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Short communication

Molecular weight effects on the gelatin/maltodextrin gel

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Abstract

The aim of this work is to demonstrate that the phase behaviour of the gelatin/maltodextrin gel can be controlled by means of the molecular weight distribution of the polymeric constituents and the cooling rate. In doing so, the technique of small deformation dynamic oscillation was used to monitor the mechanical strength of the binary gels and their melting profiles upon subsequent heating. Introduction of high molecular weight fractions induced a transformation from weakened deswelled gels to reinforced composite gels. The phase inversion point from gelatin to maltodextrin continuous gels was manipulated by decreasing the length of molecular chains of the protein and/or increasing that of the polysaccharide. The formation of maltodextrin continuous structures was further assisted by quenching the binary solutions from high temperature as opposed to slow cooling. For a given concentration of gelatin, it was possible to reduce to a third the amount of maltodextrin required for phase inversion in the mixture.

Keywords: Gelatin/maltodextrin gel; Phase behaviour; Molecular weight effects

1. Introduction

In general, interactions between a neutral and a second polymer in solution are thermodynamically unfavourable (Flory, 1953). The polymers are said to be thermodynamically incompatible and the interactions are referred to as segregative (Piculell & Lindman, 1992). In the polysaccharide–protein–water system, segregative interactions lead to macromolecular phase separation at total polymer concentrations higher than 4% (Tolstoguzov, 1986). The solution splits into two phases at thermodynamic equilibrium with one of them being rich in polymer A and depleted in B, and vice versa. Phase diagrams are constructed with points on the binodal unveiling the pattern of polymer segregation at a given composition of the mixture. Eventually, phase diagrams in gelatin–amylopectin solutions were rationalised at the molecular level using the Flory–Huggins interaction parameters of the polymeric ingredients with respect to solvent and the ingredients themselves (Durrani, Prystupa, Donald, & Clark, 1993).

Cooling of the ternary system may induce network formation which transforms the phase behaviour of the resulting gel (Watase & Nishinari, 1983; Clark, Richardson, Ross-Murphy, & Stubbs, 1983). To start with, the entropic effect of lowering the temperature will shift the binodal to lower compositions thus rearranging polymer segregation and solvent partition between phases. More to the point, however, the disorder-to-order transition and the ensuing network formation introduce enthalpic interactions between chains of the same species, which are capable of wiping out the macromolecular organisation in solution. An expedient way to demonstrate the perturbation of phase equilibria is to introduce a kinetic element in the gelation of the constituent polymers. Quenching ($\approx$ 33°C/min) of a system with a fixed gelatin concentration (5% LO-2) requires 15% maltodextrin (SA-6) for the formation of a polysaccharide continuous gel (Kasapis, Morris, Norton, & Clark, 1993a). In contrast, slow cooling at 1°C/min maintains gelatin continuous co-gels up to about 22% maltodextrin. Thus phase separated solutions with a maltodextrin-rich continuous phase at thermodynamic equilibrium (e.g. 5% LO-2 + 20% SA-6) yield protein or polysaccharide continuous gels depending on the rate of cooling (Alevisopoulos, Kasapis, & Abeysekera, 1996).

The present study employs samples of gelatin and maltodextrin with distinct molecular weight distributions which govern the structural properties of networks. Structure formation was induced by cooling binary solutions of the two hydrocolloids at distinct scan rates. The approach is used to explore the link between the gelling characteristics of polymeric constituents and the pattern of phase separation of the composite gel.

