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Carbohydrate Polymers 49 (2002) 177–183

Carbohydrate
Polymers

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Rheological investigation of the interaction between amylose and κ-carrageenan

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Received 2 April 2001; revised 27 July 2001; accepted 1 August 2001

Abstract

By combining rheological and turbidity measurements, the interaction and viscoelastic properties of amylose–κ-carrageenan mixtures were investigated under conditions allowing gelation of the former and gelation or non-gelation of the latter. Amylose concentration was kept constant (1.34 wt%) and carrageenan content was varied from 0.093 to 1.38 wt%. Amylose was dispersed in water at 150°C and its gelation was induced by quenching aqueous solutions from 80 to 25°C. When desired, carrageenan gelation was also induced by addition of 20 mM KCl. Absorbance and gel-cure profiles were highly dependent on carrageenan concentration and presence of salt. The storage modulus at 15 h depended strongly on carrageenan concentration; for concentrations <0.2%, amylose aggregation occurred rapidly and the rigidity of gels was reinforced as a result of phase separation between amylose and κ-carrageenan. Further addition of carrageenan, either without or with KCl, resulted in a maximum G' occurring at about 0.2 and 0.3%, respectively. Beyond such values a sharp decrease was observed suggesting phase inversion with carrageenan forming the continuous phase. Above 0.5%, G' increased steadily showing a predominance of carrageenan gel properties. Results support the existence of at least two different conditions in which amylose and carrageenan form the continuous and disperse phase alternately. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Amylose; Carrageenan; Polysaccharides; Rheology; Viscoelasticity; Gels

1. Introduction

Amylose is the linear component of common starch; it is a (1–4)-linked α-glucan responsible for gelation of cooked pastes upon cooling. When amylose-containing starch is blended with other macromolecules, synergistic effects may develop giving rise to spectacular increases of the viscosity of hot pastes as a result of an artificial concentration of the added polymer, in the continuous phase, induced by granule swelling (Alloncle, Lefebvre, Llamas & Doublier, 1989). When cooled, however, pastes exhibit a rather complex viscoelastic behavior. It has been suggested that phase separation, occurring as a consequence of thermodynamic incompatibility between amylose and the added hydrocolloid, may take place in the continuous phase (Alloncle & Doublier, 1990). In fact, it is well known that amylose–dextran (Kalichevsky, Orford & Ring, 1986) and amylose–amylopectin (Kalichevsky & Ring, 1987) mixtures exhibit such incompatibilities at specific conditions of temperature and composition.

In amylose solutions, gelation occurs by a short-time scale phase separation into polymer-rich and polymer-deficient regions followed by a longer-time scale crystallization in the polymer-rich phase (Miles, Morris & Ring, 1985). The first of these changes depends mainly on molecular weight (and probably on its distribution) as well as on polymer concentration. Depending on the amylose concentration and degree of polymerization (DP), different states, going from precipitates to gels and mixtures of both, are observed (Gidley & Bulpin, 1989). While rheological descriptions of amylose gelation have been documented in the literature (Clark, Gidley, Richardson & Ross-Murphy, 1989; Doublier & Choplin, 1989; Doublier, Llamas & Choplin, 1990), we are not aware of published reports discussing the rheological properties of amylose–hydrocolloid mixtures in non-starchy media. As interaction between macromolecules normally determines the final texture and properties of gels, the study of such properties is of interest because hydrocolloids are often combined with starch in order to get attractive functional properties. However, due to the presence of suspended particles the system is very complex and interpretations are more difficult. It is therefore desirable to study the interaction between amylose and hydrocolloids in particle-free systems in order to get a better understanding of the behavior of such mixtures and the

