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Mixtures of pregelatinised maize starch and κ-carrageenan: Compatibility, rheology and gelation

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Abstract

Compatibility, flow and visco-elastic properties of a pregelatinised maize starch mixed with κ-carrageenan were investigated. After cooking of the pregelatinised starch, some undissolved granules remained in solution. Aqueous mixtures of κ-carrageenan and starch were studied at 60 °C and 20 °C by combining rheological measurements and microscopic observations under conditions allowing gelation of carrageenan and non-gelation of starch. The viscometric study of mixed dilute solutions of amylose from pregelatinised starch and carrageenan showed that the components are slightly incompatible. Mixture viscosity and elastic modulus were studied at 60 °C in details as a function of mixture composition for a total polymer concentration of 3%; both were found to be significantly higher than the corresponding theoretical additive values. This finding was interpreted by starch granules excluded volume effect. At 20 °C, no noticeable increase of mixture elastic modulus was found as compared with the additive value. The absence of the synergistic effect is supposed to be due to the formation of highly inhomogeneous gels with agglomerates of undissolved granules.

Keywords: Pregelatinised maize starch; κ-Carrageenan; Visco-elastic properties; Compatibility

1. Introduction

Starch is one of the most important food hydrocolloids. It is not only used as a main ingredient of staple foods but also as a thickener, gelling agent and stabiliser. It is known that starch is not easy to dissolve. Indeed, it is often mentioned that, for example, some granules of a waxy maize starch remain undissolved after being heated at a typical temperature of 90 °C (Autio, Vesterinen, & Stolt, 2002), which obviously influences final product properties. Starch is generally considered as a composite, in which swollen gelatinised granules, composed of mainly amylopectin, are embedded into an amylose matrix. One way to make starch solutions homogeneous is to degrade it at 150 °C. Another way to help starch dissolution is to "pregelatinise" it, or, in other words, to carry out a preliminary cooking while applying a mechanical treatment in order to partially break up the granules. The influence of pregelatinisation on the rheological properties of starch itself and its mixtures with other polysaccharides has not been well studied. It was reported that although being viscous, pregelatinised starch shows reduced stickiness and self-lubricating properties as compared with an equivalent starch system (Podczeck, 1999). It also improves the dissolution of poorly soluble drugs and is a promising material to be used in tamps filling (Podczeck, 1999; Gohil, Podczeck, & Turnbull, 2004). Thus the study of pregelatinised starch and its mixtures with other food hydrocolloids should allow the development of new and interesting cold prepared or minimally heated food materials.

Blends of starch with other biopolymers are widely used in food applications. Components (in)compatibility, coupled with their individual properties (gelation, ageing,

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etc.), leads to a large variety of structures and properties of prepared materials. Phase separation is a phenomenon encountered in many food applications containing mixed biopolymers. Depending on the ratio of components, a continuous phase of one component in which the other is dispersed, or two co-continuous liquid or gel phases, can be formed. The rheology of starch–hydrocolloid mixtures will thus depend on components compatibility, their individual properties and particular experimental conditions. For example, it was shown that wheat starch/galactomannan mixture can be regarded as a suspension of 3% of starch granules dispersed in a solution of galactomannan (Closs, Conde-Petit, Roberts, Tolstoguzov, & Escher, 1999). Mixture properties can also be affected by the molecular weight of the components. For example, in wheat starch/galactomannan systems, amylose interacts with the galactomanann only if its molecular weight is higher than a critical molecular weight of about 10^6 g × mol^{-1} (Funami et al., 2005). Moreover, the addition of polysaccharide gums like guar gum, locust bean gum, konjac-glucomannan, xanthan or carrageenans to starch pastes causes an increase in viscosity and retrogradation decrease, as well as syneresis of the starch-based system (Alloncle & Doublier, 1991; Alloncle, Lefebvre, Llamas, & Doublier, 1989; Appelqvist & Debet, 1997; Bahnassey & Breene, 1994; Du Toit, Pillay, & Danckwerts, 2006; Lai, Huang, & Lii, 1999; Loisel, Tecante, Cantoni, & Doublier, 2000; Sajjan & Rao, 1987; Tecante & Doublier, 1999, 2002; Yoshimura, Takaya, & Nishinari, 1996, 1999). To explain these effects, researchers refer to different types of molecular interactions between starch and non-starch polysaccharides: thermodynamic (in)compatibility between coexisting molecules, interference of a non-gelling polysaccharide in association with the coexisting gelling one, and the exclusion effect of swollen granules (Autio et al., 2002; Bahnassey & Breene, 1994; Eidam, Kulicke, Kuhn, & Stute, 1995; Lai et al., 1999; Tecante & Doublier, 1999, 2002).

The goal of this work is to study and understand the properties of pregelatinised starch mixed with a charged hydrocolloid. κ-carrageenan was chosen as a typical charged gum that has been widely investigated. The article will thus be focused on the individual properties of pregelatinised starch and its mixture with κ-carrageenan, without a detailed interpretation of carrageenan behaviour supposing it is well known (see, for example, Nickerson & Paulson, 2004; Mangione et al., 2003; Norziah, Foo, & Karim, 2006; Rochas, 1982). The understanding of the mixture behaviour will be based on the study of its flow and gelation properties in the dilute and semi-dilute states, coupled with optical microscopy observations.

2. Materials and methods

2.1. Materials and preparation of solutions and mixtures

κ-Carrageenan (κ-car in the following) was kindly supplied by Cargill Texturizing Solutions. Its moisture content was 13% (w/w) and the material was used as received. Its molecular weight is 8.8 10^5 g/mol and its ion content (%), provided by the supplier, is summarised in Table 1.

Table 1
Ionic content in κ-carrageenan

Ions	Na^+	K^+	Ca^{2+}	Mg^{2+}
Content (%)	1.25	7.3	2.45	<0.1

Pregelatinised maize starch (pgs in the following) was kindly provided by Roquette Frères. Amylose content is 70%, as provided by the supplier. The moisture content was 10% and the material was used as received.

Powders of each sample were dispersed at room temperature in distilled water in separate flasks using a magnetic stirrer. The dispersions of κ-car and pgs were heated at 70 °C and 90 °C, respectively, and kept at this temperature for 30 min with a constant stirring. κ-carrageenan concentration used in this study varied from $C_{car} = 0.04–3\%$ and of pregelatinised starch from $C_{pgs} = 0.04–10\%$. Mixtures were obtained by adding a hot solution of pgs into the solution of κ-car with a constant stirring at 70 °C during 30 min.

When the viscometric studies of the initial solutions and of their mixtures in the dilute state were performed, both starch and carrageenan were filtered separately prior measurements, in particular in order to exclude undissolved starch granules. Cellulose acetate membrane with pore size range from 16 to 40 μm was used. Polymer concentration in starch solution after filtration was determined by drying this solution up to constant weight for 5 days at 50 °C. The amount of the polymer after filtering and drying was 38% smaller as compared with the initial amount of dispersed starch. This decrease is due to the removal of undissolved granules; the remaining solution was supposed to be composed only of dissolved amylose. When performing viscometric measurements, the real value of amylose concentration was considered.