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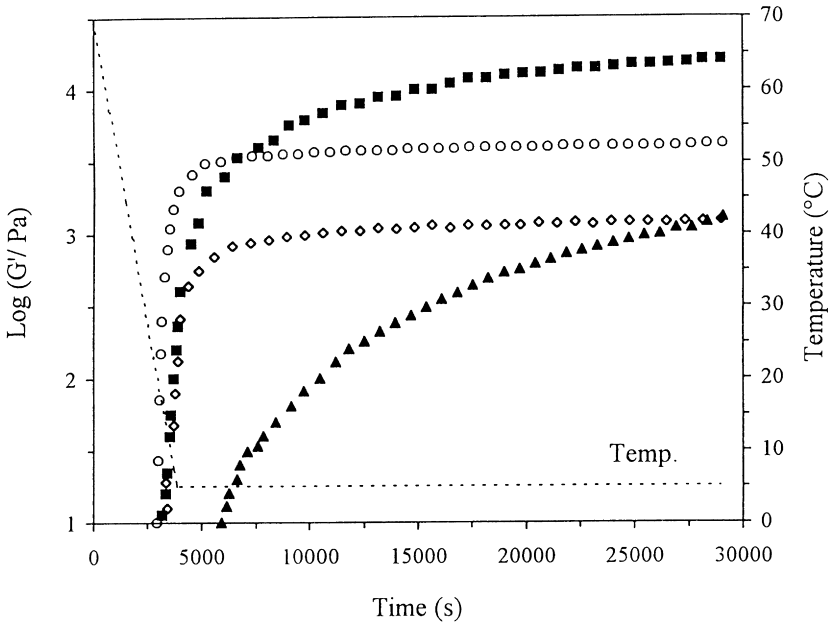

Fig. 1. Cooling-isothermal runs of 25% maltodextrin [(■) C*1906; (▲) SA-6] and 5% gelatin [(○) LO-2; (◇) PS4] samples (scan rate: 1°C/min; 0.2% strain; frequency: 1 Hz).

2. Experimental

The gelatin and maltodextrin samples were of the same botanical/animal source but varied in molecular weight. Regarding the gelatin samples, LO-2 is a high quality extract with a weight average molecular weight (M_w) of 2.1×10^5 whereas the M_w of its replacer in the composite gels is equal to 0.8×10^5 Da (PS4). Bloom values are 270 and 48 g, respectively. The maltodextrin samples (SA-6 and C*1906) are dextrins from potato starch produced by enzymic cleavage with thermally stable α-(1 → 4) amylase. Thus the α-(1 → 6) linkages remain largely unaffected yielding a degree of branching of 3.0% and 3.3% for SA-6 and C*1906, respectively (^{1}H NMR results of Kasapis, Morris, Norton, & Gidley, 1993b and F. Deleyn, personal communication). The enzymolysis released some low molecular weight material with the degree of branching being higher than the values of 2.5–2.8 expected for intact potato starch (Robyt, 1984). Systems remain mainly polymeric, albeit polydisperse, shown by the dextrose equivalent numbers (4.7 and 3.9 for SA-6 and C*1906, respectively) and the following slicing of GPC data (Alevisopoulos et al., 1996; Chronakis, Kasapis, & Richardson, 1996).

The GPC data argue that SA-6 contains higher amounts of the low molecular weight fractions (three top bands) whereas C*1906 dominates in the range of 25×10^3 to 5×10^6. This is reflected on the mechanical strength of the networks which at 25% polysaccharide yield storage modulus (G') values of 1.3 and 16 kPa for SA-6 and C*1906, respectively (Fig. 1). Besides the network strength, the high M_w fractions are responsible for steric exclusion phenomena in binary blends (Morris, 1990) and both effects are used to investigate the molecular organisation of the gelatin/maltodextrin gel.

3. Results and discussion

Fig. 1 shows typical time–temperature profiles of storage modulus for our samples. They were cooled from 70°C to 5°C at a rate of 1°C/min and held at the final temperature for 7 h. A positive trend between polymer concentration and temperature of gelation has been documented for maltodextrins ranging from ≈ 50°C to 67 min holding time at 5°C as the polysaccharide content was dropped from 50% to 15% (Chronakis et al., 1996). This relationship parallels the effect of molecular weight in Fig. 1. Thus, the short chains of SA-6 require an extended 'lag period' for gelation to occur (30 min in the isothermal run) whereas the onset of gelation for C*1906 is seen during cooling at 20°C. The latter also forms substantially stronger networks at the end of the experimental routine. In contrast, the temperature span of the onset of network formation for a 20-fold increase in gelatin concentration is rather short, i.e. 26.4–32.6°C (Michon, Cuvelier, & Launay, 1993), since the physical

