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Effects of iota-carrageenan on the rheological properties of starches

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Abstract

The phycocolloid iota-carrageenan (ι-CAR) was extracted from the Brazilian seaweed *Meristiella gelidium*. At a concentration of 5 mg ml^{-1} it was mixed with solutions of common corn starch (CS), high amylose starch (MS), waxy corn starch (WS) and YS starch (YS), to give systems at a final concentration of 25 g l^{-1}, which were subjected to rheological measurements. Each mixture gave rise to a different behaviour under dynamic rheological conditions showing a distinct degree of interaction between ι-CAR and the starch. The presence of ι-CAR in ι-CAR-WS, ι-CAR-MS and ι-CAR-CS systems resulted in synergy manifested as enhancements in thermal stability (absence of hysteresis), resulting in thermoreversible gels softer and more stable between 45 and 85 °C. In the ι-CAR-YS system, the synergistic effect occurred as an improvement in solid character, increasing the elastic nature of the gel, suggesting that the structural characteristic of YS, more regular structure with amylopectin having a low molar mass, can contribute to enhanced intermolecular binding.

Keywords: Carrageenans; Starches; Gels; Rheological properties; *Meristiella gelidium*; Solieriaceae

1. Introduction

The technological interest in polysaccharides mixtures, in particular between starch and non-starch like polysaccharides, is motivated by the ability of mixtures of these macromolecules to influence gelation capacity, emulsification, viscosity modification, stabilization of suspensions, and ability to retain water, thus providing attractive functional properties (Medina-Torres, Brito-De La Fuente, Torrestiana-Sanchez, & Alonso, 2003).

Red seaweeds produce different types of sulfated galactans, as agarans, (Duarte, Noseda, Cardoso, Túlio, & Cerezo, 2002; Duarte et al., 2004; Gonçalves, Ducatti, Duarte, & Noseda, 2002; Noseda, Viana, Duarte, & Cerezo, 2000), carrageenans (Chiovitti, Bacic, Craik, Kraft, & Liao, 2004; Falshaw, Furneaux, & Stevenson, 2005; Faria-Tischer et al., in press; Noseda & Cerezo, 1995; Viana, Noseda, Duarte, & Cerezo, 2004) and D/L-hybrid (Matsuhiro et al., 2005; Takano, Shiomoto, Kamei, Hara, & Hirase, 2003; Zibetti, Noseda, Cerezo, & Duarte, 2005).

Among food polysaccharides, carrageenans are largely used as additives frequently in combination with starches, such as native maize starch, in gelled dairy desserts (Tye, 1988). Starch imparts body and mouthfeel to the product, while carrageenan provides the appropriate texture, namely firm and brittle with kappa-carrageenan, soft and elastic with iota-carrageenan (Zobel & Stephen, 1995).

The structure of carrageenan is based on a disaccharide backbone of alternating 3-linked β-D-galactopyranose and 4-linked α-D-galactopyranose units, namely G and D units, respectively, Knutsen's nomenclature (Knutsen, Mylabodski, Larsen, & Usov, 1994). They can be recognized according to the position of sulfation (S) and the cyclization of the D units to form an anhydro ring (A). Industrial representatives are the gelling kappa- (G4S-DA), iota-carrageenan (G4S-DA2S) and non-gelling lambda-carrageenan (G2S-D2S,6S) (Van de Velde, Knutsen, Usov, Rollema, & Cerezo, 2002; Villanueva, Mendoza, Rodrigueza, Romero, & Montaño, 2004).