In all other measurements non-filtered pregelatinised starch was used. All concentrations are given in weight per cent and are calculated considering the initial moisture content.

2.2. Methods

2.2.1. Rheological measurements

Steady and dynamic shear experiments were carried out at 60 °C and 20 °C using a cone-plate geometry (cone angle 2°, plate diameter 60 mm) on a stress-controlled Bohlin Gemini® rheometer equipped with a Peltier temperature control system. Solutions and mixtures were directly introduced on the plate after the preparation, and a layer of silicone oil was put around the border of the measuring cell in order to prevent water evaporation.

The viscosity of the initial components and their mixtures were measured as a function of shear rate. Frequency sweeps of the storage (G') and loss (G'') moduli were recorded at 20 °C and 60 °C for several polymer concentrations and mixture compositions at a strain of 1%, which corresponded to the linear visco-elasticity zone. When mixtures were studied, their total polymer concentration was 3%. The experimental errors in steady and dynamic measurements were less than 10%.

2.2.2. *Capillary viscometry*

Capillary viscometry was carried out at 25 °C using an automatic Ubbelhode-type viscometer (Lauda) immersed in a thermobath. The dependence of the viscosity of the initial components on polymer concentration during dilution with water was measured. The interactions between the components were studied as follows: the initial aqueous polymer solutions of each component of equal concentrations were mixed directly in the viscometer in different proportions, under stirring, and the flow time was measured. The total polymer concentration in the mixture was kept constant at 0.04%. No buffer was used to modify mixture pH. In all cases, flow time was long enough (higher than 2 min) for the kinetic energy and drainage corrections to be neglected. The experimental errors in the viscometric measurement were less than 3%.

2.2.3. *Optical microscopy observations*

A Metallux 3 (Leitz) optical microscope, coupled with Linkam heat stage, was used in transmission mode to observe the morphology of mixtures in gel and solution states at 20 °C and 60 °C, respectively. Microphotographs were then analysed with Visilog 6.3 software in order to calculate the volume fraction of starch granules.

3. Results

3.1. *Visual observations*

The initial components and their mixtures were observed with an optical microscope at 60 and 20 °C, total polymer concentration being 3% (Fig. 1). While κ-carrageenan solution is transparent, pregelatinised starch contains some broken undissolved granules and is thus slightly opaque. The granules' volume fraction is not negligible when starch concentration exceeds 2–3%. For example, the volume fraction of undissolved granules in the mixture at 60 °C κ-car:pgs = 2:1 is 6% (Fig. 1a, pgs concentration in the mixture 1%) and in the mixture κ-car:pgs = 1:2 – around 12% (Fig. 1b, pgs concentration in the mixture 2%). When the mixture is in the liquid state, granules are homogeneously distributed all over the mixture. No liquid/liquid phase separation was noticed within the time to be taken into account for the rheological measurements. However, granules form agglomerates at 20 °C when the mixture becomes a gel (Fig. 1d). The system κ-carrageenan + pregelatinised starch is thus very complex: it is a dispersion of broken granules in a continuous phase of mixed κ-carrageenan and amylose aqueous solutions. This complexity will influence the flow and visco-elastic properties of the mixtures.

3.2. *Dilute mixtures*

3.2.1. *Viscometric results: initial components*

Before studying the interactions between mixed components, the properties of the initial systems were analysed. To do this, the dilution of each component with water was performed. Fig. 2 shows Huggins (η_{sp}/C) and Kraemer ($\ln\eta_{rel}/C$) plots of the reduced viscosity η_{sp}/C versus polymer concentration C (where $\eta_{sp} = \eta_{solution}/\eta_{solvent} - 1$, $\eta_{rel} = \eta_{solution}/\eta_{solvent}$, $\eta_{solution}$ and $\eta_{solvent}$ are solution and solvent viscosities, respectively) for amylose. As far as starch dispersion was filtered before being loaded into the viscometer, we consider that the measurements were performed on amylose solution. No aggregation of amylose was noticed within the time of experiments: flow time corresponding to a given concentration varied non-systematically within the experimental errors.

Fig. 2 shows that the intrinsic viscosity of amylose from pregelatinised starch is $[\eta] = 1.15$ dL/g and Huggins constant is around 0.3. The obtained value of intrinsic viscosity is rather close to that reported by Ring, L'Anson and Morris (1995), 0.76 dL/g. Huggins constant obtained corresponds to a polymer dissolved in a good solvent (Lapasin & Pricl, 1995). The results obtained confirm the hypothesis that during cooking of pregelatinised starch practically only amylose macromolecules were released.

Amylose overlap concentration C^* was calculated using different approaches. Classical Flory approach $[\eta]C^* = 1$ that is also applied to polysaccharide systems (see, for example, Lapasin & Pricl, 1995) gives $C^* \approx 0.9\%$. Other approaches that depend on solution temperature and sample characteristics consider $[\eta]C^* = 1.8$ for amylose of $300 < \mathrm{DP} < 2800$ at 30 °C (Gidley, 1989), resulting here in $C^* \approx 1.6\%$, or $[\eta]C^* = 1.2$ for $\mathrm{DP} \approx 3000$ at 65 °C (Miles, Morris, & Ring, 1985), resulting in $C^* \approx 1.0\%$. The inset of Fig. 2 shows our viscometric data as a function of amylose concentration multiplied by its intrinsic viscosity. The slope of the straight line is 1.1 suggesting that Flory approach should be considered and the overlap concentration is 0.9%. In the following sections this value will be compared with the overlap concentration deduced from the flow curves of pregelatinised starch and with its concentration of gelation.

The measurement of the reduced viscosity for the κ-carrageenan aqueous solution shows a behaviour that is characteristic of a polyelectrolyte with no salt added: an increase of reduced viscosity with the decrease of polymer concentration. This fact will influence the following analysis of κ-carrageenan and amylose mixture viscosity.

3.2.2. *Viscometric results: Mixture*

One of the simplest and widely used tests for the analysis of interactions in mixed polymer solutions is the measurement of mixture intrinsic viscosity versus its composition