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PII: S0144-8617(01)00317-4

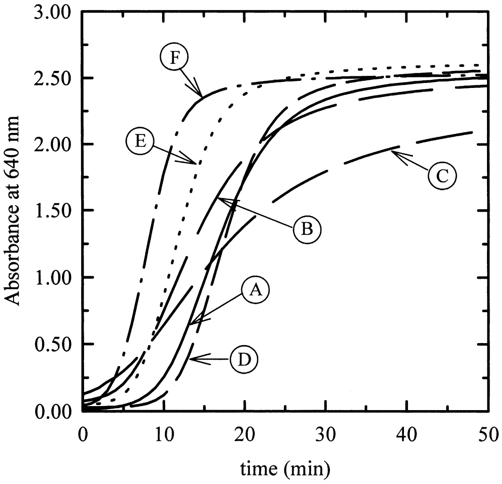

Fig. 1. Time evolution of turbidity at 25°C of amylose alone (curve A) and its mixtures with κ-carrageenan without addition of KCl. Concentrations (wt%) were: amylose 1.34, carrageenan; 0.093 (curve B), 0.17 (curve C), 0.28 (curve D), 0.34 (curve E) and 0.46 (curve F).

role played by both components. With this in mind, we report here on the rheological as well as on the aggregation behavior of amylose–κ-carrageenan mixtures in aqueous media free of suspended particles. As carrageenan can also form gels, we have investigated the rheological behavior of the admixtures under conditions leading to gelation or non-gelation of this polysaccharide. It is expected that such information could allows us to get some insights on their interaction as well as on their role in the rheological response of the blends.

2. Materials and methods

2.1. Materials

Potato amylose was supplied by AVEBE (Groningen, The Netherlands); its ion content, determined by atomic absorption, was (mg/g): 2.1 Na^+, 0.4 K^+, 0.02 Ca^{+2} and 0.013 Mg^{+2}. Its intrinsic viscosity in 0.2 N KOH at 25°C was 144 ml/g, which according to the equation $[\eta] = 6.92 \times 10^{-3} Mv^{0.78}$ (Banks & Greenwood, 1975), corresponded to a viscosity molecular weight average of 340 740 (DP ~ 2100). The κ-carrageenan sample was a gift from SKW Biosystems (France) and was used as received. Analytical grade KCl (Merck) and distilled deionized water were used throughout.

2.2. Solutions preparation

Only fresh polymer solutions were used. Carrageenan solutions were prepared in stoppered flasks: first, the powder was dispersed, either in water or in a 20 mM KCl solution, under magnetic stirring at ambient temperature (20°C) and then the dispersion was heated at 80°C during 30 min in a water–ethylene glycol bath. Amylose solutions (total volume not greater than 10 ml) were prepared as reported previously (Doublier, Coté, Llamas, & Charlet, 1992): the proper weighed amount of amylose powder and solvent (water or KCl solution) were carefully placed into a custom-made glass bulb made-up from a 15 mm diameter test tube stretched at its open end to a 5 mm diameter hollow stem. The stem was flame-sealed at about 30 mm above the tube-stem neck. The ampoule was then heated in an oil bath at 150°C for 30 min; it was occasionally stirred in a vortex mixer for few seconds and immediately returned to the bath. At the end of the heating period, the ampoule was transferred to a water–ethylene glycol bath and cooled to 80°C, then, was opened carefully and its content was immediately quenched to 25°C in the measuring devices (see below). When both polymers were blended, amylose and carrageenan solutions were prepared at twice their final concentration in the mixture and they were thoroughly mixed while still at 80°C before quenching. The evolution of the macroscopic state of the system was followed by direct visual observation as well as by optical density and rheological measurements. Amylose concentration either alone or in the mixtures was always 1.34 wt% and κ-carrageenan concentration varied from 0.093 to 1.38 wt%.

2.3. Turbidity measurements

The development of turbidity at 25°C was monitored by measuring the time course of absorbance at 640 nm in a UV/Vis spectrophotometer (Perkin Elmer Lambda 2). Measurements were made against a blank of solvent in 1 cm length cells over a period of 15 h. Evaporation was avoided by tightly covering the cells with plastic caps.