M_w	SA-6 (% of material)	C*1906 (% of material)
$< 10^3$	6.71	5.19
10^3–5×10^3	21.26	18.27
5×10^3–25×10^3	29.4	26.38
25×10^3–2×10^5	39.76	44.54
2×10^5–10^6	2.87	5.56
10^6–5×10^6	0.01	0.06

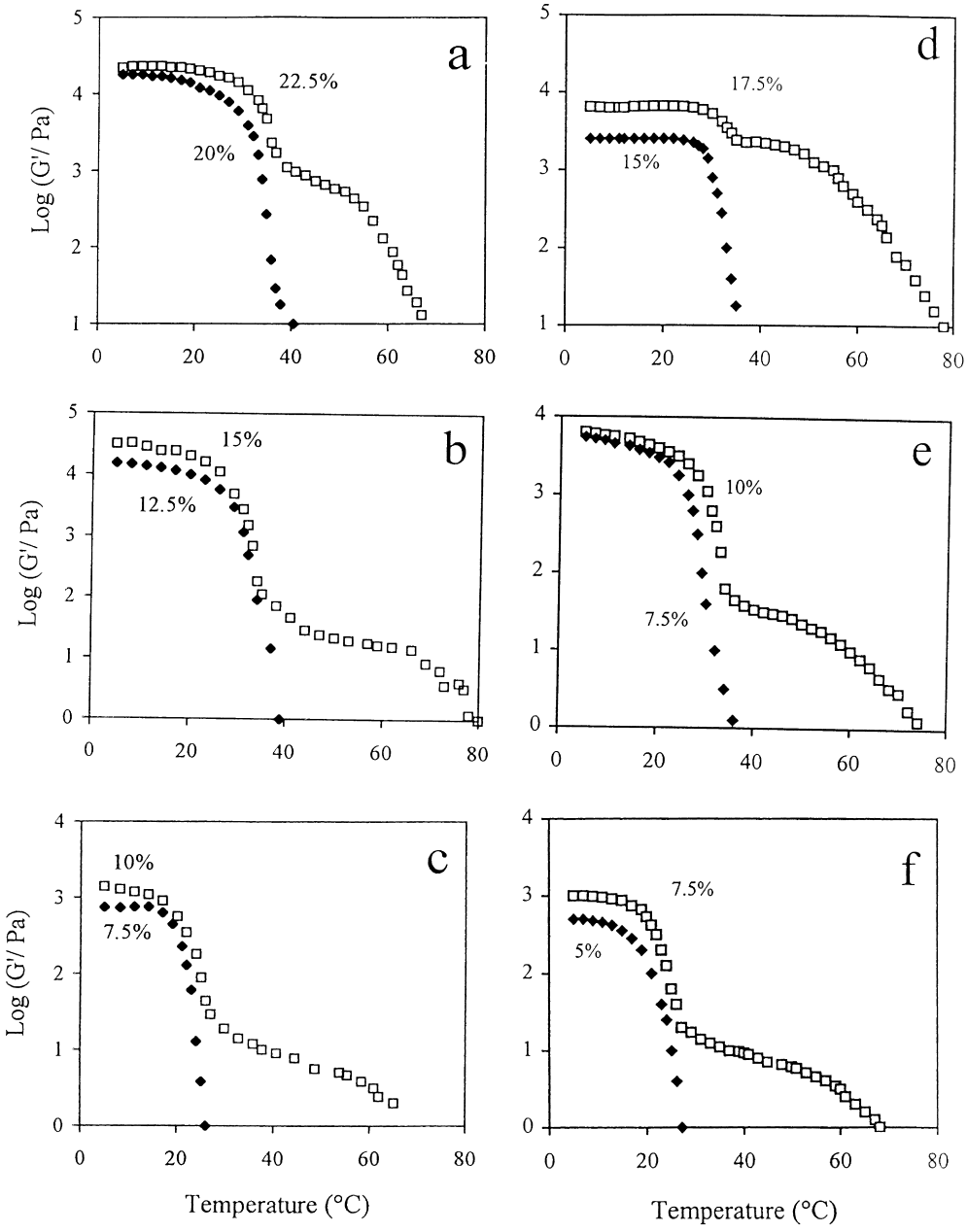

Fig. 2. Heating profiles of: (a) LO-2/SA-6; (b) LO-2/C*1906; (c) PS4/C*1906; (d) LO-2/SA-6; (e) LO-2/C*1906; and (f) PS4/C*1906 at a scan rate of 1°C/min. Samples (a)–(c) were cooled to 5°C at 1°C/min whereas samples (d)–(f) were quenched to 5°C at 33°C/min. The gelatin concentration is 5% and the maltodextrin content is shown by the individual traces.

process cannot occur at temperatures higher than the coil-to-helix transition (36°C) of the parent collagen (Djabourov, Leblond, & Papon, 1988). By analogy, increasing the molecular weight has a limited impact on the onset of gel formation (2°C in Fig. 1), but the longer chains of LO-2 form a network half-an-order of magnitude stronger than the structure of PS4.