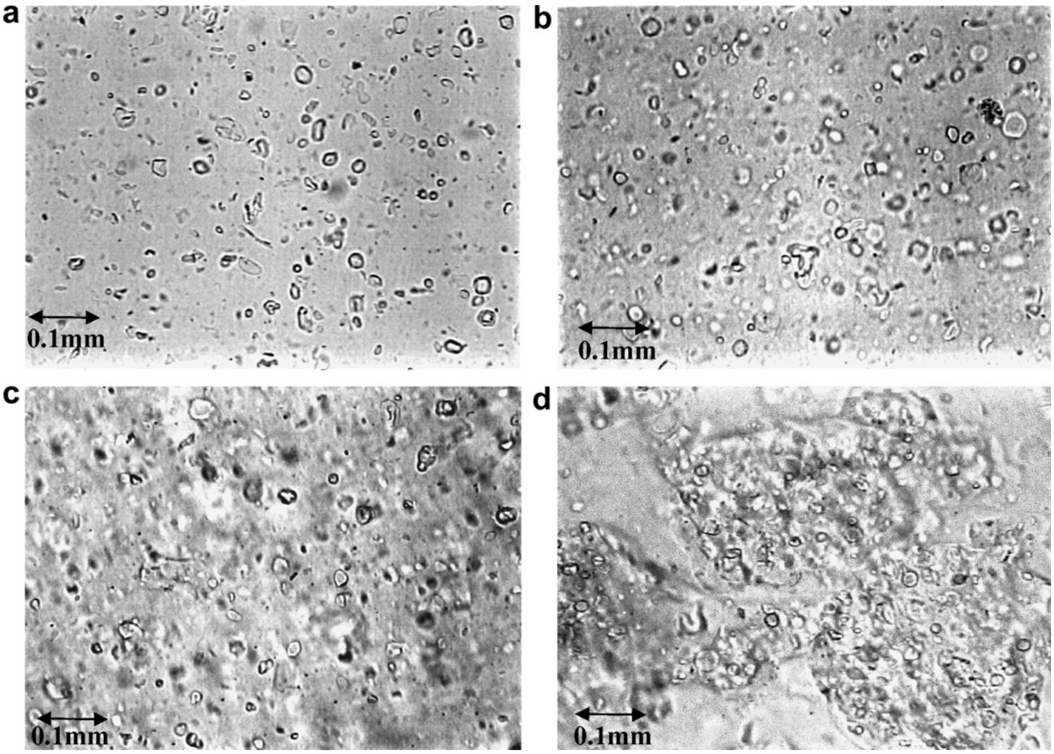

Fig. 1. Optical micrographs of liquid mixtures at 60 °C (a and b) and gels at 20 °C (c and d) with total polymer concentration 3%: (a) and (c) κ-car:pgs = 2:1, (b) and (d) κ-car:pgs = 1:2.

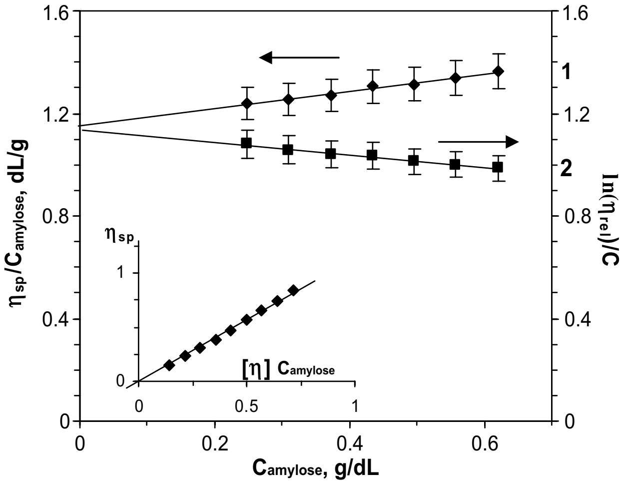

Fig. 2. Huggins (1) and Kraemer (2) plot for pregelatinised starch in water at 25 °C. Inset: Specific viscosity as a function of $[\eta]C_{\text{amylose}}$. All lines are least square linear approximations.

(see, for example, for testing the formation of interpolymer complexes: Bokias, Hourdet, Iliopoulos, Staikos, & Audebert, 1997; Bokias, Staikos, Iliopoulos, & Audebert, 1994). The experimental values of the mixture intrinsic viscosity have then to be compared with the calculated additive curve, which ignores the interactions between the components. If the deviation of experimental results from the additive curve is positive, it indicates the formation of gel-like or branched interpolymer complexes which hydrodynamic size is larger than the additive sum of the sizes of the initial components. If the deviation is negative, two options are possible: polymers are incompatible or compact complexes are formed due to strong interactions between the macromolecules leading to the decrease of solubility.

The classical way of calculating an additive curve is to measure the intrinsic viscosities of the initial components $[\eta]_1$ and $[\eta]_2$ and to calculate the mixture intrinsic viscosity at several compositions as follows: $[\eta]_{\text{add mix}} = w_1[\eta]_1 + w_2[\eta]_2$ where w_1 and w_2 are the weight fractions of each component in a given mixture (Bokias et al., 1994). However, as far as one of the component, κ-carrageenan, is a polyelectrolyte, it is not possible to use the approach described above. In our case, the specific viscosities of mixtures $\eta_{\text{sp mix}}$ of aqueous solutions at different compositions were measured. The additive curve was calculated using the following approximation (Nikolaeva, Budtova, Alexeev, & Frenkel, 2000; Nikolaeva, Budtova, Brestkin, Zoolshoev, & Frenkel, 1999; Staikos & Bokias, 1991; Staikos & Tsitsilianis, 1991; Xiang, Jiang, Zhang, Wu, & Feng, 1997; Pinteala et al., 2005):

$$\eta_{\text{sp add}} = \eta_{\text{sp1}}(C_1) + \eta_{\text{sp2}}(C_2) \quad (1)$$

$\eta_{\text{sp1,2}}$ $(C_{1,2})$ being the specific viscosity of each component at concentration C_1 and C_2 at which the polymer is present in the mixture. The values of specific viscosities $\eta_{\text{sp1,2}}$ $(C_{1,2})$ were measured in separate experiments by dilution of each component with water. The comparison of the measured and calculated values of the specific viscosities should give, in the first approximation, the indication of either complexation or incompatibility between the components.

An example of the experimental dependence of the mixture specific viscosity $\eta_{\text{sp mix}}$ on the fraction of κ-carrageenan in the mixture is shown in Fig. 3. The mixture was transparent. Eq. (1) for the additive curve allows taking into account the real behaviour of the specific viscosity of each component in the mixture, in the case where they are not complexing. Due to the polyelectrolyte effect, the specific viscosity of κ-carrageenan does not decrease linearly with dilution. This explains why the calculated dependence of $\eta_{\text{sp add}}$ as a function of mixture composition shows an upward curvature (Fig. 3, dashed line).

The results obtained (Fig. 3) show that mixture specific viscosities (points) are slightly lower than the additive curve (dashed line). Since it is known that between starch and κ-carrageenan there are no specific interactions (Autio et al., 2002), we assume that we obtained a confirmation that amylose and κ-carrageenan are slightly incompatible.

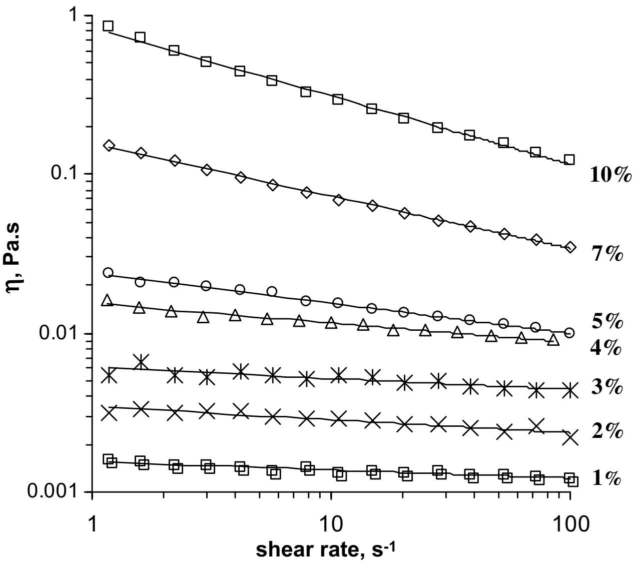

Fig. 4. Flow curves of pregelatinised starch of different concentrations at 60 °C. Lines are power law approximations.

