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Viscoelastic properties of ι-carrageenan/gelatin mixtures

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The storage (G') and loss (G'') moduli of transparent mixtures of ι-carrageenan and gelatin have been measured during gelation and melting and compared with those of gelatin and ι-carrageenan systems alone. The moduli of the mixtures were always higher than the sum of those of their components alone. Gelatin and ι-carrageenan seem to reinforce each other. Three specific temperature domains can be distinguished, delimited by the melting and helix-coil transition temperatures of gelatin and ι-carrageenan. An interpretation based on conformational changes and an attractive electrostatic interaction between the two biopolymers is suggested. The temperature dependence of G' and G'' for mixtures has been studied as a function of thermal history (time and temperature of gel ageing), sodium chloride concentration and molecular weight of the ι-carrageenan. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Food are usually complex mixtures of many components, including biopolymeric thickeners and gelling agents. Interactions between these biopolymers are important for many applications. Ingredient producers and food manufacturers wish to better understand the behaviour of biopolymer mixtures in order to optimise their use and to find new textures or new applications.

Gelatin, an animal protein produced from collagen, and ι-carrageenan, a polysaccharide extracted from red seaweed, are hydrocolloids with a long history of use as gelling agents. Their ability to form thermoreversible gels is of great importance in industrial applications (Poppe, 1992; Thomas, 1992). The sol–gel transitions of both ι-carrageenan (Rochas, 1987; Picullel *et al.*, 1992; Parker *et al.*, 1993) and gelatin (Djabourov, 1987; Djabourov *et al.*, 1988; Te Nijenhuis, 1981a, b) have been extensively studied. It is generally accepted that helix formation of ι-carrageenan chains leads to the formation of double helices. However, the nature and topology of the junction zones forming the gel are not yet understood. Several mechanisms have been suggested (Rees *et al.*, 1969; Morris *et al.*, 1980; Smidsrød, 1980). Helix formation in gelatin leads to the formation of left-handed helices which are able to self-associate, probably to form right-handed triple helices stabilised by hydrogen bonds with a structure similar to that of native collagen (Eagland *et al.*, 1974; Eldridge & Ferry, 1954). Since the coil-helix transition temperature of gelatin is usually lower than that of ι-carrageenan, so is its sol–gel transition temperature. From a fundamental point of view, it is interesting to study the effect of the state of gelatin (coil or helix, sol or gel) on the behaviour of ι-carrageenan in mixed systems.

In general, mixtures of two uncharged polymers in solution are thermodynamically incompatible (Flory, 1953), so when the polymer concentrations are high enough, phase separation will occur with each phase enriched in one of the components. Piculell and Lindman (1992) call this type of phase separation 'segregative'. The literature suggests that it can occur for neutral polysaccharide/gelatin mixtures at any pH and for anionic polysaccharide/gelatin mixtures at pHs above the pI of the gelatin (Tolstoguzov, 1986, 1990). For example, Kasapis *et al.* (1993a) observed phase diagrams typical of segregative phase separation for mixtures of maltodextrin and a limed ossein gelatin.

The viscoelastic behaviour of their maltodextrin/gelatin mixtures during melting depended on the polymer ratio. With 20 g/l of gelatin and 100 g/l of maltodextrin, the mixture behaviour was similar to that of gelatin alone, whereas with 200 g/l of maltodextrin, the mixture behaved like maltodextrin alone (Kasapis *et al.*, 1993b). The authors (Kasapis *et al.*, 1993b) propose an interpretation based on excluded volume effects. Similar

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behaviour has also been observed for a gellan/gelatin mixture at pHs below the gelatin pI (Papageorgiou *et al.*, 1994). However, the electrolyte concentration was high and under these conditions, even oppositely charged polymers can undergo segregative phase separation (Piculell & Lindman, 1992).

When the polymers are of opposite charges, e.g. an anionic polysaccharide and a protein at a pH below its pI, there is electrostatic attraction between them. This phenomenon can lead to the formation of complex. In this case the interaction is called 'associative' (traditionally called 'complex coacervation' in the gelatin literature), and when a macroscopic phase separation appears, one phase is rich in both polymers and the other is almost pure solvent (Dickinson, 1987; Piculell & Lindman, 1992). We have shown that it is the case for gelatin/ι-carrageenan mixtures (Michon *et al.*, 1996). As we showed in a previous paper, the interactions between those two species depend greatly on the pH (relative to the pI of the gelatin), the ionic strength, the polymer concentration and the polymer ratio (Michon *et al.*, 1995b).