In general, addition of hydrocolloids of phycological origin accelerates gel formation of native maize starch. This occurs with kappa-carrageenan, although it is retarded with iota-carrageenan (Eidam, Kulicke, Kuhn, & Stute, 1995). During heating of kappa-carrageenan in the potassium-form with cross-linked waxy corn starch, starch granules were more swollen and the viscoelastic behaviour of the mixture is less

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when compared to that of starch alone (Loisel, Tecante, Cantoni, & Doublier, 2000). Similarly, it was found that addition of starches accelerated gelation of kappa-carrageenan, possibly due to coupling effects between kappa-carrageenan and soluble starch molecules, and that gelation of iota-carrageenan may be retarded by the addition of rigid starch granules or accelerated when soluble granules of starch were added (Lai, Huang, & Lii, 1999). Tecante and Doublier (2002) demonstrated that the storage modulus depends strongly on the kappa-carrageenan concentration in mixtures with amylose. This points to the existence of at least two different conditions under which they form the continuous and disperse phase depending on the concentration of both.

The chemical structure of iota-carrageenan differs from that of kappa-carrageenan by the presence of an additional sulfate group in the 3,6-anhydrogalactosyl residue, which confers a more hydrophilic character to the molecule (Renn, 1997). The differences in the textural properties of iota- and kappa-carrageenan gels reflect the differences in their structures: iota-carrageenan gels consist of double helices with little or no aggregation, which renders them flexible and soft. In contrast, kappa-carrageenan gels consist of aggregated helices, these molecules do not gel without any aggregation, the kappa gel being relatively brittle and hard (Stanley, 1990).

When compared to other food biopolymers such as xanthan and gelatine, the number of dynamic oscillatory studies on carrageenans are still limited (Chen, Liao, & Dunstan, 2002) and in combination with starches, most of them have focused on kappa-carrageenan (Autio, Vesterinen, & Stolt, 2002; Lai et al., 1999; Tecante & Doublier, 2002; Verbeken, Thas, & Dewettinck, 2004). The studies on iota-carrrageenan were mainly based on systems containing casein micelles and dynamic oscillatory analyses were carried out in mixtures with gellan (Rodríguez & Tecante, 1999), mucilage gum (Medina-Torres et al., 2003), silica (Shchipunov, 2003) and with various proteins (Galazka, Dickinson, & Ledward, 2001).

As starches and carrageenans can be used in mixed systems in order to obtain desirable functional properties, we have investigated the gelation ability of mixtures of iota-carrageenan extracted from *Meristiella gelidium* (Faria-Tischer et al., in press) and starches with different levels of amylose. The rheological characteristics of the mixtures are compared and this appears attractive, since there are a high number of available seaweeds in Brazil known to be potential sources of carrageenans (Saito & Oliveira, 1990), as well as many starches from different sources.

2. Materials and methods

2.1. Algal material

Specimens of *Meristiella gelidium* were collected in Pitimbu, Paraíba State, on the northeast coast of Brazil. The iota-carrageenan fraction (M1) was obtained by aqueous extraction (1 g% w/v) at 25 °C for 15 h as previously described (Faria-Tischer et al., in press) and in this work was denominated ι-CAR.

Four different starches were investigated, namely common corn starch (CS), corn starch rich in amylose (MS), waxy corn starch (WS) and yam starch (YS). Corn Products Brazil Ingredientes Industriais Ltda, Balsa Nova, supplied MS and WS; YS was supplied by Prof. M.V. Grossmann, Universidade Estadual de Londrina, State of Paraná, Brazil; and CS were purchased from Sigma Chemical Co.

2.2. Chemical analysis

Total carbohydrate was assayed by the phenol–sulfuric method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956) using glucose as the standard. Protein was determined by the method of Hartree (1972), ash and moisture by that of Zobel and Stephen (1995), and amylose content was by that of Chrastil (1987).

2.3. Ion content

Sample of carrageenan (ι-CAR) was analysed for its ion content using atomic absorption spectroscopy in equipment Perkin Elmer, model 4100. This analysis was performed in the Instituto de Tecnologia para o Desenvolvimento-LACTEC, Curitiba, State of Paraná, Brazil.

