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Rheological study into the ageing process of high methoxyl pectin/sucrose aqueous gels

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The ageing process of high methoxyl pectin (HMP)/sucrose gels was followed at different ageing temperatures by small amplitude oscillatory experiments. Dynamic mechanical measurements allowed the characterisation of the point at which the system undergoes the sol/gel transition. The HMP/sucrose system is extremely sensitive to temperature variation during ageing, especially in the lower temperature range. The viscoelastic behaviour through the gel point changes with the ageing temperature, probably due to variations in mobility of the pectin chains, and consequently, in the lifetime of junction zones. Weaker pectin networks are formed under thermal conditions unfavourable to the development of hydrophobic interactions. Gel time and elastic modulus have a complex dependence on temperature, which could be attributed to the different thermal behaviour of the intermolecular interactions that stabilise the nonpermanent cross links of these physical networks.

INTRODUCTION

Pectins are anionic structural polysaccharides extraced from the primary plant cell wall. They consist of a linear backbone of randomly connected $\alpha(1 \rightarrow 4)$D-galacturonic acid residues partially esterified with methanol. Neutral sugars are also present, as side-chains bound to the galacturonate main chain or inserted into the main chain (rhamnose), usually in amounts of about 5 to 10% of the galacturonic acid. Pectins with degree of methylation (molar ratio of methanol to galacturonic acid) higher than 50%, named high methoxyl pectins (HMPs), form gels at pH lower than about 3·5 and when the water activity is reduced by addition of a cosolute, typically sucrose, at a concentration higher than 55% by weight. They are widely used in food formulations, mainly as gelling agents.

HMP gelation is a quite complex process, in which are involved several kinds of intermolecular interactions. The available results suggest that, in gels of HMPs, the junction zones are stabilised by hydrogen

bonds and also by hydrophobic interactions between the ester methyl groups (Walkinshaw & Arnott, 1981; Oakenfull & Scott, 1984).

The mechanical properties of HMP gels have been extensively studied, mainly by using empirical methods based on internal strength/breaking measurements and SAG techniques (Crandall & Wicker, 1986), but also by some fundamental static viscoelastic methods, like creep compliance (Kawabata, 1977; Plashchina *et al.*, 1979; Dahme, 1985) and stress relaxation (Comby *et al.*, 1986). In comparison to the studies that have been done on cured gels, only a few measurements have been reported during the HMP sol–gel transition, including small amplitude oscillatory rheological tests (Ikkala, 1986; Beveridge & Timbers, 1989; Dahme, 1982; Rao *et al.*, 1993).

It was felt that a more comprehensive study during the gel formation, using nondestructive and fundamental methods, would provide a better insight into the rheological properties of HMP/sucrose gels and would be a useful contribution to the understanding of the

gelation mechanism of these systems. Our purpose was to study the influence of temperature, on the viscoelastic properties of HMP gels, near the gel point, during the ageing process, and after maturation of the gels, by using dynamic rheological methods.

The role of hydrophobic interactions in stabilising polysaccharide networks has been studied by different techniques: the relative effects of organic solvents (Oakenfull & Scott, 1984), temperature effects (Oakenfull & Scott, 1984, 1986), and the relative influence of the lyotropic series of salts (Case *et al.*, 1992). The influence of a combined set of intermolecular interactions with different thermal sensitivity on the thermal behaviour of HMP gels, should be very important from a technological point of view. For this reason, the variation in temperature was selected as a tool to investigate the relative influence of hydrophobic interactions and hydrogen bonds on the evolution of the viscoelastic properties of HMP gels.

EXPERIMENTAL

Pectin sample

The pectin sample used was a commercial citrus pectin obtained from Bulmer (UK). Some physicochemical characteristics of the HMP are shown in Table 1. The degree of methylation was 64% as determined by gas chromatography, and the percentage of anhydrogalacturonic acid was 82% as determined colorimetrically. The intrinsic viscosity was 4·8 dl/g in 0·1 mol/litre NaCl at 25°C. The total neutral sugars were quantified by the orcinol method, as described by Montreuil *et al.* (1981). Details of the analytical procedures employed have been described elsewhere (da Silva *et al.*, 1992).

Preparation of the gels

The pectin was previously dispersed overnight in 0·1 mol/litre citrate buffer (pH 3·0) at room temperature, and then centrifuged for 1 h at 28 000 g. The dispersion was heated at 105°C in a paraffin bath for 3 min and then the required amount of sucrose was added under stirring. The heating was continued for

Table 1. Physicochemical parameters of the HMP sample[a]

Anhydrogalacturonic acid (%)[b]	81·6 ± 1·2
Degree of methylation (%)	63.6 ± 1·3
Total neutral sugars[b]	8·61 ± 0·28
Intrinsic viscosity (dl/g)	4·79 ± 0·08
Huggins coefficient (k')	0·49 ± 0·01
Structural charge density ($\bar{\lambda}$)	0·586

[a]The values shown are mean ± standard deviation of three determinations, on a dry weight basis.
[b]Measured as anhydro residues.

7 min, the lost water was replaced and the sample was transferred to the instrument plate at the desired test temperature. The time elapsed from the beginning of the heating process (total of 10 min at 105 ± 2°C) to the commencement of the test was exactly 15 min.

Rheological experiments

Dynamic rheological measurements were performed using a Carri-Med CS-50 controlled-stress rheometer, fitted with cone and plate geometry (radius 25 mm, angle 4°). After the sample was transferred to the instrument plate, the exposed surface of the sample was covered with a thin layer of low viscosity paraffin oil to avoid solvent evaporation. Two types of experiments have been carried out at several temperatures, using a small amplitude oscillatory strain of 0·03: gel formation was monitored by measuring the storage (G') and the loss (G'') moduli at a fixed frequency of 0·5 Hz as a function of time, and mechanical spectra (frequency sweeps) were recorded near the sol–gel transition and after maturation of the gels. Accurate temperature control (within ±0·1°C throughout the experiments) was achieved with a Peltier system at the bottom plate.