The aim of the present work was to study the influence of thermal history, electrolyte concentration and molecular weight of the ι-carrageenan on the viscoelastic properties of gelatin/ι-carrageenan mixtures under associative conditions (pH below the gelatin pI, 0.2M NACl) in order to understand how they behave and interact in such mixtures.

EXPERIMENTAL

The gelatin sample was a first extract acid-process sample produced from pig skin by S.B.I. (isoelectric point 8.8). The sample was thoroughly ion-exchanged during manufacture. The ion content is negligible. The manufacturer's specifications were: Bloom 301 (gel strength at a concentration of 6.67% after 16 h at 10°C) and viscosity 5.4 mPa/s (6.67% concentration at 60°C in deionised water). Two ι-carrageenan samples were used, both were produced from cultivated *Eucheama denticulatum.* One from seaweed grown in Madagascar (i1) and the other (i2) from the Philippines. ^{13}C NMR, carried out as described previously (Parker *et al.*, 1993) showed that i2 contained 7±1 mol% of the kappa form. Contamination of i1 by the kappa form was estimated to be of the same order, using the elasticity/temperature method described by Parker *et al.* (1993). The cation contents of the two samples were similar: $Na^+ \approx$ 40 mol%/$K^+ \approx$ 60 mol%, Ca^{2+} and Mg^{2+} <0.3 mol%. The only free anions detected were chloride, which represented <2 mol% of the total anions, the rest being carrageenan sulphate groups. Gel permeation chromatography analysis with PEO calibration gave the following weight-average molecular weights in daltons: gelatin, 180 000; i1, 1 000 000; i2, 700 000.

A 4 g/l solution of sample i1 was depolymerised progressively using ultrasound. Three solutions were obtained. Their degree of polymerisation was estimated by measuring their Newtonian viscosities at 20°C using a Contraves LS30 viscometer. The Newtonian viscosity of the initial solution was 46 mPa/s and those of the degraded samples were 26, 10 and 6 mPa/s, after 2, 10 and 30 min of ultrasonic degradation, respectively.

Master solutions of gelatin and ι-carrageenan (160 and 16 g/l, respectively) were prepared separately and mixed with distilled water in various proportions in order to obtain a series of mixtures with a final concentration of 80 g/l of gelatin and various ι-carrageenan concentrations. 500 ppm NaN_3 was added to prevent microbial degradation. The hot mixtures were stirred at 60–70°C for about 10 min, then the pH was adjusted to 7.0 and the sodium chloride concentration to 0.2M. The gelatin concentration, pH value and sodium chloride concentration were chosen from those studied previously (Michon *et al.*, 1995b) in order to obtain gels which were transparent, and apparently compatible, over the whole temperature range studied.

Dynamic viscoelastic measurements were performed using a Rheometrics Fluids Rheometer (RFR-7800) or a Rheometrics Fluids Spectrometer (RFS II) both fitted with coaxial cylinders. Solutions were placed in the rheometer at 67°C. A thin layer of paraffin oil was added to prevent sample dehydration. All measurements were made in the linear viscoelastic domain, whether the sample was in the sol or gel state.

Melting temperatures (called T_{mg} for gelatin, T_{mi} for ι-carrageenan and T_{mm} for their mixtures) were determined by the critical point method described previously (Michon *et al.*, 1993, 1995a). At the critical point of gel–sol (or sol–gel) transition, the storage modulus G' and the loss modulus G'' follow a power-law with the same exponent Δ, as a function of the oscillation frequency ω:

$$G'(\omega) \propto G''(\omega) \propto \omega^{\Delta}$$

Thus, the following relation holds for all ω:

$$\tan\delta = \frac{G''}{G'} = \text{constant}$$

The critical melting temperature is that at which plots of $\tan\delta$ vs temperature for different frequencies cross each other (see, for example, Fig. 2 in Michon *et al.*, 1995a). Frequency sweeps are performed from 0.01 to 25 rad/s. The melting temperature was measured to a precision of better than 0.5°C as the present systems gave sufficently precise data in the sol state. The advantage of this method is that the melting temperature is rigorously defined and frequency independent. However, the measurement time is long, as a frequency sweep must be carried out at each temperature.