2.4. Solution preparation

Two different sample preparations were applied and only fresh polymer solutions were used. The mixtures of starches (CS, MS, WS and YS) and carrageenan were prepared in closed tubes at a total concentration of 2.5% (w/v). (I) Initially the carrageenan ($5\ \mathrm{g\ l^{-1}}$) was solubilised for 30 min in distilled water with magnetic stirring at 25 °C. After solubilisation, the starch ($20\ \mathrm{g\ l^{-1}}$) was added to the solution of carrageenan to a total volume not greater than 5 ml, and the mixture was dispersed at 25 °C by magnetic stirring for 1 h. In the isolated systems the starches ($25\ \mathrm{g\ l^{-1}}$) were solubilised at 25 °C by magnetic stirring for 1.5 h. (II) Considering that the molecular interactions among other factors depend on the swelling-solubility of starches, the YS plus (ι-CAR mixture was also prepared with prior heating at 85 °C. The red algal polysaccharide ($5\ \mathrm{g\ l^{-1}}$) was solubilised in distilled water for 30 min under magnetic stirring at 25 °C. After solubilisation the starch ($20\ \mathrm{g\ l^{-1}}$) was added and the mixture was then dispersed at 85 °C under magnetic stirring for 1 h. Similarly, YS alone ($25\ \mathrm{g\ l^{-1}}$) was solubilised at 85 °C under magnetic stirring for 1.5 h. Then, in preparations I and II, the material was sequentially autoclaved for 30 min, refrigerated for 18 h and maintained at 25 °C, ready to begin the rheological tests at this temperature.

2.5. Rheological measurements

Oscillatory analyses were carried out using a model RS 75 Haake Rheometer with C-60/2° and pp35/Ti sensor. For constant temperature studies at 25 °C a BC-5 Haake model bath was employed and the temperature was carried out with a Peltier system with heating (5–85 °C) and cooling gradients (85–5 °C) at a rate of 0.066 °C s^{-1}. The viscoelastic properties, storage moduli (G') and loss moduli (G'') were determined using small amplitude oscillatory shear flows at frequencies ranging from 0.05 to 10 Hz.

2.6. Sweelling studies

The pastes of YAM (25 g l^{-1}) and ι-CAR (5 g l^{-1})-YAM (20 g l^{-1}) were dried (in the disc form), accurately weighed and placed in a small bottle containing water bath at 25 °C. The weight of hydrating samples was measured after 15 min, after which no difference in the weight was observed. The excess swelled water was removed by gentle blotting and the weight of swollen hydrogels was calculated by subtracting the boat weight from the total weight (Polnok, Verhoef, Borchard, Sarisuta, & Junginger, 2004). The experiment was repeated three times. The swelling ratio (Q) is defined as

$$Q = W_s - W_d \qquad (1)$$

where W_s is the weight of the swollen hydrogel and W_d is the weight of dried hydrogel.

2.7. Optic microscopy analysis

The mixture ι-CAR (5 g l^{-1})–YAM (20 g l^{-1}) was prepared as described in Section 2.4. The methylene blue solution at 10% and iodine dyes were used to identify carrageenan and starch, respectively. Sections were photographed using an Olympus CH30RF100 compound microscope (Olympus Optical Co. Ltd, Japan).

3. Results and discussion

3.1. Chemical analyses

The chemical composition of the starch samples, in terms of carbohydrate, protein, moisture, ash and amylose, are shown in Table 1. It can be seen that different levels of amylose exist ranging from 27.5 to 66% (Table 1). These are important to evaluate the real capacity for the model starches to interact with carrageenan, since this is based on the proportion of amylose to amylopectin.

A cation analysis demonstrated that besides Na^+ (30 mol%), Ca^{2+} (6.2 mol%) and Mg^{2+} (6.8 mol%), ι-CAR contains mainly a potassium ion (K^+ 57 mol%). A main K^+-form was also detected in samples of iota-carrageenan prepared from *Eucheuma denticulatum*, those of kappa-carrageenan from *K. alvarezii*, and from industrial carrageenans, having K^+ to Na^+ close to 2.33 mol.% (Parker, Brigand, Miniou, Trespoey, & Vallée, 1993), and to the iota-carrageenan from *M. gelidium* was determined as 1.90.