To take advantage of the disparate viscoelasticity of the two materials we came up with mixtures where the reinforcement of one component should be at the expense of its partner. Fig. 2(a) depicts the transition from a gelatin to a maltodextrin continuous network in the LO-2/SA-6 mixture where the cooling (1°C/min)/isothermal run was followed by a heating scan at the same rate. The first wave of structural loss (gelatin melting) is halted at 37°C due to the thermally stable maltodextrin matrix which is capable of supporting the liquid gelatin inclusions. Replacement of SA-6 with C*1906 reinforces the maltodextrin network which is able to phase invert the LO-2/C*1906 mixture at a lower concentration (15% in Fig. 2(b)). This pattern of phase behaviour is further assisted by substituting PS4 for LO-2 with the maltodextrin taking over at 10%

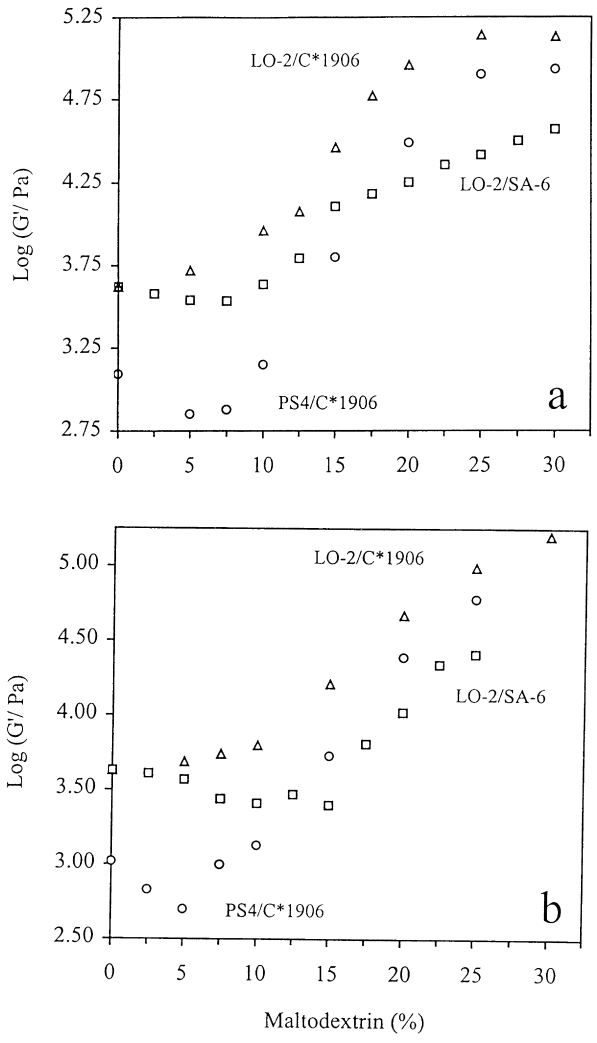

Fig. 3. Development of storage modulus as a function of maltodextrin concentration for our three co-gels during cooling from 70° to 5°C at: (a) 1°C/min; and (b) 33°C/min. In both cases samples were left at the final temperature for 7 h.