3.3. Semi-dilute mixtures

3.3.1. Steady-state flow of the initial components and of their mixtures at 60 °C. Viscosity versus mixture composition for semi-dilute systems

The flow of the initial solutions (Figs. 4–6) and of their mixtures (Fig. 7) was studied at 60 °C in order to avoid starch retrogradation. Pregelatinised starch shows a shear-thinning behaviour for concentrations higher than 1% (see Fig. 4). The reasons are (i) the polymer concentration that is higher than the overlap one and (ii) the presence of undissolved granules that start to interact and influence the flow at volume fractions higher than 10%, which corresponds to starch concentrations greater than 1.5% (see Section 3.1). The viscosity versus shear rate dependences can be approximated using classical power law $\eta = K\gamma^{n-1}$, where η is viscosity, K is a constant, γ is shear rate and n is flow index. The latter varies from 0.95 for $C_{\text{pgs}} = 1\%$ to 0.53 for $C_{\text{pgs}} = 10\%$. The κ-carrageenan solutions (Fig. 5) show a Newtonian flow behaviour for concentrations lower than 2–2.5%: $n = 0.94$ for $C_{\text{car}} = 2.5\%$. The 3% κ-carrageenan solution is, in fact, in a gel state, as it will be shown in the following. Because in these conditions it is a very weak gel, it flows and breaks at the same time, which explains the slope change of the flow curve (upper curve in Fig. 5).

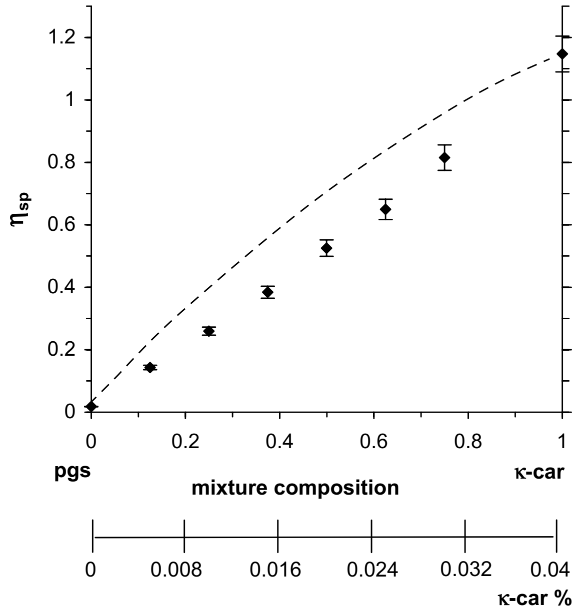

Fig. 3. Mixture specific viscosity as a function of composition (points); total polymer concentration is 0.04%, temperature 25 °C. Dashed line corresponds to the additive curve calculated according to Eq. (1).

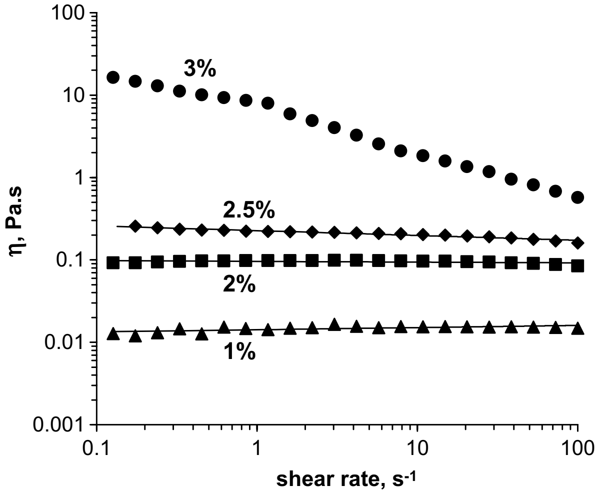

Fig. 5. Flow curves of κ-carrageenan of different concentrations at 60 °C. Lines are power law approximations.

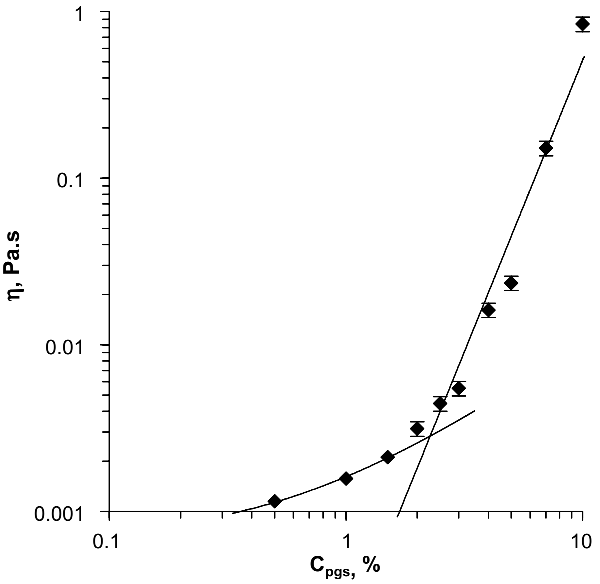

Fig. 6. Viscosity of pregelatinised starch at 60 °C taken from the flow curves at shear rate of 1 s^{-1} as a function of starch concentration; lines are linear and power-law approximations.

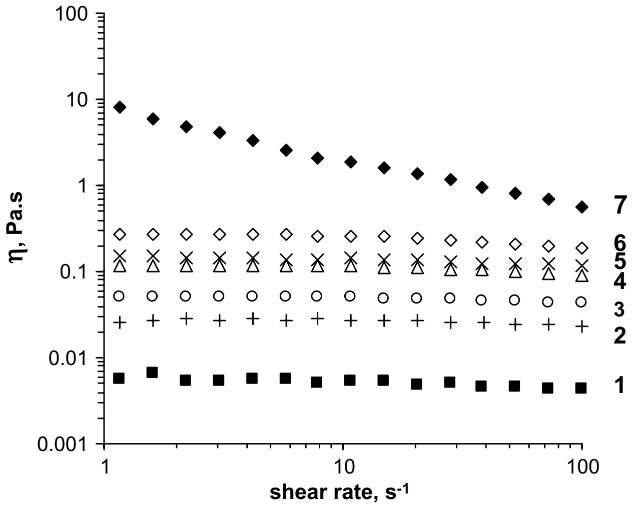

Fig. 7. Flow curves at 60 °C for mixtures with total polymer concentration 3% of different compositions κ-car:pgs = 1:5 (2), 1:2 (3), 1:1 (4), 2:1 (5) and 5:1 (6); initial systems: pgs of 3% (1) and κ-car of 3% (7).