2.4. Rheological measurements

Low amplitude oscillatory shear tests were carried out at 25°C in a strain rheometer (Fluids Spectrometer RFS II, Rheometrics) using the cone and plate (diameter 5 cm, angle 0.04 rad) geometry. Samples were quenched by placing them directly onto the plate. The fixture rim was covered with paraffin oil to prevent evaporation. The following in-sequence protocol was used for each preparation: (1) a time evolution (gel-cure) of the storage and loss moduli at 1 rad/s over a period of 15 h and (2) a mechanical spectrum at constant strain. In general, both were carried out at 10% strain which was found to be within the zone of linear viscoelasticity; in some cases, however, 2% strains were used.

3. Results

3.1. Systems without added KCl

3.1.1. Time evolution of turbidity

Amylose gelation can be easily monitored by turbidity measurements and rheological means (gel-cure profiles)

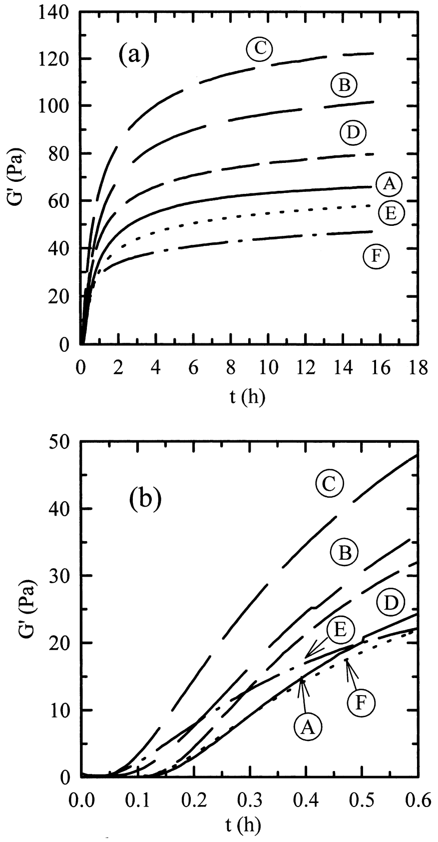

Fig. 2. Time evolution of G' at 25°C of amylose alone and mixtures with κ-carrageenan without addition of KCl: (a) over a 15 h period, (b) initial period (<1 h). Concentrations are those shown in Fig. 1.

(Doublier & Choplin, 1989; Ellis & Ring, 1985; Miles et al., 1985). Figs. 1 and 2 show typical profiles for a 1.34% amylose dispersion (curves A) and amylose–carrageenan mixtures without KCl (curves B–E). In amylose alone, absorbance (Fig. 1, curve A) started to increase at about 5 min and then turbidity build-up was quite rapid. This time has been defined as the 'cloud time', t_C, which can be taken as an index for the kinetics of the gelation process (Doublier & Choplin, 1989). In amylose alone, opaque systems (absorbance higher than 2) were developed in about 20 min. It is worth noting that absorbance has no sound meaning when such high values are reached. However, its rate of increase provides another means to evaluate the gelation kinetics. The physical basis of amylose gelation is well documented (Clark et al., 1989; Ellis & Ring, 1985; Gidley, 1989; Gidley & Bulpin, 1989; Miles et al., 1985). A two-step mechanism is involved; in the first step, turbidity increases as a result of phase separation into polymer-rich and polymer-deficient regions while in the second step, crystallization of amylose chains takes place. It is the combination of both steps that leads to the development of the polymer network.