The sol–gel transitions were mostly studied during melting (from gel to sol) and once during gelation (from sol to gel). To study gel melting, the system was first cooled from 67°C to the ageing temperature (T_a), usually 28°C. As the viscoelastic properties of gelatin gels are strongly time- and thermal history dependent, all systems containing gelatin were held for 15 min at 40°C, to allow thermal equilibrium to be attained, before cooling below the helix-coil transition temperature ($T_{h\text{-}cg} \sim 42°C$) determined by optical measurements. This step was omitted when ι-carrageenan was studied alone. The gel ageing time (t_a) was arbitrarily taken to start when the temperature fell below 40°C, it was usually 90 min. At the end of the gel ageing time, the gel was melted by increasing the temperature in steps of 1°C every 30 min. To study gel formation, G' and G'' were measured whilst cooling from 60°C to 40°C in 1°C steps every 15 min, followed by a temperature ramp of 0.6°C/min from 40 to 28°C.

SOL–GEL TRANSITION TEMPERATURES OF SINGLE COMPONENTS AND MIXTURES

Viscoelastic properties during melting

The evolution of G' and G'' during melting was studied for three systems: 80 g/l gelatin alone, 2 g/l ι-carrageenan (i2) alone and a mixture containing 80 g/l gelatin and 2 g/l ι-carrageenan. The thermal history was identical for systems containing gelatin. We checked that the rheological properties of systems containing ι-carrageenan alone were at equilibrium at the end of each step of temperature. The ageing temperature was 28°C and the ageing time was 90 min. Figure 1 shows the storage and loss moduli as a function of temperature for the three systems.

The *gelatin system* melted close to 33°C. G' fell from 50 to 0.02 Pa over a range of 6°C, G'' fell from 4 to 0.2 Pa over the same temperature range. At temperatures above 35°C, G' and G'' were too low to be measured. This phenomenon corresponds to the disappearance of the gelatin network.

The *ι-carrageenan system* melted close to 50°C. Between 28 and 45°C, G' decreased slowly and regularly, falling by less than an order of magnitude. From 45 to 55°C the decrease was more pronounced. G'' increased slightly between 28 and 47°C, then fell rapidly during the melting process.

The melting of the mixed gel was complex and seemed to be governed by several phenomena. As the temperature increased, the system weakened regularly. Three distinct temperature domains could be distinguished. These domains are marked a, b and c on Fig. 1. Initially, from 28 to 29°C, G' for the mixture was equal to that of the gelatin alone. However, at all higher temperatures, both G' and G'' for the mixture were higher than for either of the biopolymers alone. Therefore, it seems that the presence of gelatin reinforces ι-carrageenan gels and vice versa.

Domain (a) is similar to gelatin alone

Initially, there is a slight shoulder in both G' and G'', which then decrease rapidly between 29 and 33°C. Nevertheless, this decrease is more gradual than for gelatin alone.

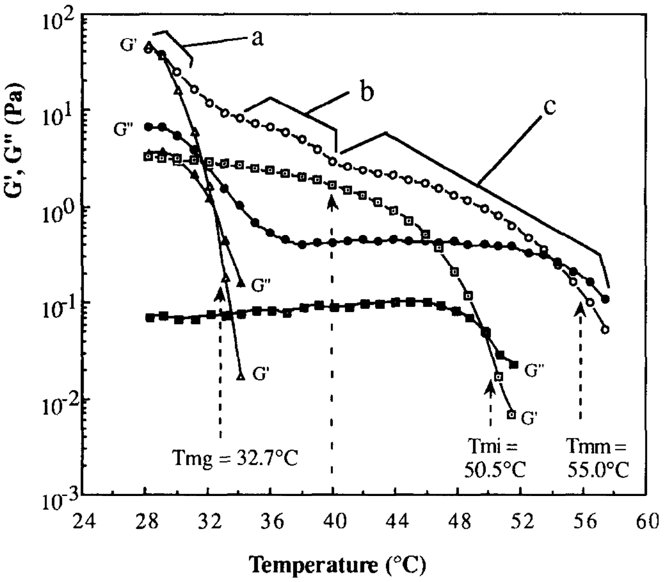

Fig. 1. Comparison of G' and G'' during melting of three systems: gelatin 80 g/l (△, ▲), ι-carrageenan i2 2 g/l (□, ■) and the mixture gelatin 80 g/l + ι-carrageenan i2 2 g/l (○, ●). Pulsation: 1 rad/s, strain amplitude: 1–20%, 0.2M NaCl, $T_a = 28°C$, $t_a = 1$ h 30. (a), (b), (c): see text. T_{mg}, T_{mi} and T_{mm} are the melting temperatures of gelatin alone, ι-carrageenan alone and gelatin / ι-carrageenan mixtures, respectively.