3.2. Flow behaviour of starches and mixed starches-ι-carrageenan

The viscoelastic behavior was determined under dynamic conditions for starches and ι-CAR-starch mixtures over a frequency range of 0.05–10 Hz. Linear G^* deformations of less than 5% were observed under stresses lower than 0.5 Pa (data not shown). Fig. 1 indicates the variation of G' and G'' as a function of frequency under 1% deformation at 25 °C for CS (25 g l^{-1}) and for the ι-CAR (5 g l^{-1})–CS (20 g l^{-1}) mixture. The mechanical spectrum of CS (25 g l^{-1}) (Fig. 1A) shows that the storage modulus (G') was at least three times greater than the loss modulus (G''), at all examined frequencies, characteristics of a gel behaviour, which showed a dependence of the frequency above 1 Hz. The presence of ι-CAR (5 g l^{-1}) altered the gel structure of CS (20 g l^{-1}), when compared with result of CS alone, since the mixture gave rise to a viscoelastic solution (Fig. 1B), as shown by a crossover of G' and G'' at 0.2 Hz.

Similar behaviour was also obtained with MS alone and also in its mixture with ι-CAR (5 g l^{-1}) (data not shown). The difference between the moduli in the paste formed by MS (25 g l^{-1}) characterizes this system as a weaker gel, and after addition of carrageenan the physical properties were modified and a viscoelastic solution was formed. For WS (25 g l^{-1}) and mixture ι-CAR (5 g l^{-1})–WS (20 g l^{-1}), both moduli were dependent on the frequency, typical of a viscoelastic solution (data not shown). In mixtures with CS or MS, presence of ι-CAR (5 g l^{-1}) altered the viscoelasticity, when compared with each of the starches; with WS, the mixture gave rise to

Table 1
Chemical composition (g%) of starch samples

Sample	Carbohydrate[a]	Protein[b]	Moisture[c]	Ash[c]	Amylose[d]
MS[e]	91.5	0.19	8.5	0.045	66.0
WS[e]	89.0	0.26	9.0	0.04	0
YS[f]	88.0	0.1	12.9	0.09	36.0
CS[e]	88.0	0.2	10.7	Tr	27.5

[a] Method of Dubois et al. (1956).
[b] Method of Hartree (1972).
[c] Method of Zobel and Stephen (1995).
[d] Method of Chrastil (1987).
[e] Described by Freitas et al. (2003).
[f] Described by Freitas, Paula, Feitosa, Rocha, and Sierakowski (2004).

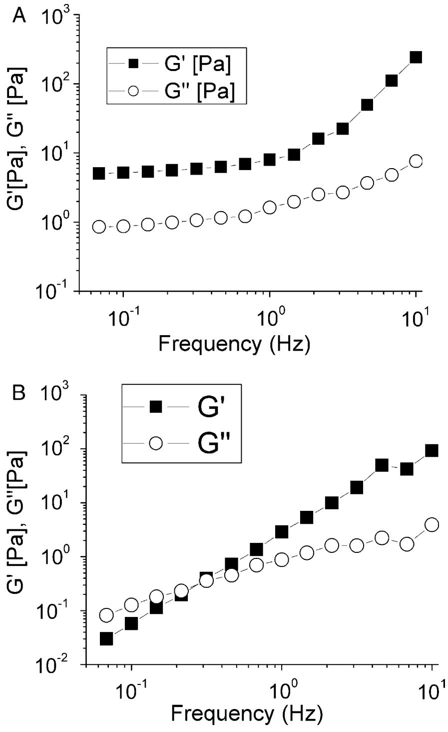

Fig. 1. Frequency dependence of the storage (G'), loss modulus (G'') at deformation of 1% for: (A) CS (25 g l^{-1}) and (B) ι-CAR (5 g l^{-1})–CS (20 g l^{-1}) mixture.

a more viscoelastic solution. In all rheograms of the mixtures, the moduli were frequency-dependent and an overlap of G' occurred at frequencies greater than 0.2 Hz.