RESULTS AND DISCUSSION

Cure experiments and gel time

A typical cure curve for a 1·1% HMP gel (60% (w/w) sucrose, pH 3), showing the evolution of the storage (G') and the loss modulus (G'') at constant frequency as a function of the ageing time (t), is shown in Fig. 1.

The general behaviour of the dynamic moduli is typical of biopolymer gel systems. The beginning of the gelation process is dominated by the viscous behaviour of the system ($G'' > G'$) and the elastic behaviour dominates the final stages of the experiment ($G' \gg G''$). Both moduli increase as a result of the increasing junction zones density, but the storage modulus rises more sharply until it intercepts and then exceeds the loss modulus. During the first 8 h, the storage modulus had a great variation covering about two orders of magnitude, whereas that of G'' was approximately one order. After this rapid increase, resulting from the rapid formation of junction zones into the polymer network, the storage modulus keeps increasing slightly and continuously as a result of the slower formation and rearrangement of junction zones, reaching the pseudo-plateau region. Even after 3 days ageing, G' continues to increase steadily in this region, as could be evidenced by plotting G' as a function of log (t). This nonequilibrium behaviour should result from a continuous reorganisation of the network, a behaviour that was also found for other biopolymeric systems (te Nijenhuis, 1981; Clark & Ross-Murphy, 1987).
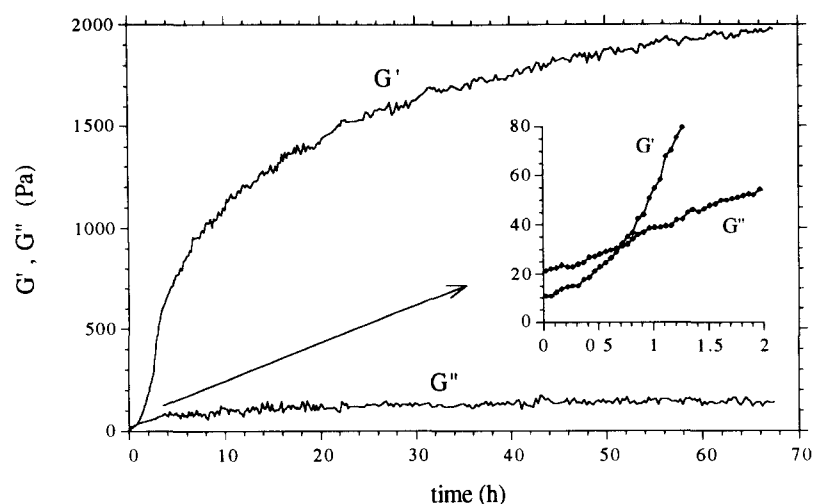
Fig. 1. Cure curve for a 1·1% HMP sol/gel (pH 3, 60%(w/w) sucrose), recorded at 20°C and 0·5 Hz, showing the evolution of the storage (G') and the loss (G'') moduli as a function of the ageing time.

Dynamic mechanical measurements allow the direct determination of the moment at which the system undergoes the sol/gel transition. However, an unambiguous rheological criterion to detect the gel point is still a matter of controversy.

The studies of Winter and coworkers (Winter & Chambon, 1986; Chambon & Winter, 1987; Winter, 1987) on cross-linking chemical gels have shown that the time of the $G'-G''$ cross-over is not a universal property of the gel point; the time of interception might be close to, but not identical with, the sol/gel transition time. They proposed a new mechanical definition of the gel point based on the observation that the entire relaxation spectrum is affected by the gelation transition. Power law relaxation at the gel point seems to be a more general property, common to chemical gels (Chambon & Winter, 1987; Scanlan & Winter, 1991) and to physical gels from synthetic (te Nijenhuis & Winter, 1989; Lin *et al.*, 1991) or biological macromolecules (Cuvelier *et al.*, 1990; Michon *et al.*, 1993). According to this concept, the dynamic moduli also follow a power law dependence upon oscillatory frequency, with the same exponent (n):

$$G'(\omega) \propto G''(\omega) \propto \omega^n \tag{1}$$

It was further demonstrated that the relaxation exponent is not a universal parameter for gelation. Depending on the specific nature of the polymer network, values in the range of 0·1–0·9 have been reported (Chambon & Winter, 1987; te Nijenhuis & Winter, 1989; Lin *et al.*, 1991; Muller *et al.*, 1991; Scanlan & Winter, 1991).

To apply the $G'-G''$ cross-over criteria to localise the gel point, G' should be identical to G'' over a large frequency range and not just an interception at a specific frequency value. This criterion is thus limited to network polymers that relax following a power law with a relaxation exponent $n = 0·5$.

Also shown in Fig. 1 is the cross-over G' and G'', occurring at an ageing time of about 41 min. However, the time of the $G'-G''$ cross-over at 20°C and for a HMP concentration of 1%(w/w) was found to be dependent on the oscillatory frequency (Fig. 2). Clearly, the moment of the $G'-G''$ cross-over depends on the frequency of the dynamic experiment, and should not be used as a criterion to identify the critical gel point.