Domain (b) between 33 and 40°C

There is a second shoulder in G' up to 40°C, where G' decreases more abruptly once again to reach a third shoulder.

Domain (c) is similar to ι-carrageenan alone

There is a gradual decrease in G' and little change in G'' between 40 and 50°C, then both moduli decrease rapidly between 50 and 60°C. The latter phenomenon corresponds to the melting of the ι-carrageenan gel. The temperatures over which both the gradual decrease and the sharp decrease occur are about 6°C higher for the mixture than for the ι-carrageenan alone.

Influence of thermal history on the viscoelastic properties of the mixture (Figs 2 and 3)

Whilst ι-carrageenan systems evolve rapidly at a given temperature, this is not the case for gelatin at temperatures below T_{mg} (about 33°C). Therefore, the influence of the gel ageing temperature (T_a) and time (t_a) on the viscoelastic behaviour during melting was studied.

Influence of t_a (Fig. 2)

The mixture whose behaviour was discussed in the previous section was cooled to 28°C, and then heated in the same way as previously, but the ageing time was varied: 1 h 00, 1 h 30, 4 h 00 and 16 h 30. Figure 2 shows the storage modulus measured whilst heating. Between 40 and 58°C, G' was independent of the ageing time, and the behaviour of the mixture was characteristic of ι-carrageenan. However, differences occurred at lower temperatures, undoubtedly due to changes in the gelatin network, whose evolution is known to be slow and continuous (Te Nijenhuis, 1981a, b). Note that the longer t_a:

(i) the smaller was the inflexion of the curve, close to T_{mg}, which defines the end of domain *a* in Fig. 1, in fact this domain did not exist after the longest ageing time

(ii) the larger the stabilisation by ι-carrageenan below 40°C (domains a and b). So the reinforcement of the gelatin network proceeds slowly.

Influence of T_a (Fig. 3)

The thermal history was as described above, with $t_a = 4$h and various values of T_a: 28, 30, 32, 35, 37, 40 and 44°C. Above 40°C, G' curves superimposed well, so the viscoelastic properties were not affected by the thermal history at lower temperatures. However, differences occurred below 40°C.

When T_a was lower than T_{mg}, the curves had an inflexion point at temperatures around T_{mg}, corresponding to a partial disappearance of the gelatin network.

The higher the gel ageing temperature, the weaker the gel below 40°C. The moduli below 40°C for the two highest ageing temperatures exactly parallel the behaviour of ι-carrageenan alone, displaced by 6°C.

Comparison of G' and G'' during gelation and melting (Fig. 4)

Figure 4 shows that during gelation G' increased regularly with decreasing temperature. There was no second shoulder, between 34°C and 40°C. Thus, it appears that being below the temperature of coil-helix transition, $T_{c\text{-}hg}$, is a necessary, but not a sufficient, condition for reinforcement of the ι-carrageenan