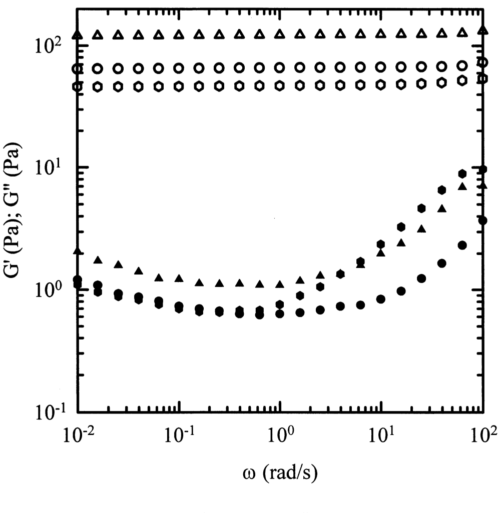

Fig. 3. Mechanical spectra, G' (void), G'' (filled), of KCl-free gels of amylose alone (circles), and its mixtures with 0.17% (triangles) and 0.46% (hexagons) carrageenan. Test conditions were 25°C and 10% strain.

Addition of carrageenan without KCl had effect on t_C and on the rate of turbidity build-up. In general, once turbidity began to increase, mixtures attained an essentially constant absorbance within the first hour following mixing and quenching. The rate at which this happened was, however, dependent on carrageenan concentration. As shown in Fig. 1, addition of a small amount (0.093%) of carrageenan resulted in an earlier increase ($t_C < 2$ min: curve B) and a faster build-up during the first 20 min, which leveled off in a similar way to amylose alone. Further addition (0.17%), decreased yet the cloud time ($t_C < 1$ min: curve C) and accelerated notably turbidity development within the first 10 min but afterwards a slower build-up and a lower final absorbance were observed. This behavior, however, changed upon further addition of carrageenan; for a concentration of 0.28% (curve D) a behavior similar to amylose alone was observed with essentially equal final absorbances but with $t_C \sim 7$ min. At higher concentrations (0.34%: curve E and 0.46%: curve F) an earlier turbidity development (about 3 and 1 min, respectively) with respect to that of curves A and D was observed and also a faster build-up and higher final absorbance. Nevertheless, further addition up to 0.74 and 1.38% (not shown) resulted in a behavior very similar to that of curve B. The major changes occurred within the first hour and although absorbance increased still slightly after this lapse, the relative positions of the curves shown in Fig. 1 at 50 min, were kept to the end of the 15 h test period.

3.1.2. Gel-cure profiles

Fig. 2 shows the change with time of the storage modulus resulting from cooling aqueous solutions of amylose and its carrageenan mixtures without KCl. The storage and loss moduli (this latter not shown) increased steadily but the former did it more appreciably. In all systems, the storage modulus never attained a constant value after 15 h; therefore, for practical reasons, values of G' at this time, herein after designated as G'_{15}, were taken for further analysis. From the gel-cure profiles (Fig. 2a), the gel time, t_G, (time at which G' over-crossed G'') was estimated together with

Table 1
Gel time values of systems with and without KCl

Carrageenan concentration (%)	t_G (s) without KCl	t_G (s) with KCl
0	272	337
0.093	371	128
0.17	101	–
0.28	398	–
0.34	370	–
0.46	123	–
0.74	143	–
0.92	129	–

the G'_{15} and G''_{15} values. The modulus G'_{15} was always greater than G''_{15} by about one to one and a half logarithmic decade depending on carrageenan concentration (Fig. 3). It is an accepted practice to determine the gel time at the cross over of dynamic moduli from gel-cure profiles, even though some other criteria can be used (Ross-Murphy, 1991). Table 1 shows the gel times determined by this procedure. The cross over of G' and G'' occurred at about 0.007 Pa for amylose alone gels, from 0.07 to 0.13 Pa for carrageenan concentrations up to 0.46%, and 0.25 Pa, 0.40 Pa for carrageenan contents in the mixture of 0.74 and 0.92%, respectively. In amylose alone systems, t_G was about 6 min, whilst G'_{15} was around 60 Pa. Carrageenan concentration had a noticeable effect on t_G as well as on the growth kinetics and G'_{15} and G''_{15} values. Carrageenan concentrations of 0.093% (B) and 0.17% (C) exhibited a faster increase of G' and had higher G'_{15} values than amylose alone (A). For 0.28% (D) intermediate values were observed but for 0.34% (E) and 0.46% (F) values were lower than for amylose alone.