With the purpose of finding the moment at which the dynamic moduli exhibit a power law dependence upon oscillatory frequency (eqn (1)), with the same relaxation exponent (n), the viscoelastic behaviour at the beginning of gelation was also analysed. At chosen stages of the gelation process, the time sweep experiments were
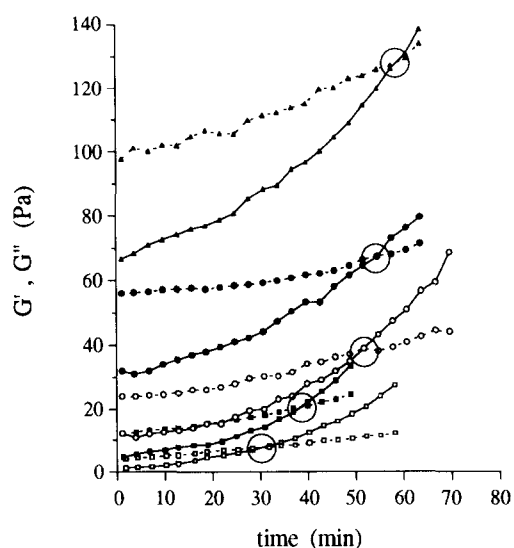

Fig. 2. Storage modulus (G') and loss modulus (G'') as a function of the ageing time, recorded at different oscillatory frequencies, for 1% HMP (60% sucrose, pH 3): (□) 0·50 rad/s; (■) 1·58 rad/s; (○) 5·0 rad/s; (●) 15·8 rad/s; (△) 50·0 rad/s. Continuous lines denote G' and dashed lines G''.

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interrupted, and the storage (G') and the loss modulus (G'') were measured as a function of frequency, at successive time intervals. By doing that it was also possible to follow the continuous evolution of the viscoelastic properties through the gel point.

During the beginning of gelation most of the rheological changes are related to macromolecular aggregation and are expected to occur mostly at relatively long time scales, i.e. the measurements at low frequencies would be the most important. However, taking into account that the gelation proceeds during the measurement and it is in the beginning of gelation that the rheological properties change more quickly, the measurements should be quick enough to decrease the effect of time. Therefore, an intermediate frequency range was chosen in order to balance these contradictory requirements.

Figure 3 shows the evolution of the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ during the initial period of gelation at 20°C. Each frequency sweep took about 5 min. The times shown for each mechanical spectrum are the average times of each experiment.

A congruent behaviour of G' and G'' over the entire experimental frequency range was not observed. A similar power law dependence on frequency of both moduli over the entire frequency range, with an exponent of about 0·6 (Fig. 3(a)), was observed to occur before the $G'-G''$ cross-over. After this point, the tendency of the storage modulus towards a limiting value at low frequencies begins to be evident, suggesting

the existence of permanent elasticity characteristics of a solid material. Both moduli change smoothly as the gelation proceeds, with G' and G'' approaching each other and crossing in a continuous fashion.

Effect of temperature

Hydrogen bonds, hydrophobic interactions and electrostatic interactions contribute to build up the HMP/sucrose networks. How the structure of this kind of network is affected by temperature during its formation has not yet been established, and was one of the purposes of this work. Given the different temperature dependence of these different kinds of intermolecular interactions, important temperature effects in the viscoelastic behaviour of HMP gels are expected to occur. Two different methods were employed to analyse the thermal behaviour of the HMP/sucrose systems: (a) by quenching the dispersions at fixed ageing temperatures; and (b) by quenching the gels, previously matured for 48 h at 20°C, at different temperatures.

Effect of temperature on the ageing process and gel point
Gel cure experiments have been performed on the HMP–sucrose systems at several ageing temperatures. some of the cure curves obtained are shown in Fig. 4. The storage modulus continued to increase as a function of time for all the temperatures studied, even after ageing for 4 days (results not shown).
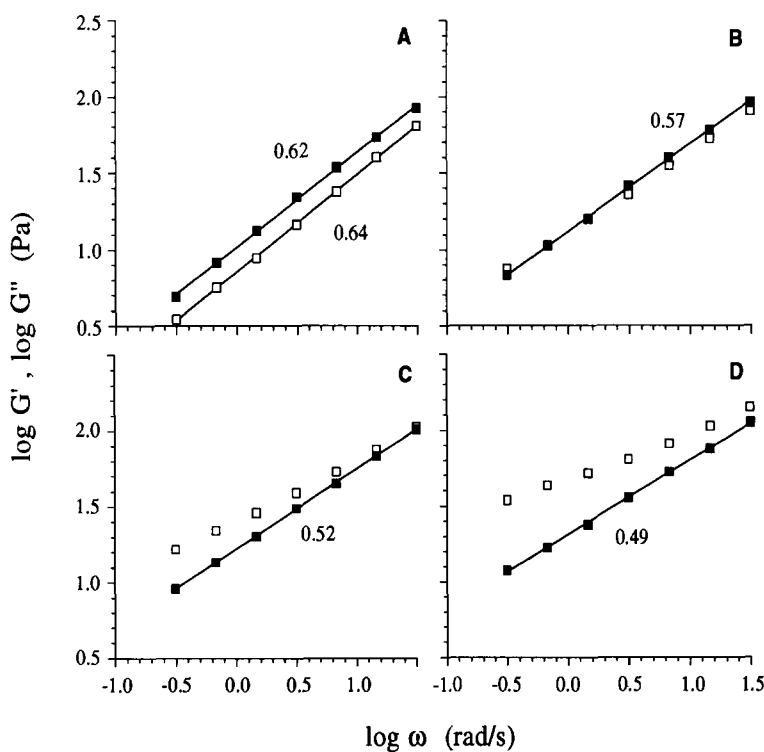