Viscosities of the pregelatinised starch at a low shear rate (1 s^{-1}) were plotted versus C_{pgs} (Fig. 6), and the overlap concentration C^*_{pgs} was determined as the last concentration that fits the linear approximation in the dilute regime. In general, characteristic parameters such as C^* or the slopes in dilute or concentrated regimes should be calculated from the plot done at zero shear rate viscosities, but they were not achievable with our apparatus. While at low starch concentrations the flow behaviour is practically Newtonian, at concentrations higher than 3% the viscosity values presented are underestimated due to shear thinning. Thus, the real slope values at starch concentrations above 3% must be higher than the one obtained here: 3.5. As compared with pure amylose solution, such a high value is partly due to the presence of undissolved parts of starch granules that occupy more and more of volume with the increase of starch concentration and lead to the increase in starch viscosity. C^*_{pgs} is around 2% (Fig. 6). Considering that pregelatinised starch is composed of 62% of amylose as found after filtration, and if the presence of other poorly dissolved starch substances do not strongly influence the flow properties except increasing the solution viscosity (as compared with a pure amylose solution), a very rough estimation gives $C^*_{pgs} \times 0.6 \approx 1.2\%$ that should correspond to pure amylose overlap concentration. This value is not far from the one obtained with viscometric experiments, $C^* \approx 0.9\%$.

The flow of κ-carrageenan + pregelatinised starch mixtures with the total polymer concentration being 3% at 60 °C is shown in Fig. 7. The pure 3% κ-carrageenan exhibits strong shear thinning behaviour (curve 7), whereas the pregelatinised starch is weakly shear thinning with $n = 0.94$ (curve 1). The flow behaviour of the mixtures at the compositions studied is practically Newtonian and viscosity values are in-between the ones of the initial components. These results are not surprising since, first, a noticeable shear-thinning in carrageenan solution can be observed at concentrations above 2.5–2.6%, while the maximal concentration of κ-carrageenan in the mixtures studied was 2.5% (mixture 6 in Fig. 7), and second, κ-carrageenan and starch are not forming any complexes which could modify the flow.

The next step is to check if mixture viscosity follows the mixing law: Viscosity versus mixture composition for mixtures with a total polymer concentration of 3% was plotted (Fig. 8); viscosity values were taken at $\gamma = 1\ s^{-1}$ from Fig. 7. The additive dependence was calculated in two ways. The first one (dashed line) was done in accordance with Arrhenius mixing law:

$$1\mathrm{n}\eta_{\mathrm{add\ A}} = \phi_1 1\mathrm{n}(\eta_{1,3\%}) + \phi_2 1\mathrm{n}(\eta_{2,3\%}) \qquad (2)$$

where $\varphi_{1,2}$ are weight fractions of each component in the mixture, $\eta_{1,3\%}$ and $\eta_{2,3\%}$ are viscosities of each component at 3%. Because the application of Arrhenius law is criticised and was proved not working well for mixed polymers (see, for example, Haley & Lodge, 2004), and is oversimplified for such a complex system as κ-carrageenan + pregelatinised starch, another way of additive viscosity calculation was used. It is a sum of the experimental values of each component viscosity (solid line) at the concentration it is present in the mixture, $\eta_i(C_i)$, taken from the flow curves of the initial components (Figs. 4 and 5) at $\gamma = 1\ s^{-1}$:

$$1\mathrm{n}(\eta_{\mathrm{add\ B}}) = 1\mathrm{n}(\eta_1(C_1) + \eta_2(C_2)), \qquad C_1 + C_2 = 3\% \qquad (3)$$

Both approaches are the simplest approximations that do not take into account any special interactions leading to the formation of interpolymer complexes or to synergism between the components. It should be noted that as compared with κ-carrageenan, starch viscosity is very low (see Fig. 7), and thus the additive viscosity calculated according

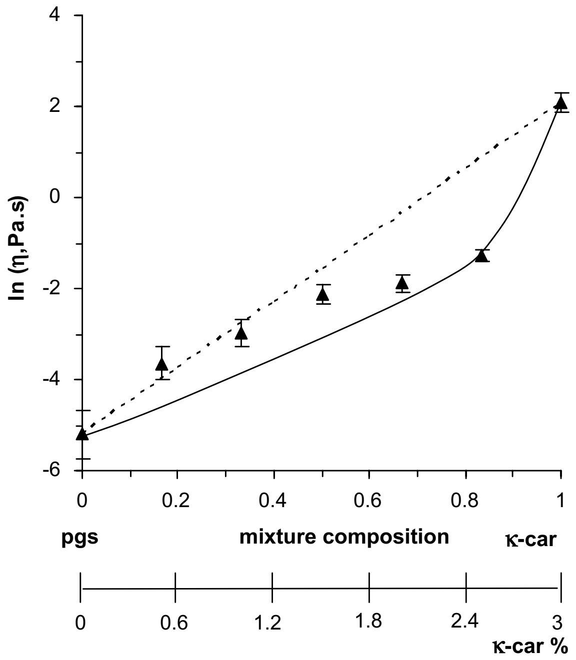

Fig. 8. Viscosity of the mixture of semi-dilute solutions (total polymer concentration 3%) as a function of mixture composition, at shear rate $1\ s^{-1}$ and 60 °C. Dashed line corresponds to the additive viscosity calculated according to Arrhenius law (Eq. (2)); solid line is the additive sum calculated according to Eq. (3).

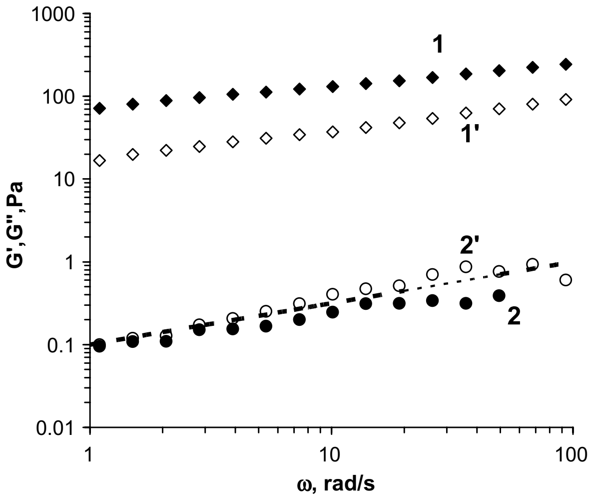

Fig. 9. G' (solid) and G'' (hollow) of pregelatinised starch as a function of frequency at 60 °C for different concentrations: 10% (1 and 1′) and 3% (2 and 2′). Dashed line corresponds to $G' \sim \omega^{0.5}$.