Fig. 2b shows the early stages of the gel-cure process shown in Fig. 2a for amylose alone (curve A) and its mixtures with carrageenan (B–F). Addition of carrageenan resulted in a faster start-up of the storage modulus. The relative position of curves A–D on a short time-scale was the same as that observed over the longer time-scale shown in Fig. 2a. However, unlike the long time-scale behavior, the short-time scale behavior of the modulus at higher carrageenan concentrations (curves E and F) was similar to amylose alone (A). Amylose gelation proceeded steadily but the presence of carrageenan reinforced the rigidity of the system.

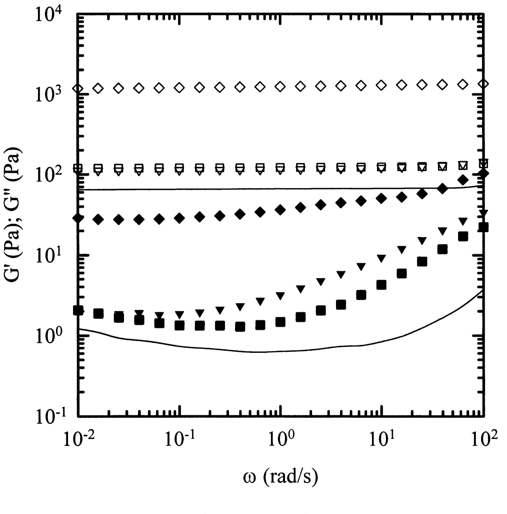

Fig. 4. Mechanical spectra, G' (void), G'' (filled), of KCl-free gels of mixtures with 0.74% (squares), 0.92% (inverted triangles) and 1.38% (lozenges) carrageenan. Continuous lines show the moduli of amylose alone gels. Test conditions were 25°C and 10% strain.

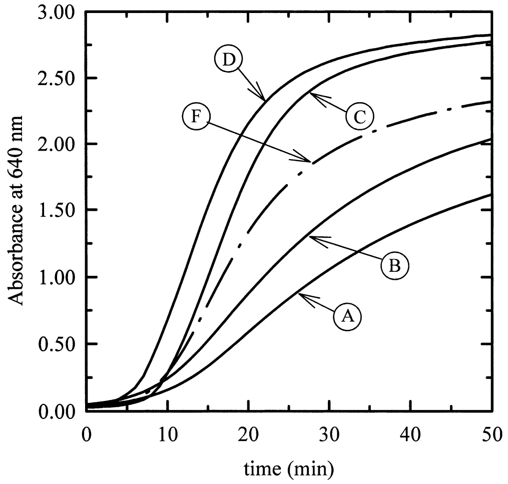

Fig. 5. Time evolution of turbidity at 25°C in amylose alone (curve A) and its mixtures with κ-carrageenan with addition of 20 mM KCl. Concentrations are those shown in Fig. 1.

3.1.3. Viscoelastic behavior of gels

Typical spectra of KCl-free gels are shown in Figs. 3 and 4. The spectra were obtained immediately after the end of the gel-cure period and therefore, moduli values were practically the same as those at 15 h. The mechanical spectrum of amylose alone shows a typical gel behavior with G' essentially independent of frequency and G'' showing a concavity (Fig. 3). The presence of a minimum in the loss modulus has been observed in other physical gels like PVC and gelatin gels (te Nijenhuis, 1997). This has been associated with the existence of a relaxation mechanism, which should be present at lower angular frequencies. The corresponding spectra of the admixtures were also characteristic of gel materials with both moduli being similar in behavior to those of amylose alone. However, G' of the mixture with 0.17% carrageenan was higher than the corresponding to amylose alone and a further increase to 0.46% carrageenan yielded lower G' values. As shown in Fig. 4, further addition of carrageenan not only resulted in higher moduli over those of amylose alone but also in a significant change of shape of spectra. As carrageenan concentration increased, the loss modulus became less frequency-dependent which confirms the formation of more rigid gels.

