks when exposed to large changes in solvent composition (Tanaka, 1981, 1992).

Finally, there are some central issues that remain unresolved:

- why do segregative interactions sometimes cause phase separation and sometimes lead to precipitation?
- why do some polymers precipitate, or cause precipitation, while others do not?
- what factors determine which component is precipitated and which remains in solution?

These would be obvious targets for future research.

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.

References

Abdulmola, N. A., Hember, M. W. N., Richardson, R. K., & Morris, E. R. (1996). Application of polymer blending laws to starch–gelatin composites. *Carbohydrate Polymers*, *31*, 53–63.

Clark, A. H. (1987). The application of network theory to food systems. In J. M. V. Blanshard & P. Lillford (Eds.), *Food structure and behaviour* (pp. 13–34). London: Academic Press.

Durrani, C. M., Prystupa, D. A., Donald, A. M., & Clark, A. H. (1993).

Phase-diagram of mixtures of polymers in aqueous solution using Fourier-transform infrared spectroscopy. *Macromolecules*, *26*, 981–987.

Flory, P. J. (1953). *Principles of polymer chemistry*. Ithaca, NY: Cornell University Press.

Kasapis, S., Morris, E. R., Norton, I. T., & Gidley, M. J. (1993). Phase equilibria and gelation in gelatin/maltodextrin systems. Part 2. Polymer incompatibility in solution. *Carbohydrate Polymers*, *21*, 249–259.

Manoj, P., Kasapis, S., Hember, M. W. N., Richardson, R. K. & Morris, E. R. (2000). Complex interactions in co-gelation of whey protein isolate or bovine serum albumin with potato maltodextrin. *Food Hydrocolloids*, submitted for publication.

Mohammed, Z. H., Hember, M. W. N., Richardson, R. K., & Morris, E. R. (1998). Application of polymer blending laws to composite gels of agarose and crosslinked waxy maize starch. *Carbohydrate Polymers*, *36*, 27–36.

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*, *43*, 113–122.

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, 43*, 123–141.

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*, *43*, 133–141.

Takayanagi, M., Harima, H., & Iwata, Y. (1963). Viscoelastic behaviour of polymer blends and its comparison with model experiments. *Memoirs—Faculty of Engineering Kyushu University*, *23*, 1–13.

Tanaka, T. (1981). Gels. *Scientific American*, *January*, 110–123.

Tanaka, T. (1992). Phase transitions in gels. In R. S. Harland & R. K. Prud'homme (Eds.), *Polyelectrolyte gels* (pp. 1–21). Washington, DC: American Chemical Society.

Tolstoguzov, V. B. (1995). Some physico-chemical aspects of protein processing in foods. Multicomponent gels. *Food Hydrocolloids*, *9*, 317–332.