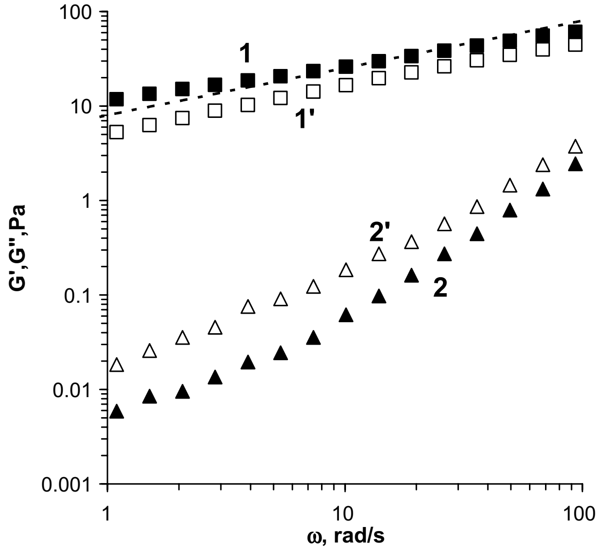

Fig. 10. G' (solid) and G'' (hollow) of κ-carrageenan as a function of frequency at 60 °C for different concentrations: 3% (1 and 1′) and 1% (2 and 2′). Dashed line corresponds to $G' \sim \omega^{0.5}$.

to Eq. (3) practically coincides with the viscosity of κ-carrageenan alone. This calculated additive dependence is much more realistic than the one built according to Arrhenius mixing law and will be used in the following for the comparison with experimental data.

At low κ-carrageenan fractions, mixture viscosity (Fig. 8) noticeably exceeds $\eta_{\mathrm{add\ B}}$ values; at high κ-carrageenan fractions mixture viscosity coincides with $\eta_{\mathrm{add\ B}}$. The transition occurs at carrageenan fractions in the mixture higher than 0.5–0.6 ($C_{\mathrm{car}} > 1.5$–2%). These results will be discussed together with the ones obtained on mixtures gelation and gelling properties of κ-carrageenan in Section 4.

3.3.2. Visco-elastic properties at 60 °C of the initial components and their mixtures

The angular frequency dependence of the elastic G' and viscous G'' moduli for the initial components and their mixtures was studied at 60 °C (Fig. 9 for pregelatinised starch, Fig. 10 for κ-carrageenan and Figs. 11 and 12 for their mixtures). The goal was to investigate if and how mixing influences the visco-elastic behaviour.

For pure components (Figs. 9 and 10), the elastic modulus becomes higher than the viscous one when polymer concentration is greater than 3–3.5% for both systems. However, the values of G' or G'' of κ-carragenan and pregelatinised starch of the same concentration differ by two orders of magnitude: for example, for 3% at 1 rad/s $G'_{\mathrm{car}} \approx 10$ Pa and $G'_{\mathrm{pgs}} \approx 0.1$ Pa. According to Winter and Chambon theory (Winter & Chambon, 1986), $G' \sim \omega^{a}$; $G'' \sim \omega^{b}$ and the gel point is reached when $a = b = 0.5$. Thus pregelatinised starch is near its gelation point at 3% (curves 2, 2′ and dashed line in Fig. 9) and κ-carragenan solution of 3% just overpassed it (curves 1, 1′ and dashed line in Fig. 10). With the increase of starch concentration, the elastic modulus becomes less frequency dependent at $\omega > 1$ rad/s (see curve 1 in Fig. 9 for $C_{\mathrm{pgs}} = 10\%$), however a real rubber plateau is not reached even for 10% system. Pregelatinised starch can be thus considered as a weak gel at $C_{\mathrm{pgs}} > 3\%$ with G' higher than G'' but with a noticeable dependence on the angular frequency (Clark & Ross-Murphy, 1987). Similar results were found for maize starch (Alloncle & Doublier, 1991); cross-linked waxy corn starch

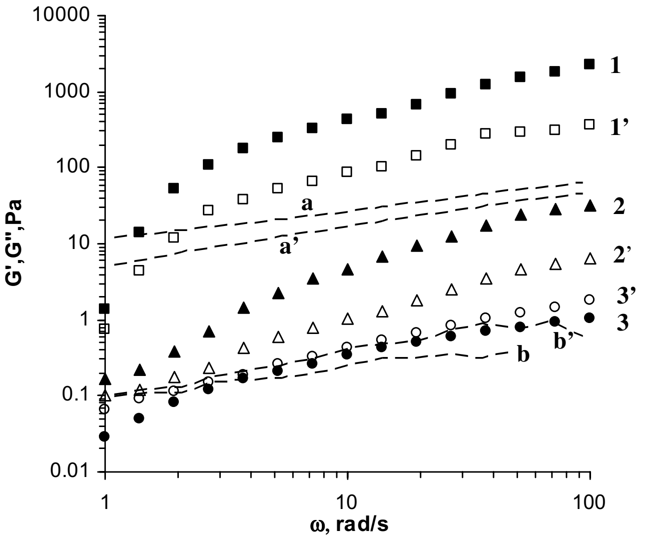

Fig. 11. G' (solid) and G'' (hollow) of pregelatinised starch + κ-carrageenan mixtures of total polymer concentration 3% at 60 °C of different compositions κ-car:pgs = 2:1 (1 and 1′), 1:2 (2 and 2′), 1:5 (3 and 3′). Dashed lines correspond to G' (a and b) and G'' (a′ and b′) of 3% initial components: κ-car (a and a') and pgs (b and b').

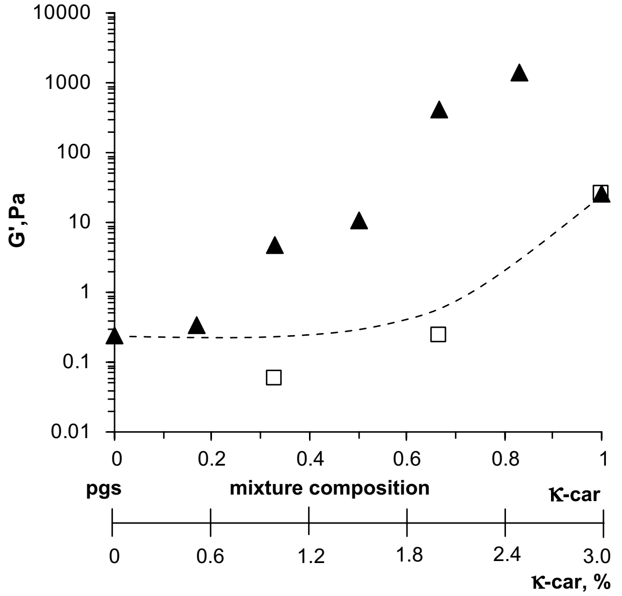

Fig. 12. Elastic modulus of pregelatinised starch + κ-carrageenan mixtures (solid) of total polymer concentration 3% at $\omega = 10$ rad/s and 60 °C as a function of mixture composition. Hollow points are G' values of carrageenan alone at its corresponding concentration in the mixture, taken from Fig. 9; dashed line is an approximate additive dependence.

showed higher elastic modulus and was less frequency dependent in the same conditions (Tecante & Doublier, 1999; Loisel et al., 2000). κ-carragenan of 3% at 60 °C is also a weak gel, but both systems are pourable fluids. For $C_{car} < 3\%$ κ-carrageenan shows a liquid-like behaviour with $G' < G''$ and strong frequency dependence.