The rheograms of YS alone (25 g l^{-1}) and ι-CAR (5 g l^{-1}) –YS (20 g l^{-1}) mixture showed a different behaviour, when compared to other starches. The mechanical spectrum of YS showed typical gel behaviour, with G' being greater than G'' and with the elastic modulus less dependent on frequency. An almost identical behaviour was observed with the ι-CAR-YS mixture. The tan δ plot (Fig. 2) indicated that the values are greater for starch alone (0.21 at 1 Hz), thus characterising the paste as a strong gel. In the mixture, the value of tan δ was lower (0.14 at 1 Hz), showing that the gel strength is greater in the mixture, as a result of a positive synergistic effect, arising from the presence of ι-CAR in this system.

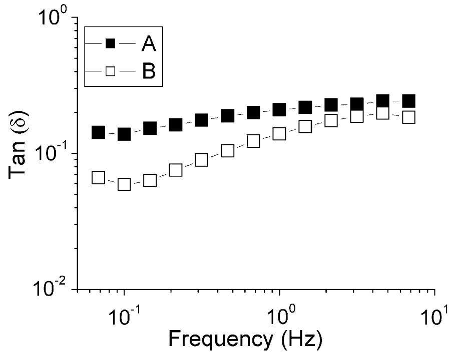

Fig. 2. Frequency dependence of tan δ on: (A) YS (25 g l^{-1}) and (B) ι-CAR (5 g l^{-1})–YS (20 g l^{-1}) mixture. At deformation of 1%.

From the above it appears that, ι-CAR does not interact to the same degree with CS, MS and WS starches, and presence of hydrocolloid weakens the network formed. But, with YS at the same concentration its presence resulted in an increase of the rigidity of the gel.

Since, a greater interaction was observed in the ι-CAR (5 g l^{-1})–YS (20 g l^{-1}) system, we sequentially evaluated the interaction between these two polymers, heating them together at 85 °C, as described in Section 2.6 (II). The pre-heating of these polysaccharides permitted a better solubilisation of the starch and increased the interaction between the molecules, as shown in Fig. 3. The rheograms demonstrated the gel behaviour of the starch alone and the mixture, but in the mixture the moduli were greater showing a better interaction.

It is generally accepted that the aqueous media of cooked starch can be described as biphasic systems, formed by a continuous and a disperse phase. In many practical situations, swollen starch particles are the dominant structural feature (Steeneken, 1989). In mixed systems, the situation remains the same, but a further complication arises since the continuous phase is itself an aqueous mixture of amylose and added hydrocolloid; without considering the possible solubilisation of the amylopectin during pasting (Tecante & Doublier, 1999). Depending on the ratio of the biopolymers and the gelling technique, one of the biopolymers forms a continuous phase into which the other is dispersed, or two continuous networks in a bicontinuous system can be formed (Autio et al., 2002). Tecante and Doublier (2002) observed that, in mixtures of

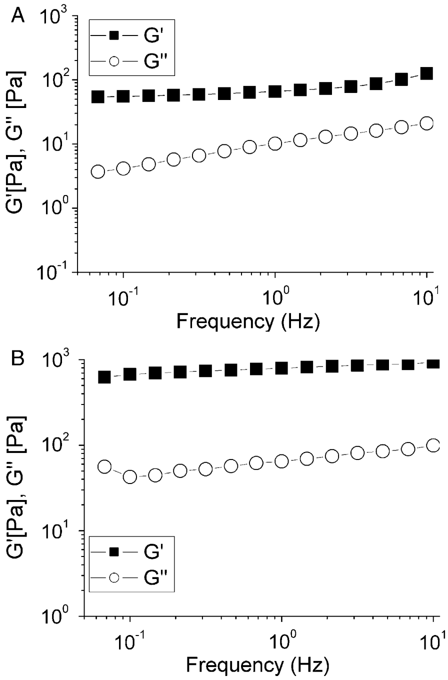

Fig. 3. Frequency dependence of the storage (G'), loss modulus (G'') at deformation 1% for: (A) YS alone (25 g l^{-1}) pre-heated at 85 °C and (B) ι-CAR (5 g l^{-1})–YS (20 g l^{-1}) mixture pre-heated together.

potato amylose (1.34 wt%) and kappa-carrageenan at concentrations between 0.3 and 0.5%, the amylose is the dispersed with carrageenan being the continuous phase.