Fig. 3. Mechanical spectra ($\square$, G'; $\blacksquare$, G'') recorded at 20°C at several ageing times in the vicinity of the $G'-G''$ cross-over (1% (w/w) HMP, 60% (w/w) sucrose, pH 3): (A) 25 min; (B) 34 min; (C) 44 min; (D) 54 min. For this cure test, the cross-over of G' and G'' at 0·5 Hz occurred at about 39 min. The numeric values denote the slope of the straight lines.
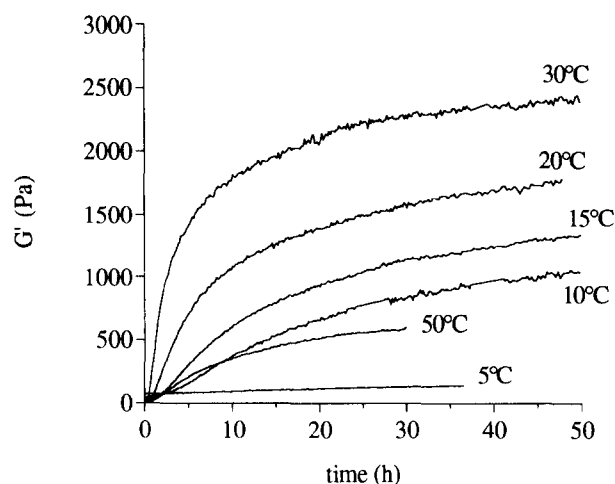
Fig. 4. Storage modulus (G') plotted against ageing time for 1% HMP sol/gel (pH 3·0, 60% (w/w) sucrose), measured at 0·5 Hz and 3% strain, at several ageing temperatures.

The dynamic shear moduli were very sensitive to the temperature. The particular behaviour at low temperatures should be noted. In the beginning of the cure experiment at 5°C, G' is higher than G''. Aggregation phenomena, possibly involving hydrogen bonding, must be responsible for the high values of G' in this initial phase of the gelation process. However, the ageing

process evolves slowly and monotonously. After a 48 h ageing period at 5°C, the gel modulus reached a lower value than at higher temperatures, and the difference between the dynamic moduli was smaller. This should be a direct consequence of the important role of hydrophobic interactions in stabilising the HMP network. This kind of interaction is weak at low temperatures, and therefore, at low ageing temperatures, weaker gels are obtained.

On the other hand, hydrophobic interactions become stronger at higher temperatures, increasing the connectivity of pectin chains into the network structure, resulting in the increase of the elastic modulus from 5 to 30°C. The gel becomes softer at higher temperatures because other interactions, like hydrogen bonds, are now weakened.

The viscoelastic behaviour near the gel point also changes as a function of temperature (Fig. 5). Mechanical spectra were recorded at different stages of the pectin network formation. Frequency sweeps performed in the vicinity of the gel point are shown in Figs 6–8.

At lower ageing temperatures, the HMP/sucrose system seems to be characterised by lower relaxation exponents at the sol/gel transition, around 0·4 to 0·55. The HMP/sucrose system when aged at 5°C is characterised by a slow evolution of the viscoelastic behaviour through the gel point, with a power law behaviour
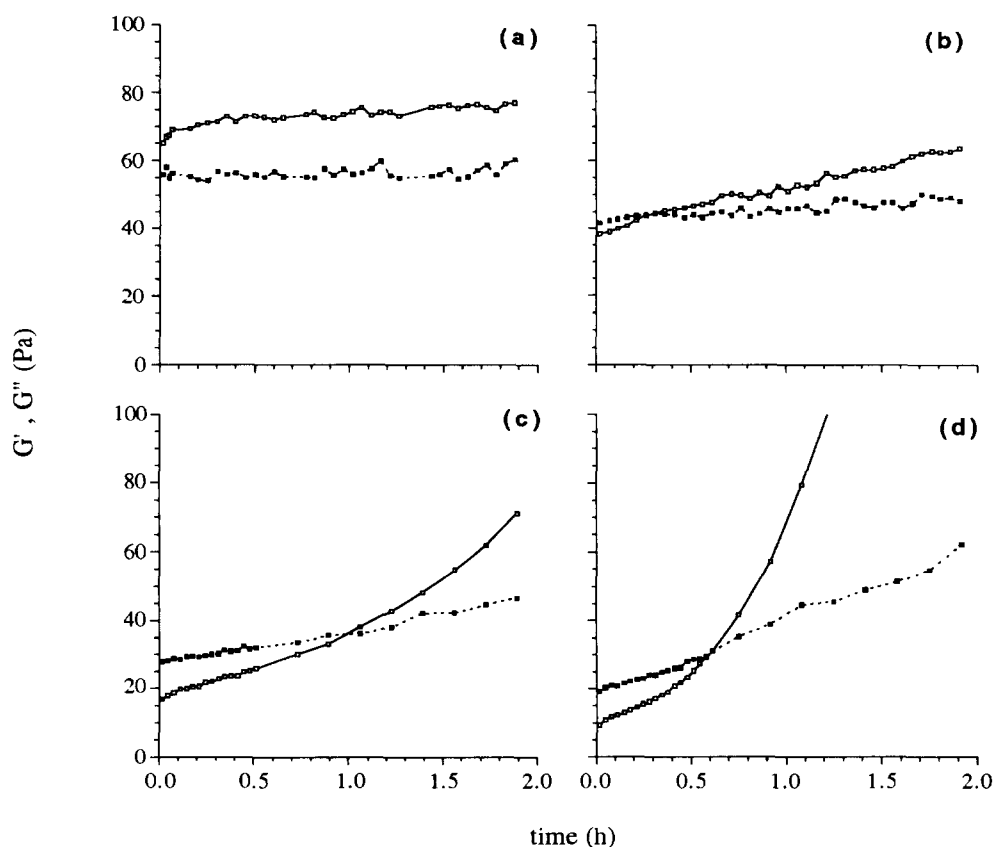