An example of elastic and viscous moduli of mixtures with total polymer concentration 3% at 60 °C are presented in Fig. 11 together with G' and G'' of the initial components at 3%. In all mixtures containing more than 0.5% of κ-carrageenan, the elastic modulus (filled points) dominates the viscous one (open points). G' is frequency-dependent and thus these mixtures can be considered as weak gels. Visco-elastic properties of the mixture containing 0.5% of κ-carrageenan, κ-car:pgs = 1:5 (see 3 and 3′ in Fig. 11), coincide with the ones of pure 3% pregelatinised starch (b and b′ in Fig. 11): it is close to its gelation point, the presence of κ-carrageenan practically does not play any role. On the contrary, mixtures containing more than 2.0% of κ-carrageenan show G' higher than that of 3% carrageenan alone. This can be clearly seen in Fig. 12 where an example of G' at 10 rad/s is plotted as a function of mixture composition together with G'_{car} and approximate additive dependence (dashed line). Because starch elastic modulus is very low and thus difficult to measure at $C_{pgs} < 3\%$, the additive dependence, on one hand, cannot be built in a proper way, but on the other hand, it should not be very different from the elastic modulus of κ-carrageenan alone. Fig. 12 shows that higher is carrageenan concentration in the mixture, more G' deviates from the additive dependence. Above $C_{car} > 0.5\%$ (mixture composition κ-car:pgs = 1:5) carrageenan dictates the rheological (elastic) behaviour and mixture G' is significantly reinforced even in the hot state, contrary to κ-carrageenan + cross-linked waxy corn starch system (Tecante & Doublier, 1999) but similar to κ-carrageenan + amylose mixture (Tecante & Doublier, 2002).

3.3.3. Visco-elastic properties of the mixture and the initial components at 20 °C

In this section, visco-elastic properties of the initial components and their mixtures at 20 °C are investigated. The elastic and viscous moduli were recorded for different angular frequencies. Figs. 13 and 14 show the results obtained for the initial components just after cooling to 20 °C, and Fig. 15 – G', G'' of mixtures and G' of κ-carrageenan alone, all aged for two days at 20 °C in the rheometer. Ageing was chosen mainly to increase starch elastic properties: it resulted in doubling of G'. However, the values of starch moduli even after ageing were too small (for example, around 0.4 Pa at 1 rad/s) as compared with the ones of κ-carrageenan or mixtures, and thus are not shown. For κ-carrageenan, ageing induced a slight G' increase, not more than by 20% as compared with the values shown in Fig. 13.

The mechanical spectra for pure components demonstrate two different behaviours. For κ-carrageenan alone (Fig. 13) a strong gel is obtained whatever the concentration: $G' > G''$ and moduli are independent of frequency in the range analysed. For pregelatinised starch, the behaviour at 20 °C (Fig. 14) is almost the same as at 60 °C (Fig. 9): the moduli are frequency dependent and gelation occurs at starch concentration around 2–3% ($G' = G''$). The values of starch moduli are negligible compared to κ-carrageenan alone, for example at 3% and 1 rad/s $G'_{pgs} = 0.18$ Pa and $G'_{car} = 2580$ Pa.

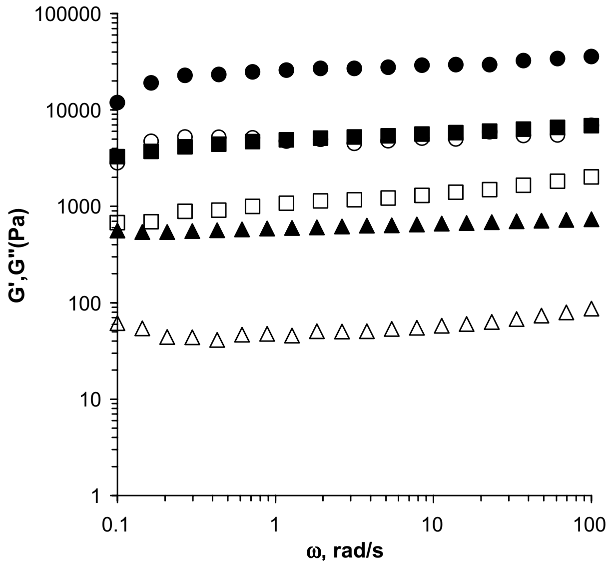

Fig. 13. G' (solid) and G'' (hollow) of κ-carrageenan as a function of frequency at 20 °C for different concentrations: 3% (● and ○), 2% (■ and □) and 1% (▲ and Δ).

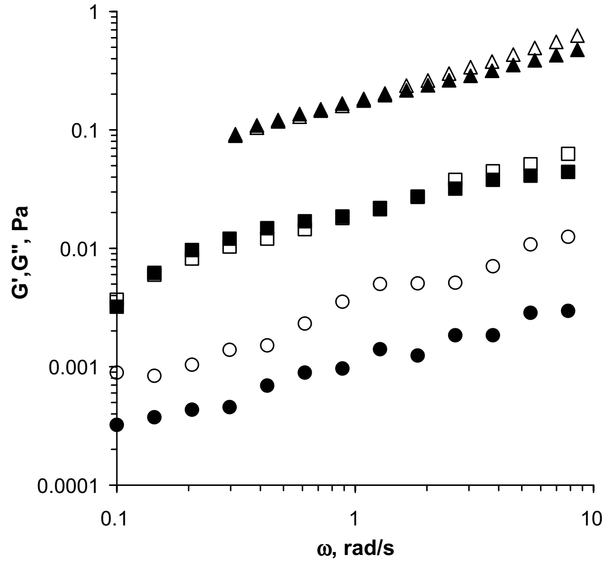

Fig. 14. G' (solid) and G'' (hollow) of pregelatinised starch as a function of frequency at 20 °C for different concentrations: 3% (▲ and Δ), 2% (■ and □) and 1% (● and ○).

For 2-day-old mixtures, results on Fig. 15 indicate that strong gels are obtained whatever the composition. G'' values are not shown in order not to overload the graph; they were lower than G' by one order of magnitude (see Fig. 16 where G' and G'' are given as a function of mixture composition at $\omega = 1$ rad/s). The overall behaviour of the mixture is dominated by κ-carrageenan with $G'_{\text{mixture}} \geqslant G'_{\text{car}}$ (Fig. 16), except at low carrageenan concentrations $C_{\text{car}} < 0.5\%$ (composition κ-car:pgs = 1:5), where elastic modulus is slightly lower for mixture than for κ-carrageenan alone, whatever the frequency (Fig. 15).