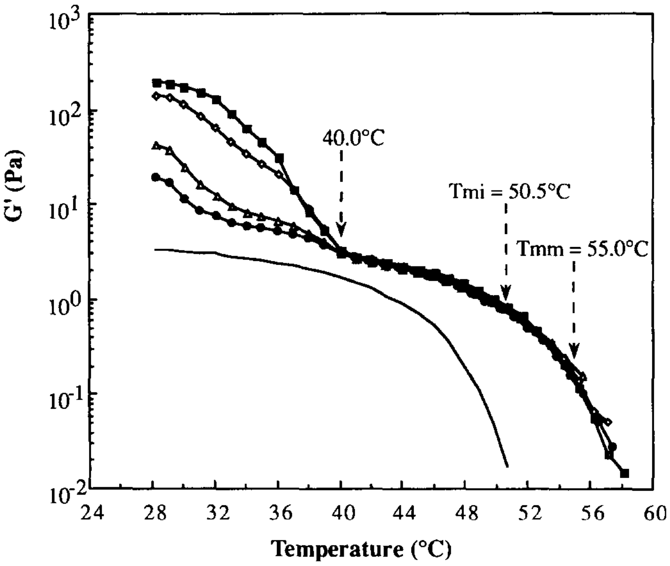

Fig. 2. Effect of the ageing time (t_a) on G' during melting. ι-carrageenan i2 (2 g/l) / gelatin (80 g/l). t_a: 1 h 00 (●), 1 h 30 (△), 4 h (◇) and 16 h 30 (■). G' of ι-carrageenan i2 (2 g/l) (—) is also shown for comparison. Pulsation: 1 rad/s, strain amplitude 1–20%, 0.2M NaCl, $T_a = 28$°C.

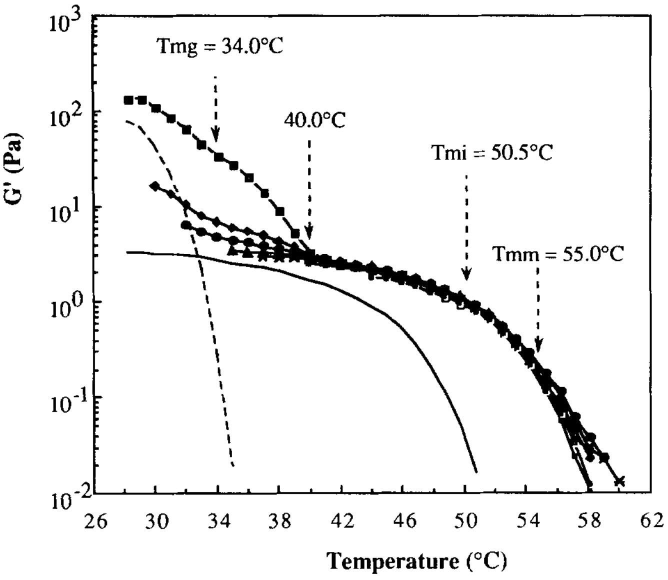

Fig. 3. Effect of the ageing temperature (T_a) on G' during melting. ι-carrageenan i2 (2 g/l)/gelatin (80 g/l). T_a: 28°C (■), 30°C (◆), 32°C (●), 35°C (▲), 37°C (✖), 40°C (■) and 44°C (■). G' of ι-carrageenan i2 (2 g/l) (—) and gelatin (80 g/l) (— —) are also shown for comparison (T_a = 28°C). Pulsation: 1 rad/s, strain amplitude 1–20%, 0.2M NaCl, t_a = 4 h.

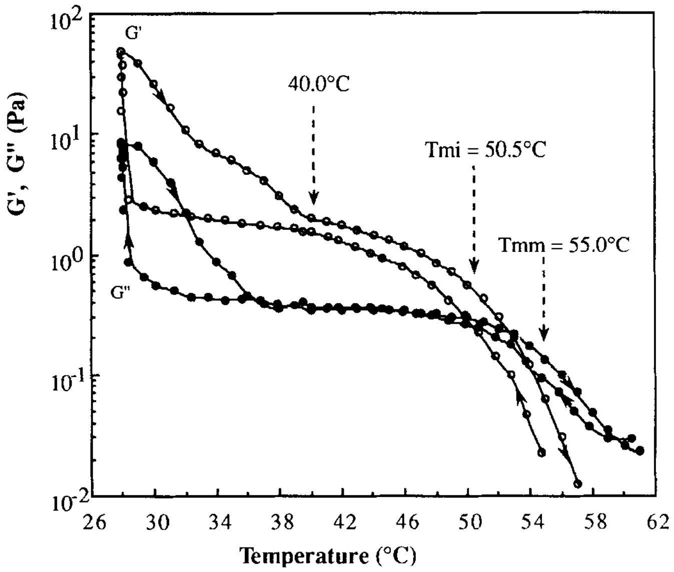

Fig. 4. Variation of G' (○) and G'' (●) during gelation and melting for a ι-carrageenan i2 (2 g/l) / gelatin (80 g/l) mixture. Pulsation: 1 rad/s, strain amplitude 1–20%, 0.2M NaCl, T_a = 28°C and t_a = 1 h 30.

network by gelatin over this temperature range: previous organisation of the gelatin at lower temperatures is also required.