Fig. 5. Initial period of gelation showing the evolution of the dymamic moduli for 1% (w/w) HMP dispersions (60% (w/w) sucrose, pH 3·0), at different ageing temperatures: (a) 5°C; (b) 10°C; (c) 15°C; (d) 20°C. Open symbols denote G' and filled symbols G''.
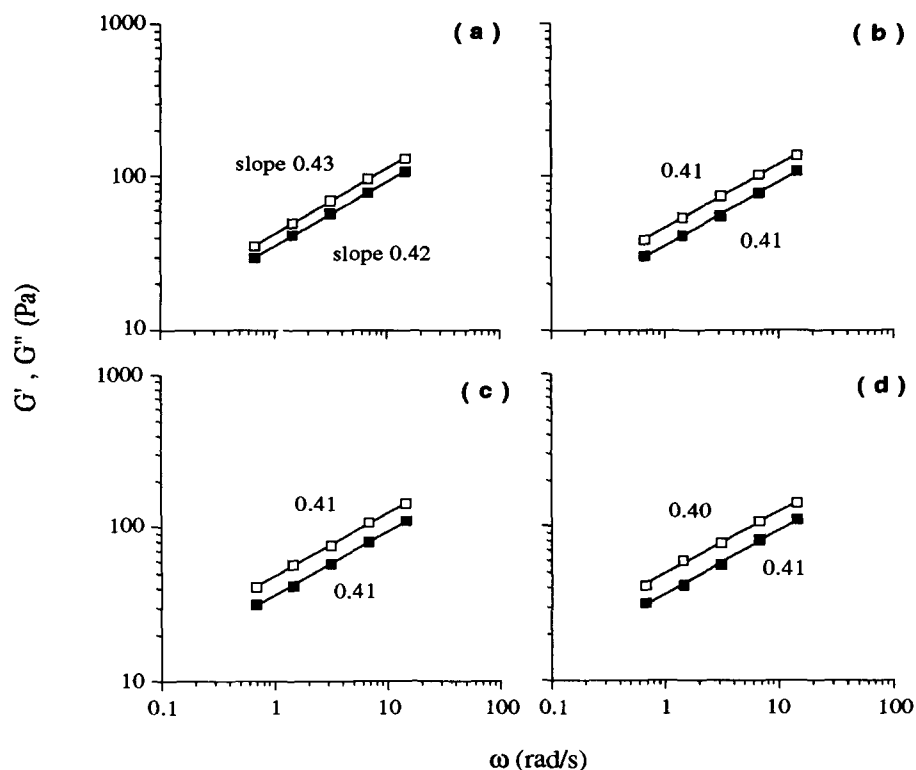
Fig. 6. Mechanical spectra recorded at different times in the initial period of gelation of a 1% (w/w) HMP dispersion (60% (w/w) sucrose, pH 3·0), at 5°C ageing temperature: (a) 8 min, (b) 45 min; (c) 118 min; (d) 189 min. Open symbols denote G' and filled symbols G''.
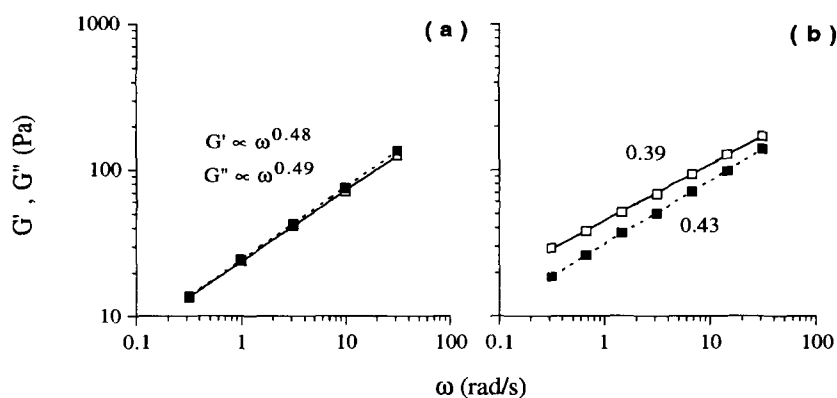

Fig. 7. Mechanical spectra recorded at different ageing times for a HMP/sucrose dispersion cured at 10°C; (a) 15 min; (b) 124 min. (Same legend as Fig. 6.)

of the dynamic moduli with a similar critical exponent over an extended period of time (Fig. 6).

In contrast, at higher ageing temperatures, the viscoelastic behaviour through the gel point is qualitatively and quantitatively different. For temperatures higher than 15°C, the evolution of the dynamic moduli is quicker, and occurs with a first tendency to an elastic plateau at low frequencies, with $G' > G''$ at low frequencies, and G' and G'' superimposed at higher frequencies. For ageing temperatures in the range 20–60°C, the viscoelastic behaviour near the gel point is qualitatively similar (see Fig. 3 for results at 20°C). The main differences are the $G'-G''$ cross-over time, which

decreases as the temperature increases, and the magnitudes of the dynamic moduli near this point, which decrease as the temperature increases. Power law dependence upon oscillatory frequency of both moduli, with the same relaxation exponent (n), was found to occur for values of n in the range 0·60–0·65.