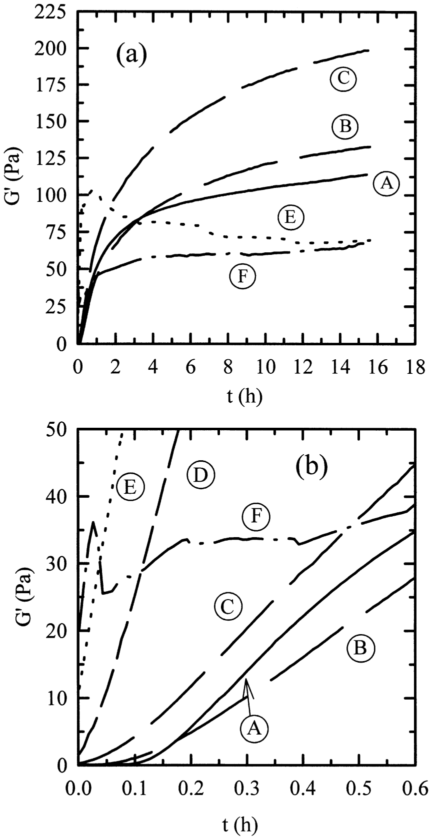

Fig. 6. Time evolution of G' at 25°C of amylose alone and its mixtures with κ-carrageenan with addition of 20 mM KCl: (a) over a 15 h period, (b) initial period (<1 h). Concentrations are those shown in Fig.1.

3.2. Systems with added KCl

3.2.1. Time evolution of turbidity

A similar trend was observed in KCl-containing mixtures as shown in Fig. 5. The rate of build-up was also function of carrageenan concentration. Addition of 0.093–0.28% (curves B–D) notably resulted in faster kinetics over amylose alone (curve A), but further addition to 0.34 (not shown) and 0.46% (curve F) resulted in a slowing-down. In KCl-free systems a change in trend was observed at 0.17%, whereas in KCl-containing samples this change appeared at 0.34%. In KCl-added mixtures t_C values from 2 to 5 min were observed with no sharp distinction among samples during the early time-scale of measurements. The final absorbance values were higher than their KCl-free counterparts. Presence of KCl had a significant effect depending on carrageenan concentration; amylose alone and mixtures with 0.093 and 0.34% carrageenan exhibited slower kinetics, while 0.17, 0.28 and 0.46% exhibited faster kinetics than their KCl-free counterparts.

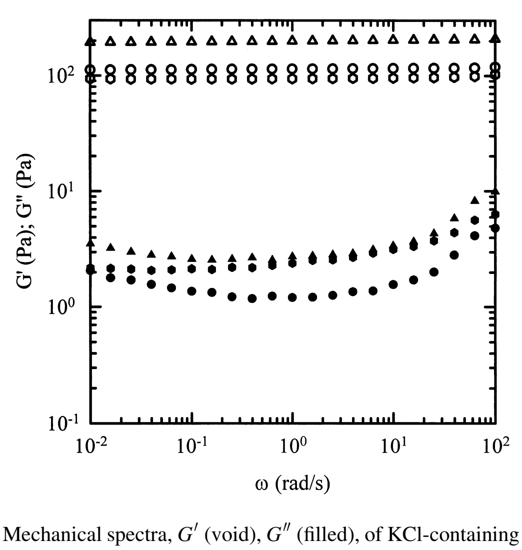

Fig. 7. Mechanical spectra, G' (void), G'' (filled), of KCl-containing gels of amylose alone (circles), 0.17% (triangles) and 0.46% (hexagons) carrageenan. Test conditions were 25°C and 10% strain.