The storage modulus during gelation was always lower than that during melting. The difference between the two depended on the temperature. The largest difference occurred at temperatures below $T_{c\text{-hg}}$ and was probably due to the organisation of gelatin chains. However, there were also differences in the temperature range from 40 to 60°C. We have checked that they were not solely due to kinetic effects caused by the different lengths of time step during heating and cooling (30 min/°C and 15 min/°C, respectively). An alternative explanation is that the difference was due to the increased structuring once the system had been at temperature below $T_{c\text{-hg}}$. Note that the curve for a mixture aged above $T_{c\text{-hg}}$ (T_a = 44°C) in Fig. 3 is slightly below the others.

Effect of concentration on the gel melting temperature (Fig. 5)

Melting temperatures were determined as explained above (T_a = 28°C, t_a = 1 h 30) for systems with a range of concentrations of ι-carrageenan (i2), both with and without 80 g/l gelatin. The results are shown in Fig. 5. For each ι-carrageenan concentration, T_{mm} is higher

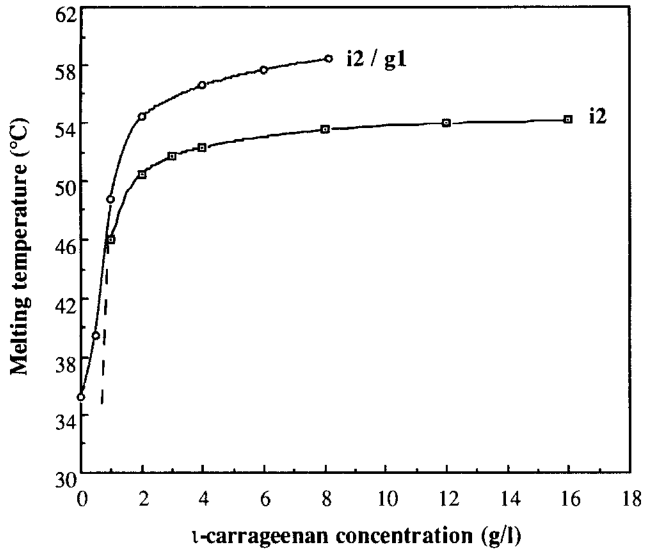

Fig. 5. Effect of concentration on the melting temperatures of ι-carrageenan alone (□) and of mixtures containing gelatin (80 g/l) (○). 0.2M NaCl.

than T_{mi}. Thus, in presence of gelatin, the ι-carrageenan network is more stable than the ι-carrageenan alone network. At the highest ι-carrageenan concentrations, T_{mi} seems to reach a maximum, which is lower than most of the T_{mm} values of the mixtures. This phenomenon is another proof that segregative interactions are not involved in gelatin/ι-carrageenan mixtures in our experimental conditions.

Effect of electrolyte concentration (Fig. 6)

As electrostatic attraction between the two biopolymers is a possible explanation for the evolution of G' and G'' during melting, the effect of electrolyte concentration has been studied, since it would be expected to have a large effect on such an interaction. In addition, we know that T_{mi} rises with increasing ion concentration. The analysis of the phase composition of very dilute mixtures showed that in both distilled water and 0.2M NaCl mixtures separated into two phases, one containing most of the biopolymers, and the other almost pure solvent (Michon *et al.*, 1996). So the phase separation, at least in 0.1 and 0.2M NaCl, was associative.

Three mixtures (gelatin 80 g/l / ι-carrageenan 2 g/l) were prepared containing 0.1M, 0.2M and 0.3M NaCl. The thermal history described above was used with T_a = 28°C and t_a = 1 h. Figure 6 shows the evolution of their storage moduli during melting. As the NaCl concentration increases, the curves are shifted to higher temperatures. This corresponds to the effect of counter-ions concentration on the viscoelastic properties of ι-carrageenan (Parker *et al.*, 1993). The same dependence is observed for its optical activity: the coil-helix transition temperature, determined from this technique, increases with increasing sodium concentration (Nilsson & Piculell, 1989). The melting temperature (T_{mm}) increases in the same way. On the other hand, at temperatures lower than about 36°C, the G' level after 1 h at 28°C decreases with increasing sodium concentration, as if the gelatin network had more difficulty in organising itself when that of ι-carrageenan was stronger. We checked that the NaCl concentrations had no effect on the viscoelastic properties of the gelatin alone. Finally, the sudden change in G' level at 40°C is less abrupt when the sodium concentration increases and at 0.3M NaCl it has almost disappeared, as if the interactions between ι-carrageenan and gelatin were screened by an electrolyte. The melting curve at this electrolyte concentration is simpler (only two shoulders, no domain (b)) and