Depending on temperature, the junction zones are stabilised by a different set of interactions. This affects the network structure and the viscoelastic behaviour at the gel point. Differences in the relaxation exponent due to network imperfections were found for chemical cross-linking gels with ratios of reactants lower than the stoichiometric ratio (Chambon & Winter, 1987; Muller et
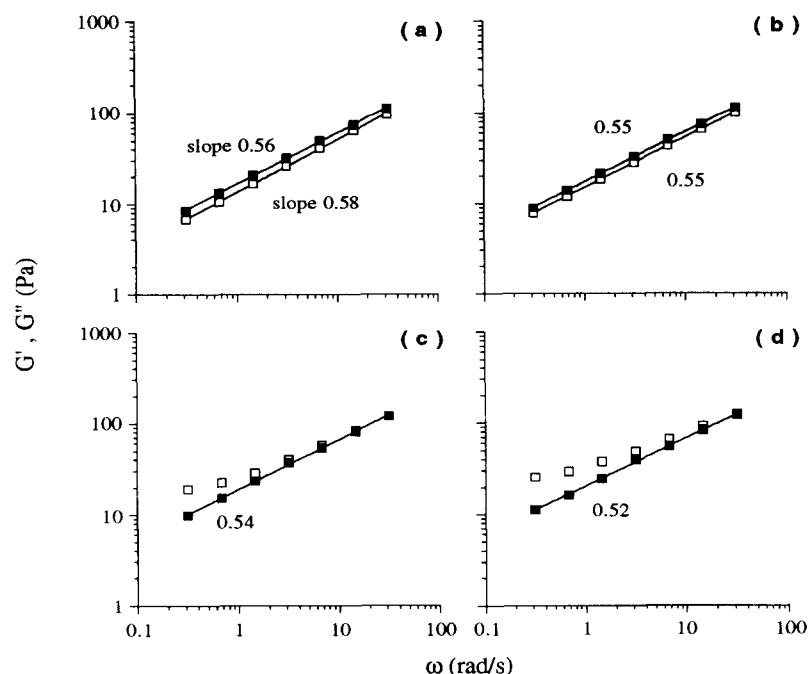
Fig. 8. Mechanical spectra recorded during ageing at 15°C: (a) 34 min; (b) 41 min; (c) 68 min; (d) 84 min. (Same legend as Fig. 6.)

al., 1991). Also, for the thermoreversible physical gel of gelatin, the relaxation exponent was found to be dependent on concentration and thermal history (Michon *et al.*, 1993). When the ageing temperature is lowered, the critical exponent seems to decrease, and the difference in the value predicted by the percolation theory (de Gennes, 1979), 0·72, increases. Under thermal conditions not favourable to the formation of additional hydrophobic interactions (lower temperatures), the formation of a weaker network is likely to occur, where the mobility of the pectin chains is increased and the lifetime of junction zones is decreased. Consequently, a higher number of pectin chains does not contribute effectively to the multiconnected network, introducing irregularities into its structure. This idealised network will have a different structure if compared with other physical gel systems undergoing sol/gel transition, for which the predictions of the scalar percolation theory have been experimentally confirmed (Tokita *et al.*, 1984; Axelos & Kolb, 1990).

The relatively low reproducibility of quantitative measurements of the gel time (repeated measurements of the time at which both dynamic exhibited power law with the same critical exponent, or at which $G' = G''$, gave errors between 5 and 10%) can be attributed to the complex composition of the systems and to the gel preparation process; the temperature history of the dispersions during the preparation and loading into the rheometer should be a critical parameter. However, it should be mentioned that the incertitude in the magnitude of the critical exponent n, measured at each ageing temperature, was much lower, in the range of 2–3%. To analyse the viscoelastic behaviour in the vicinity of the

gel point in order to find the moment of the power law relaxation behaviour, taking for example the moment when the loss angle (δ) is independent of frequency (Chambon & Winter, 1987; Winter, 1987), we should have enough, and accurate, dynamic rheological data before and after the gel point. This was not the case for all the ageing temperatures studied. This fact, associated with the slow evolution of the dynamic moduli near the gel point for temperatures below 20°C, makes very difficult the accurate determination of the gel point based on the moment for which the dynamic moduli exhibit a power law dependence upon oscillatory frequency, with the same relaxation exponent.

For practical reasons, an apparent gel time (GT_a) was defined as the time elapsed from the moment when the sample reached the study temperature until the crossover of the storage (G') and loss (G'') moduli, at a fixed frequency of 0·5 Hz. It was verified that this point was dependent on frequency and also, and perhaps more interesting, the dependence on frequency also changed with temperature. We should recall that this parameter is not an intrinsic property of the material, since this critical phenomenon cannot be dependent on the frequency of the dynamic experiment.

At 5°C, important macromolecular aggregation occurred in our system, and the apparent gel time could not be estimated because it was shorter than the time elapsed before the beginning of the cure experiments. The apparent gel time has a complex dependence on temperature (Fig. 9). If we assume that this time is directly related to a gelation rate ($1/GT_a$), following the criterion of Oakenfull and Scott (1986), the results obtained are not in total accordance with those
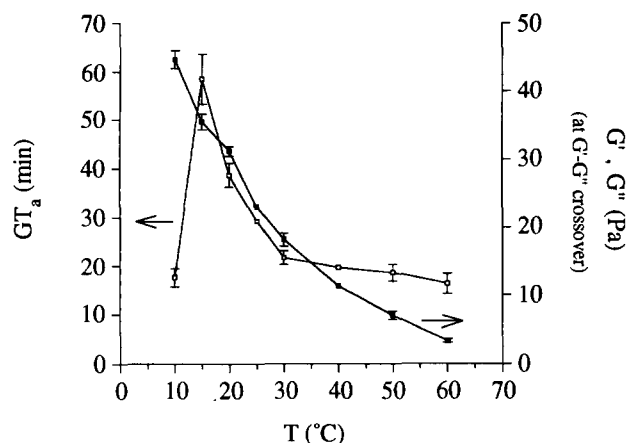
Fig. 9. Effect of the ageing temperature on the apparent gel time (GT_a) and on the dynamic moduli magnitudes at the interception point of G' and G'' for a 1% HMP/60% sucrose dispersion. Vertical bars represent standard deviation values obtained in triplicate measurements.

obtained by these authors for the gelation rate of similar systems. The differences we found, especially in the higher temperature range, can be explained in terms of the different method used by those authors to describe the gel point.