Carrageenan gelation occurs more or less immediately as a function of helix formation, although this does not always lead to gelation (Piculell, Borgstrom, Chronakis, Quist, & Viebke, 1997). In agreement with Rochas and Rinaudo (1980), a 0.5% concentration of carrageenan is sufficient to promote gelation and under this condition the rheological behaviour of carrageenan is dominant. Considering that the conditions for gelation of both kappa- and iota-carrageenan are closely related to those necessary for the helix–coil transition and that this conformational transition occurs as a function of temperature (Rees, Morris, Thom, & Madden, 1982), we have evaluated the effect of temperature on the rheological behaviour of these mixtures, since its variation could improve the interaction between the helices (starch and carrageenan).

3.3. Effect of temperature on the viscoelastic behaviour of gels

Melting and viscoelastic behaviour may differ greatly depending on the origin of the biopolymer and gelling conditions. If there are no specific interactions between the two components, the melting transitions maintain their positions in the composite gels. Since, a variation of temperature can influence the interaction between the polymers, after observing the variation of the moduli as a function of frequency, we examined the influence of temperature on viscoelastic and melting behaviour of the starch pastes alone and in mixtures with iota-carrageenan.

The behaviour of gel from corn starch rich in amylose (MS 25 g l^{-1}) showed that it did not melt, but in a cooling procedure there was a proportional decrease of the both moduli (G' and G'') at temperatures lower than 50 °C, showing that it was unstable to thermal variations (Fig. 4A). However, a substitution of 20% of the MS by ι-CAR improved strength and thermal stability of the gel (Fig. 4B). It can be observed that variation of temperature influences the interaction between polysaccharides, since there was greater synergistic effect in the temperature range from 45 to 85 °C (a greater difference between the moduli), and the presence of ι-CAR also resulted in an improvement of gel characteristics, such as better gel resistance to temperature variation as demonstrated by the lack of hysteresis. These results show that a starch paste alone is highly susceptible to temperature and in the presence of ι-carrageenan there is a marked interaction, resulting in a more stable gel, compared to MS alone. Very similar results were observed in binary system formed by ι-CAR-CS (data not shown).

The next paste analysed was that of WS (25 g l^{-1}) and the effect of temperature on its viscoelastic behaviour, as well as on the mixture with ι-CAR, as shown in Fig. 5. WS alone did not melt between 5 and 85 °C and no hysteresis was observed. The rheogram of the paste formed by ι-CAR (5 g l^{-1})–WS (20 g l^{-1}), is distinct from that observed for a xyloglucan with amylopectin interaction (Freitas, Gorin, Neves, & Sierakowski, 2003), demonstrated an interaction, shown by an increase of the moduli (Fig. 5B). In addition, the presence of iota-carrageenan did not modify the thermal stability of the mixture, since it did not melt, and a greater difference between the moduli was found between the temperature range of 50–85 °C.