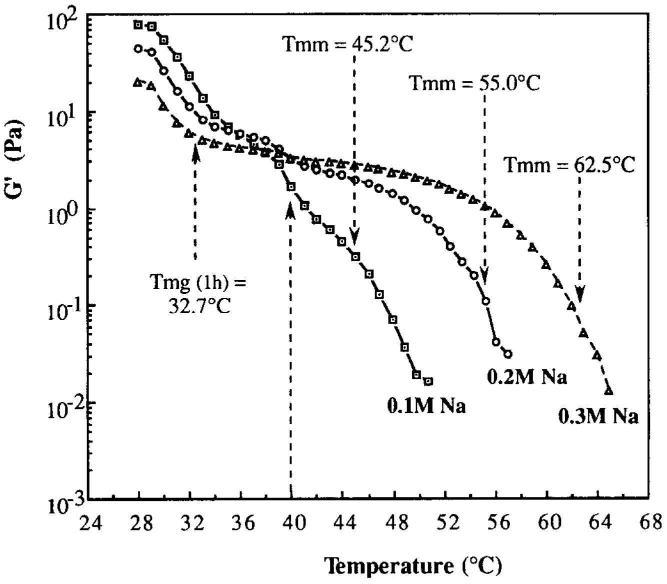

Fig. 6. Effect of the sodium chloride concentration on G' during melting. ι-carrageenan i2 (2 g/l) / gelatin (80 g/l). Pulsation: 1 rad/s, strain amplitude 1–20%, T_a = 28°C, t_a = 1 h 30.

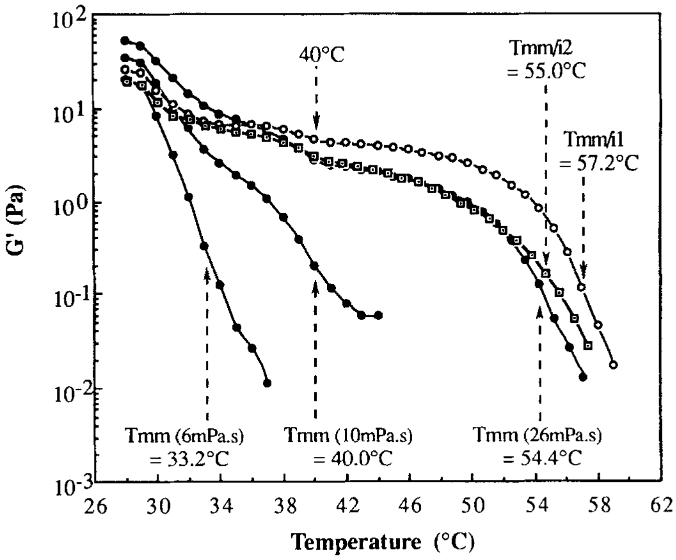

Fig. 7. Effect of the molecular weight of the ι-carrageenan on G' during melting. ι-carrageenan (2 g/l)/gelatin (80 g/l). (○) mixture containing undepolymerised i1, $\eta = 46$ mPa/s, (●) mixtures containing depolymerised i1, $\eta = 26$ mPa/s, $\eta = 10$ mPa/s and $\eta = 6$ mPa/s; (▫) mixture containing i2. Pulsation: 1 rad/s, strain amplitude 1–20%, 0.2M NaCl, $T_a = 28$°C, $t_a = 1$ h.

similar to those observed in segregating mixtures by Papageorgiou *et al.* (1994).

Effect of the molecular weight of ι-carrageenan (Fig. 7)

Figure 7 shows the variation of G' during melting of mixtures containing undepolymerised i1 and i2, and i1 depolymerised to various extents ($T_a = 28$°C, $t_a = 1$ h). The higher the molecular weight of the ι-carrageenan, the higher the melting temperature of the mixture and the more noticeable the third shoulder in G'. The curve for the 6 mPa/s sample shows that when the molecular weight was too low for gel formation at temperatures above T_{mg}, the behaviour of the mixture was similar to that of gelatin alone. Note that the curve for the 26 mPa/s sample of i1 and that for i2 are very similar. So, the differences observed between mixtures containing ι-carrageenans i1 and i2 can probably be explained by their differing molecular weights.