3.2.2. Gel-cure profiles

In systems containing KCl (Fig. 6a and b) some striking differences were observed. Solutions with 0.28% (curve D) and 0.34% (curve E) carrageenan exhibited a much faster increase of G' than amylose alone (curve A), 0.093% (curve B) and 0.17% (curve C) blends. Mixtures with 0.34% and 0.46% (curve F) carrageenan exhibited an overshoot; the former at about 18 min with $G' \sim 95$ Pa, whereas the latter at about 2 min with $G' \backsim 36$ Pa. After this overshoot, the storage modulus of both mixtures converged to a storage modulus of about 70 Pa (Fig. 6a). As in the case of KCl-free mixtures, the ‘pseudo equilibrium’ storage modulus of 0.093% (B) and 0.17% (C) was greater that that of amylose alone (Fig. 6a).

Although it was not always possible to appreciate sharply the over crossing of moduli due to background noise at low torques, t_G values of all mixtures were determined and are shown in Table 1. The trend observed was not well defined; in fact values increased and decreased apparently in a random way with 0.28% exhibiting the highest time followed by amylose alone, 0.093% and 0.34%, which had roughly the same gel time, 0.17, 0.74, 0.92, and 0.46% which displayed the lowest one. It is worth saying that t_C exhibited a similar behavior and in general it was lower than t_G with maximum (360 s) and minimum (60 s) values occurring at the same carrageenan concentrations than for t_G without KCl. As mentioned earlier, in the presence of KCl no sharp distinction was observed for t_C, and it was possible to get t_G values only for the concentrations shown in Table 1; a significant reduction was observed upon addition of carrageenan and for higher contents G' was always greater than G'' from the start of the gel-cure experiment and their difference increased with carrageenan proportion.

3.2.3. Viscoelastic behavior of gels

Gels with KCl exhibited essentially the same behavior as those without the salt, but with greater values of both moduli. As shown in Fig. 7, admixtures exhibited the typical behavior of self-supporting gels with the rubbery plateau

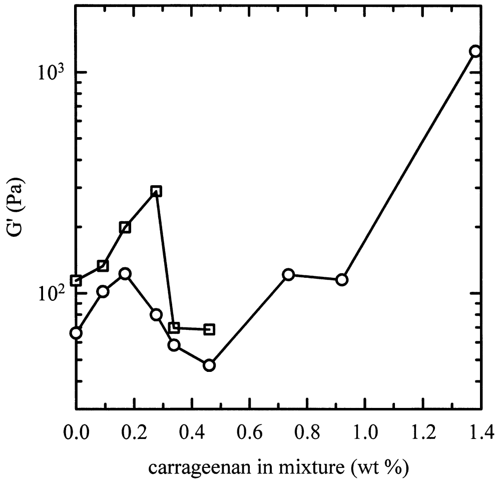

Fig. 8. Variation of the storage modulus with carrageenan concentration without KCl (circles) and with 20 mM KCl (squares).

over all the oscillation frequency and the storage modulus higher than the loss modulus. The concavity of the loss modulus present in the KCl-free counterparts was also observed. However, such concavity disappeared at lower carrageenan concentrations. For example, the storage modulus curve of 0.46% carrageenan with KCl (Fig. 7) was similar in shape, though not in values, to that of 1.38% without KCl (Fig. 4). In the presence of KCl the rigidity of co-gels developed at lower carrageenan concentrations.

4. Discussion

Absorbance and rheological data show that addition of relatively small amounts of carrageenan accelerated amylose gelation to a certain extent, beyond which further addition retarded gelation and affected the rigidity of the resulting co-gels. These effects occurred either with or without KCl, but when this salt was present co-gels exhibited a higher rigidity with respect to their salt-free counterparts. Interesting results are obtained when the storage modulus of the admixtures, with and without KCl, is plotted against carrageenan concentration (Fig. 8). Moduli of KCl-containing gels are higher than their corresponding salt-free mixtures. Maximum moduli are observed at 0.18 and 0.28% carrageenan in the absence and in the presence of KCl, respectively. Beyond the maximum, G' drops significantly below the value of amylose alone gels. For example, KCl-containing co-gels with 0.34% carrageenan, have lower G' than the corresponding amylose alone gel. The same behavior is observed in KCl-free mixtures with 0.46% carrageenan. However, the effect is more noticeable when KCl is present. Addition of this salt certainly plays a role even without carrageenan; for example, G' of amylose alone gels with KCl is almost two times greater than the corresponding without KCl.