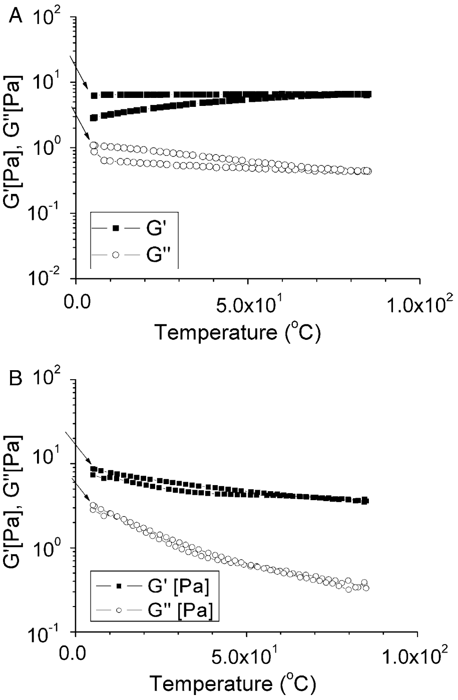

Fig. 4. Temperature dependence of the storage (G'), loss modulus (G'') for: (A) MS (25 g l^{-1}) and (B) ι-CAR (5 g l^{-1})–MS (20 g l^{-1}) mixture. At 1 Hz and deformation of 1%. (→) shows the initial heating.

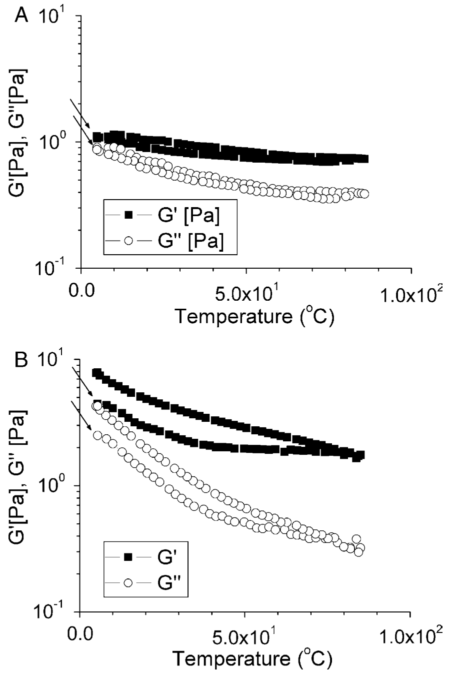

Fig. 5. Temperature dependence of the storage (G'), loss modulus (G'') for: (A) WS (25 g l^{-1}) and (B) ι-CAR (5 g l^{-1})–WS (20 g l^{-1}) mixture. At 1 Hz and deformation of 1%. (→) shows the initial heating.

Apparently, in this case, a heating in the rheometer on stress (σ) of 0.6 Pa was necessary to give a more stable and rigid complex, because high values of both moduli (G' and G'') were obtained on heating from 5 to 85 °C and subsequent cooling to 5 °C.

Although, the influence of ι-CAR in mixtures with MS and WS demonstrate strong interaction, reflecting the susceptibility of hysteresis and improvement of storage modulus, some differences can be observed. The increase of the moduli was proportionally equal for the mixtures with MS or WS, the interaction between iota-carrageenan and WS was apparently greater during cooling, suggesting strong interaction of both the starch and carrageenan helices, and this stable interaction (without thermal hysteresis) was not disrupted by reheating from 5 to 85 °C (data not shown). But in the mixture containing MS, the rheological characteristics and apparently the interaction were independent of heating or cooling.

Between ι-CAR ($5\,\mathrm{g\,l^{-1}}$)–YS ($20\,\mathrm{g\,l^{-1}}$) and YS alone ($25\,\mathrm{g\,l^{-1}}$) (Fig. 6), there was formation of a stable gel over the temperature range of 5–85 °C, as represented by the higher value of elastic modulus (G'), compared to the loss modulus (G''). However, a thermal hysteresis can be observed, as demonstrated by variation of the moduli in the procedure heating–cooling, showing that there was aggregation of the starch helices after heating.

When we analyse the behaviour of the system YS and ι-CAR-YS prepared with prior heated at 85 °C, the rheograms (Fig. 7) were very similar to those shown in Fig. 6. However, in this case a greater interaction was obtained with the mixture, as observed by an increase in the moduli. The pre-heating probably gave rise to increased starch solubility and thus improved its interaction with ι-CAR.