The 'final' viscoelastic behaviour of the HMP gels changes with the ageing temperature to which the system has been submitted. Some mechanical spectra recorded for 36 h aged gels are shown in Fig. 10. Qualitatively, between 15 and 50°C the behaviour is characteristic of a typical biopolymer gel: the molecular rearrangements are very reduced within the network with time scales in the range of 0·003–30 s, G' is higher than G'' throughout the frequency range and is almost independent of frequency (ω), and a power law dependence of the complex viscosity upon ω is observed. Especially for lower temperatures the behaviour changes to that of weak gels, with a higher dependence on frequency for the dynamic moduli. An increase of the loss modulus can be seen at higher frequencies, possibly related to the effect of dynamic entanglements (Clark & Ross-Murphy, 1987).

The elastic modulus of cured gels has also a complex dependence on ageing temperature (Fig. 11). Usually, for disordered biopolymers, the aggregation process leading to the building of the gelled network shows a different temperature dependence, with the elastic modulus and the rate of gelation decreasing when the temperature increases. Some examples are the studies on gelatin gelation of te Nijenhuis (1981), where the
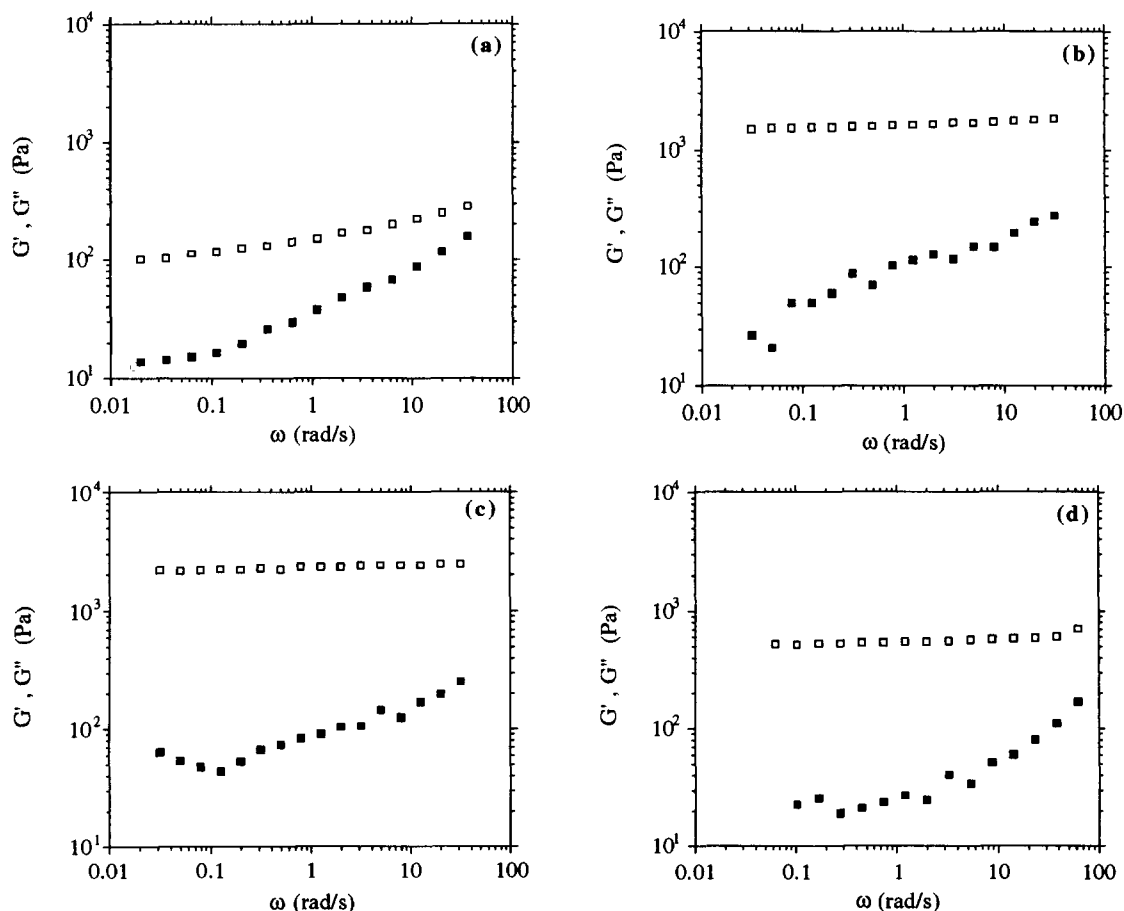

Fig. 10. Mechanical spectra for a 1% HMP gel (pH 3·0, 60% (w/w) sucrose) measured after 36 h of ageing at different temperatures: (a) 5°C; (b) 20°C; (c) 30°C; (d) 50°C. Open squares—storage modulus (G'); filled squares—loss modulus (G'').
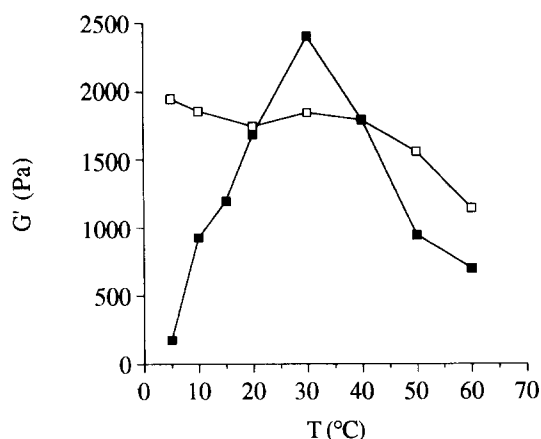
Fig. 11. Temperature effects on the modulus of a 1% HMP/ 60% sucrose (pH 3·0) gel: (■) apparent equilibrium storage modulus measured after 36 h of ageing at different temperatures, and (□) storage modulus measured on cured gels at 20 C, and equilibrated at the actual temperature of measurement. Measurements were performed at 0·5 Hz and 3% strain. Relative standard deviation values obtained from triplicate measurements did not exceed 6%.

mechanism is regulated by intermolecular triple helix formation, and the work of Durand *et al.* (1990) on low methoxyl pectin gelation mediated by ionic complexation with calcium cations.