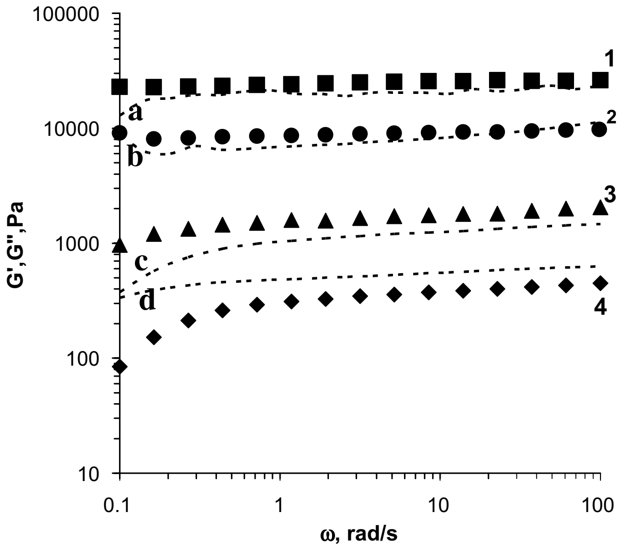

Fig. 15. Elastic modulus of pregelatinised starch + κ-carrageenan mixtures (solid) with total polymer concentration 3% at 20 °C aged for 2 days of different compositions κ-car:pgs = 5:1 (1), 2:1 (2), 1:2 (3), 1:5 (4) and G' for κ-car alone (dashed lines) at 2.5% (a), 2% (b), 1% (c) and 0.5% (d).

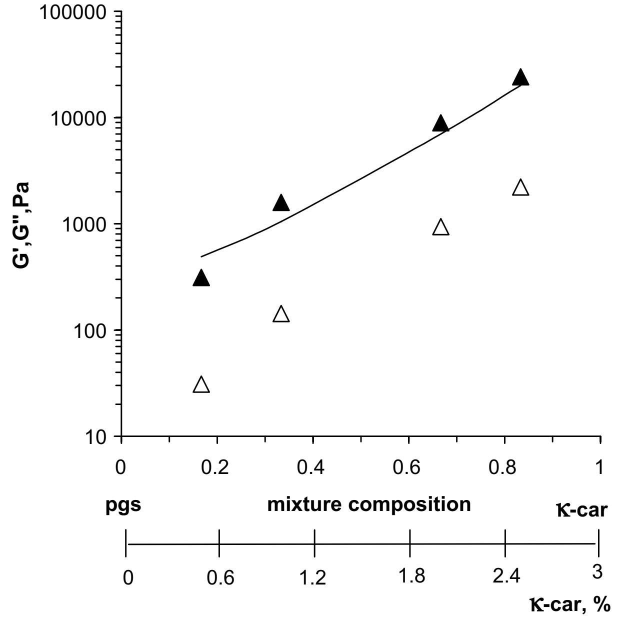

Fig. 16. G' (solid) and G'' (hollow) of pregelatinised starch + κ-carrageenan mixture as a function of mixture composition with total polymer concentration 3% at 20 °C and frequency 1 rad/s aged for two days; line corresponds to G'_{car}.

4. Discussion

Rheological properties of solutions of pregelatinised starch, κ-carrageenan and their mixtures in the dilute and semi-dilute states have been described above. Here we shall focus on the comparison of mixture properties with the corresponding additive values, or in other words, on the interpretation of results presented in Figs. 3, 8, 12 and 16.

Two important aspects in the structural organisation of κ-carrageenan + pregelatinised starch mixtures have to be taken into account. The first is that amylose and κ-carrageenan show a slight incompatibility, without any phase separation in the liquid state. We could thus expect that after being mixed at elevated temperature and then cooled down, phases should separate during gelation. A co-network of a strong carrageenan gel and a weak amylose gel with granules incorporated is formed. The phase separation in carrageenan/amylose mixtures in the gel state was already suggested by Tecante and Doublier (2002), who demonstrated, using turbidimetry, that gelation time of carrageenan + amylose mixture differs from the one of pure amylose solution. The same authors also reported that amylose gels were reinforced or weakened depending on the amount of carrageenan added. They attributed these phenomena to the phase separation and phase inversion in carrageenan/amylose solutions.

The second aspect is that non-dissolved starch granules are present in κ-carrageenan + amylose mixture. Carrageenan does not penetrate into the granules, because it is strongly incompatible with amylopectine: being mixed these solutions are separating. We prepared some mixtures of carrageenan and amylopectine solutions of concentrations and proportions studied rheologically, and we saw a clear phase separation. This non-penetration leads to a so-called "excluded volume effect": an increase of local carrageenan concentration due to the presence of swollen starch granules. This phenomenon was discussed by Tecante and Doublier (1999), for κ-carrageenan + crosslinked waxy corn starch system.

Such a complicated organisation results in a different rheological response depending on the state of the mixture (gel or solution) and on mixture composition. Fig. 8 (dependence of mixture viscosity on its composition at 60 °C) shows that at high starch concentration in the mixture, i.e. at mixture compositions lower than 0.5, mixture viscosity η_{mix} is higher than the corresponding additive values $\eta_{\text{add B}}$, and at low starch concentrations $\eta_{\text{mix}} \approx \eta_{\text{add B}}$. The reason is that higher is starch concentration in the mixture, and thus larger is the amount of granules, more noticeable is the excluded volume effect.

The elastic properties of κ-carrageenan + pregelatinised starch mixture at 60 °C (Fig. 12) show the overall similar trend – higher mixture G'_{mix} than the additive G'_{add}, but the difference between G'_{mix} and G'_{add} is much more pronounced than between η_{mix} and $\eta_{\text{add B}}$ and appears at other mixture compositions. The reason of $G'_{\text{mix}} > G'_{\text{add}}$ is the same as for viscosity increase: the excluded volume effect due to the presence of starch granules. It should also be kept in mind that at 60 °C only one of the components, κ-carrageenan, exhibits gel-like properties, and this occurs only when a certain carrageenan concentration, around 3%, is reached (Fig. 10). Thus the synergistic effect is shifted towards higher carrageenan concentrations in the mixture. We can thus conclude that in the liquid state the visco-elastic properties of the mixtures are determined by carrageenan and this is due to the presence of undissolved starch granules leading to the excluded volume effect.

Surprisingly, we did not obtain any synergistic effect when the system is in a real gel state, at 20 °C aged for 2 days (Fig. 16). Tecante and Doublier (2002) reported a strong reinforcement of amylose gel due to the addition of carrageenan when the latter was in the continuous phase and formed a strong network. We assume that in our case the undissolved granules that agglomerated during gelation leaded to the formation of an inhomogeneous system and "erased" the expected reinforcement.

5. Conclusions

The properties of aqueous dilute and semi-dilute pregelatinised starch and its mixtures with κ-carrageenan were studied in details at 60 °C and 20 °C. Pregelatinised starch cooked at 90 °C is composed of amylose solution and undissolved granules that occupy around 6% of the volume for 1% starch system. In dilute state, mixtures of amylose and κ-carrageenan demonstrated a slight incompatibility. In semi-dilute regime, the viscosity and elasticity of 3% mixtures at 60 °C were higher than the corresponding calculated additive values, indicating κ-carrageenan concentrating due to granules excluded volume effect. At 20 °C, practically no increase of the elastic modulus was recorded because of the agglomeration of non-dissolved starch granules and the formation of highly inhomogeneous gels. The presence of the undissolved granules thus leads to the increase of visco-elastic characteristics of the mixture in the liquid state and to their decrease in the gel state.

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