(PS4/C*1906 blend in Fig. 2(c)), a concentration less than half of that required in the first instance.

Clearly, there is an antagonistic effect operating between the two polymers, whereby weakening of the gelatin network or reinforcement of the structure of maltodextrin promotes an early phase inversion in the gel. Quenched preparations of LO-2/SA-6, LO-2/C*1906 and PS4/C*1906 phase invert earlier than the corresponding slow-cooled mixtures. Quenching triggers simultaneous gelation of both components thus 'freezing' the mixture in a microstructure that bears parentage to the maltodextrin-rich continuous solutions (Fig. 2(d)–(f)). Phase inversion in LO-2/SA-6, LO-2/C*1906 and PS4/C*1906 requires 17.5%, 10% and 7.5% maltodextrin, respectively, an amount which is 2.5–5% less than that for the slow-cooled counterparts.

The dramatic consequences of changing the average chain length of two components are not confined to the phase inversion regime of their mixtures. Fig. 3(a) reproduces the development of storage modulus as a function of maltodextrin concentration for mixtures subjected to slow cooling but a similar story emerges from the quenched counterparts (Fig. 3(b)). The initial drop in strength of the LO-2/SA-6 systems relates to clear single-phase solutions which form gelatin networks upon cooling. This is followed by the gelation of maltodextrin within the pores of the gelatin network thus effectively deswelling it (for a quantitative treatment of the reduction in G' see Morris, 1998). Phase separation in solution takes place during slow cooling at levels of maltodextrin above 10% and results in concentrated phases which strengthen the gelatin-continuous gels; according to the melting profile of Fig. 2(a), systems remain gelatin continuous until 22.5% maltodextrin is added to the mixture. Observe that in the case of quenching, 17.5% maltodextrin is required to induce phase separation with a polysaccharide supporting matrix thus reinforcing the modulus of the composite gel (Figs. 2(d) and 3(b)).

Substitution of C*1906 for SA-6 encourages an earlier phase separation between gelatin and the longer maltodextrin chains seen by the immediate rise in storage modulus values of the LO-2/C*1906 mixture. The upward trend continues at higher levels of the polysaccharide where stronger maltodextrin-continuous gels are formed due to increased steric exclusion ability and gelling performance of the C*1906 macromolecules. As shown in Fig. 3(a), values of G' at 30% maltodextrin are 135 and 37 kPa for LO-2/C*1906 and LO-2/SA-6, respectively.

Replacement of LO-2 with PS4 has a double effect on the structure of gelatin-dominated composites (PS4/C*1906). Thus, there is a dramatic drop in the strength of gelatin continuous gels in the presence of up to 10% C*1906, and within this concentration range the familiar trough of deswelled gelatin gels reappears (as in the case of LO-2/SA-6 samples). Both phenomena can be rationalised on the basis of shorter PS4 chains showing weaker gelling properties and increased compatibility with the C*1906 segments, which upon ordering deswell the gelatin network. In the LO-2/SA-6 mixture the increased miscibility is facilitated by the shorter SA-6 molecules, as compared to those of C*1906. Finally, 10% and 7.5% of C*1906 are needed to phase invert the gels formed by slow cooling and quenching (Fig. 2(c) and 2(f), respectively). Regardless of the cooling rate, the rigidity of the PS4/C*1906 composite approaches the elevated values of the maltodextrin-continuous LO-2/C*1906 sample (Fig. 3(a) and 3(b)), since the strength of both mixtures beyond the phase inversion point is increasingly dominated by the supporting matrix of C*1906.

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