The different behaviour of the HMP/sucrose systems could be explained by the opposing effects of temperature on both types of interaction that stabilise these kinds of gels. Hydrophobic interactions are strengthened when the temperature increases (Oakenfull & Fenwick, 1977), whereas hydrogen bonds and electrostatic interactions weaken with increasing temperature. The contribution from electrostatic interactions should be small, since the degree of ionisation of the carboxyl groups of the pectin molecule is low, due to the low pH value. Hydrogen bonding at low temperatures could be responsible for the important aggregation phenomena. With increasing temperature, the increase in entropy of the solvent reduces the hydration of the pectin chains, and hydrophobic interactions could provide the most important contribution to the macromolecular interaction. Each kind of intermolecular interaction alone is not strong enough to build up a stable HMP network. It is in an intermediate temperature range that both kinds of interaction can together contribute to form a network with the highest elasticity. The results obtained at 5 C, compared with the behaviour exhibited by the HMP/ sucrose system when the temperature is increased are clear evidence of the very important role of hydrophobic interactions in the network structure of HMP gels.

Quenching the gels at different temperatures after maturation

The influence of temperature on the storage modulus of 1% HMP gels matured at 20°C is also shown in Fig. 11. Above 20 C, the modulus shows a similar dependence

on temperature to that observed for the ageing process at different temperatures, with the same apparent maximum around 30°C and a qualitatively similar decline above 30°C, although it is much less sensitive to temperature. However, below 20°C, it is markedly reduced when gelation is carried out below this temperature, whereas after maturation at 20 C, a decrease in temperature leads to a slight increase in modulus.

Similar results to those obtained for the influence of temperature on the storage modulus of matured gels at 20°C have been obtained by Oakenfull and Scott (1984), for the effect of temperature on the rupture strength of HMP gels. Hydrophobic interactions that could develop during maturation of HMP/sucrose gels at 20°C, once they have been formed, appear to be unaffected by decreasing temperature, despite the fact that they could not develop at low temperatures. We can even observe a slight increase in the elastic modulus, likely due to enhanced hydrogen bonding and decrease in the molecular motion. The additional interactions that could be developed at 5 C seem to be perfectly reversible, since when the temperature is again increased to 20 C, the dynamic moduli decreased to values similar to those they had before.

Above 50 C, temperature has a clear effect on the viscoelastic behaviour of a HMP gel matured at 20 C. Increasing the temperature to 60°C decreases the storage modulus to about 65% of its value at 20 C. After ageing at 60 C, and when the temperature is decreased again to 20 C, the gel is not able to recover all of its initial viscoelastic properties, attaining only about 80% of the G' value. This indicates that some of the interactions that stabilise a HMP gel, when aged at 20°C, are irreversibly disrupted by increasing the temperature. As can be seen in Fig. 12, the general viscoelastic behaviour has also changed. When the
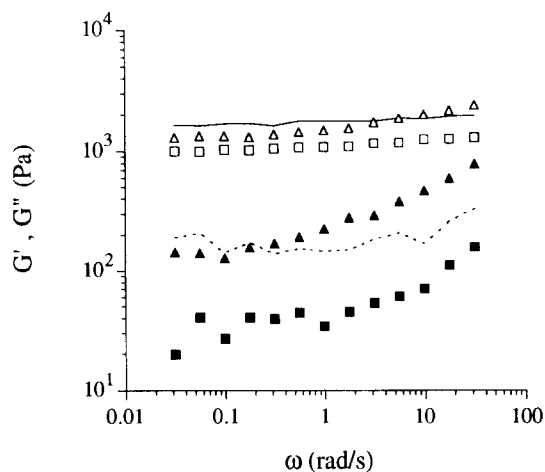

Fig. 12. Mechanical spectra recorded for a 1% HMP gel after ageing at 20°C during 60 h (——, G'; ·······, G''), after an additional ageing at 60°C during 13 h (□, G'; ■, G''), and after 24 h again at 20°C (△, G'; ▲, G'').

pectin gel was submitted to ageing at 60°C, followed by a second period of ageing at 20°C, not only did the G' not attain the previous value, but also showed a higher dependence upon oscillatory frequency, and a lower difference between the storage and the loss modulus, especially at high frequencies. This indicates that the network structure has changed, and that the molecular rearrangements are now easier.

Most biopolymer gels do not follow the thermal behaviour described by the theory of rubber elasticity, due to the structural organisation of the junction zones and to the appreciable degree of order generally found in the polymer chains between junction zones. The typical behaviour shown by the polysaccharide gels where hydrogen bonding or electrostatic interactions are the only significant interactions that stabilise the polymer network, e.g. carrageenan gels (Watase & Nishinari, 1987) and alginates (Andresen & Smidsrød, 1977), is the monotonous decrease of the modulus with increasing temperature. This behaviour has been interpreted as enthalpy driven elasticity, rather than an entropic nature of the chains elasticity. The HMP gels have a different behaviour. A different temperature dependence of the gel modulus was found in different temperature ranges. Even in the intermediate temperature range where the modulus slightly increases with increasing temperature, this behaviour should not be attributed to a rubber-like behaviour, in view of the structural organisation of the HMP network, but rather to the behaviour of the nonpermanent cross links of the ·gel and to the opposing effects of increasing temperature on hydrophobic interactions and hydrogen bonding that stabilise these cross links.

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