In KCl-free mixtures, results show that addition of small amounts of carrageenan, lower than about 0.2%, promote amylose aggregation and gelation but owing to the non-gelling conditions of carragenan (absence of salt and low concentration), amylose forms the continuous phase in which carrageenan is dispersed; the overall effect is a reinforcement of amylose gels which is also affected by amylose concentration in the continuous phase. Beyond the maximum G', the drop of final absorbance suggest some difficulties for amylose to form a gel, while the drop of storage modulus even below that of amylose alone suggest a phase inversion. This time carrageenan forms the continuous phase, still under non-gelling conditions, in which a weak amylose gel is dispersed. Above 0.46%, carrageenan begins to dominate the rheological behavior because it gradually reaches its gel forming concentration in KCl-free medium which is near 1% at 25°C (Rochas & Rinaudo, 1980; Rochas, 1982). As carrageenan concentration increases there is a transition from non-gelling to gelling conditions. Fig. 8 shows that such transition seems to occur between 0.72 and 0.92%, so the essentially constant value of G' is not fortuitous. This is confirmed by the fact that at these concentrations the mechanical spectra (Figs. 3 and 4) of mixtures are no longer similar in shape to the spectra of amylose alone and mixtures with low carrageenan concentration. Finally above 1%, carrageenan networks form the continuous phase in which amylose is dispersed. In KCl-containing systems the situation is somewhat similar but this time gelling conditions favor formation of carrageenan networks. Below 0.28%, amylose forms the continuous phase in which carrageenan gel is dispersed, hence higher moduli are observed. Beyond the maximum G', the continuous phase is formed by carrageenan networks in which gelled amylose is dispersed.

5. Conclusions

Amylose–κ-carrageenan blends of different rheological behaviors can be obtained depending on carrageenan concentration and presence of KCl. Turbidity and rheological measurements were useful to follow the evolution with time of the macroscopic state and characteristics of the blends. There is enough experimental evidence to postulate the existence of three different conditions the occurrence of which depends mainly on carrageenan concentration but that are observed either in the presence or absence of KCl. The first condition, which occurs at carrageenan concentrations lower than about 0.3%, comprises the existence of a continuous phase formed by amylose in which carrageenan is dispersed in the form a macromolecular solution when KCl is not added and a macromolecular network when KCl is present. This condition is characterized by higher moduli over amylose alone and more rigid materials when KCl is present. The second condition, which occurs between 0.3 and 0.5% carrageenan, is characterized by a phase inversion in which amylose becomes the dispersed phase and carrageenan the continuous phase. When KCl is present co-gels are formed with a weak carrageenan network and an ill-formed amylose gel. This condition is characterized by a noticeable drop of turbidity and plateau storage moduli over that of amylose gels alone. A third condition exists above 0.5%, in which carrageenan constitutes still the continuous phase and amylose the disperse phase but with a larger influence of the former on the rheological properties. In the absence of KCl carrageenan passes from a macromolecular solution to a macromolecular network with a noticeable increase of G', while in the presence of KCl carrageenan is always as a macromolecular network. This last condition is characterized by a remarkable increase in the rigidity of gels with carrageenan largely dominating the rheological properties of the blends.

Acknowledgements

We thank INRA for the research grant (to A. Tecante) which enabled this work to be carried out at Nantes. We also thank Sylvie Durand for her skilled technical support throughout this work.

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