DISCUSSION

Gelatin and ι-carrageenan interact under our experimental conditions (Michon *et al.*, 1995b, 1996). An unusual evolution of G' during melting has been observed and interpreted in terms of associative electrostatic interactions which have been confirmed by an analysis of the phase composition in very dilute, macroscopically phase-separated systems. From the observations on one-phase, transparent systems described above, a few hypotheses based on the same mechanism of associative interactions can be made.

Between the gelatin coil-helix transition temperature and the mixture melting temperature (domain (c) in Fig. 1): in the absence of macroscopic phase separation, it is difficult to distinguish between associative and segregative incompatibility. The excluded volume effects inducing segregative phase separation is sometimes used to explain synergistic rheological effects. In that case, each component is at a higher concentration in its own phase than its overall concentration would suggest, and thus forms stronger, higher melting gels. However, such an effect cannot explain the increase in the melting temperature (T_{mm}) and in the storage modulus caused by the addition of gelatin. Even for very high concentrations of ι-carrageenan, T_{mi} is still below T_{mm} (see Fig. 4). On the other hand, we note that the mixture's G' curve (domain c) is equivalent to that of the ι-carrageenan alone shifted by +6°C, a phenomenon which is also observed when NaCl is added. So, the increase in T_{mm} could be simply due to the increase in ionic strength due to the addition of gelatin to a ι-carrageenan/water system which leads to a stabilisation and then to an increase in the melting point of the ι-carrageenan network. However, the addition of 8% gelatin to a ι-carrageenan solution leads to an increase of the ionic strength of about 0.01M which should induce an increase of the melting temperature of < 1°C. Therefore, an attractive electrostatic interaction is a more plausible cause of this phenomenon: gelatin chains in coil form could connect the double helices of ι-carrageenan and stabilise the ι-carrageenan network. Thus, the polycation effect is much more important in the stabilising phenomenon than the sole ion effect. At 50°C, the mixture is still gelled, whereas the ι-carrageenan alone has melted. Thus, the gelatin/ι-carrageenan interactions lead to a stabilisation of the ι-carrageenan network.

Between the gelatin melting temperature (T_{mg}) and the gelatin coil-helix transition temperature (about 40°C) (domain b in Fig. 1): gelatin chains are in helical form and can associate to form triple helices. However, over this temperature range, only the longest triple helices are stable. For each junction the major part of the three gelatin chains concerned is used, so the loose ends are not long enough to participate in another junction, making network formation impossible (Te Nijenhuis, 1981b). This explains the lack of measurable G' above 34°C for the gelatin alone. How can we explain the slight increase in G' in presence of ι-carrageenan? Here again electrostatic interactions could play a role in the structure of the system: ι-carrageenan chains could connect gelatin triple helices and form a mixed ι-carrageenan/gelatin network, which reinforces that of ι-carrageenan. They could also protect gelatin junction zones when the temperature increases. Actually, if T_a is chosen in the temperature domain below 40°C, but above the melting temperature of gelatin alone, no G' second level is observed below 40°C (Fig. 3). So, between 33°C and 40°C, a mixed gel is formed and could be qualified as a 'partially coupled gel'. It would consist of:

ι-carrageenan/ι-carrageenan interactions stabilised by hydrogen bonds which lead to the formation of a continuous network,

gelatin/gelatin interactions stabilised by hydrogen bonds, but insufficient to form a continuous network alone,

ι-carrageenan/gelatin electrostatic interactions which lead to a reinforcement of the ι-carrageenan network. The viscoelastic properties are similar to those of a pure ι-carrageenan system, but the moduli are much higher.

Below the melting temperature of gelatin (domain a in Fig. 1), the rapid decrease in the moduli would be due to the disappearance of most of the triple helices of gelatin, which are no longer stable at temperatures above 28°C. A totally coupled mixed gel consisting of ι-carrageenan/ι-carrageenan and gelatin/gelatin junctions, both able to form gels, connected by gelatin/ι-carrageenan electrostatic interactions would be formed. In this temperature domain the gelatin network prevails and imposes its viscoelastic behaviour.

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