This mixture is gelatinised. But one can observe a dissociation of junction zones after heating within the gel networks in both systems (starch alone and mixture), which is reflected by thermal hysteresis. A commonly observed indication of association of carrageenans is the occurrence of thermal hysteresis in the conformational transition, so that the coil-to-helix transition occurs in a temperature interval lower than that of the helix-to-coil transition. The cooling transition is generally believed to reflect the equilibrium between coils and helices in solution, whereas the heating transition reflects the increased stability of associated helices after cooling (Picullel, 1995). Our results show that interactions between polysaccharides are more favourable after heating, suggesting that in the cooling process the helices cooperate better.

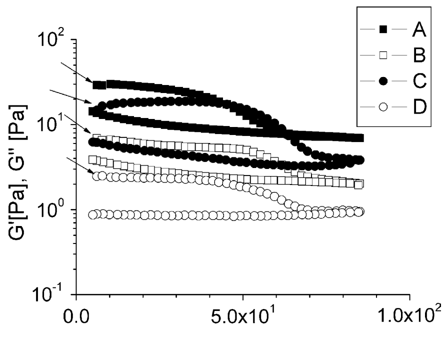

Fig. 6. Temperature dependence of: (A) storage modulus (G') and (B) loss modulus (G'') of ι-CAR ($5\,\mathrm{g\,l^{-1}}$)–YS ($20\,\mathrm{g\,l^{-1}}$) mixture and (C) storage modulus (G') and (D) loss modulus (G'') of YS alone ($25\,\mathrm{g\,l^{-1}}$). At 1 Hz and deformation of 1%. (→) shows the initial heating.

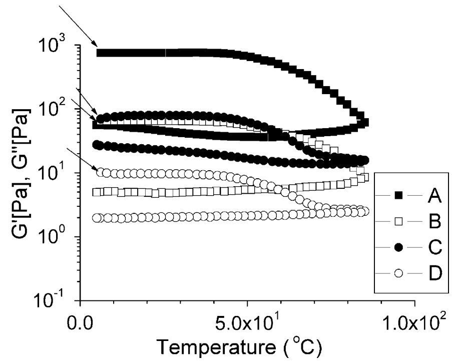

Fig. 7. Temperature dependence of: (A) storage modulus (G') and (B) loss modulus (G'') of ι-CAR ($5\,\mathrm{g\,l^{-1}}$)–YS ($20\,\mathrm{g\,l^{-1}}$) mixture, and (C) storage modulus (G') and (D) loss modulus (G'') of YS alone ($25\,\mathrm{g\,l^{-1}}$) with previous heating at 85 °C. At 1 Hz and deformation of 1%. (→) shows the initial heating.

To characterise the rheological properties of the pre-heated preparation of YS alone and with ι-CAR-YS in a better way, we have performed Cox-Merz experiments, where the Cox-Merz relationship is shown in Eq. 2

$$\eta^*(\omega) = \eta(\dot{\gamma})\omega = \dot{\gamma} \tag{2}$$

where η^* is the complex viscosity, η is the apparent shear viscosity, ω is the frequency of oscillation (rad/s), and $\dot{\gamma}$ is the shear rate (1/s). If complex viscosity plotted against the frequency is consistently higher than the apparent viscosity plotted against shear rate, elastic gel-like structure exists (Bot, Smorenburg, Vreeker, Pâques, & Clark, 2001; Han, Campanella, Guan, Keeling, & Hamaker, 2002; Martin, Freitas, Obayashi, & Sierakowski, 2003). The Cox-Merz plots show that in both samples the complex viscosity is greater than the apparent viscosity (Fig. 8), confirming the systems as containing really strong gels. But the plots also demonstrate that the elastic nature observed as the ratio of complex viscosity to apparent viscosity is much higher than in the mixture, thus showing a more solid character for this system.

The swelling experiments demonstrated that the presence of ι-CAR affected the swelling ratio (Q) of the hydrogel. It was found that its value for YAM ($25\,\mathrm{g\,l^{-1}}$) and the mixture ι-CAR ($5\,\mathrm{g\,l^{-1}}$)–YAM ($20\,\mathrm{g\,L^{-1}}$) as 0.8 ($\pm$0.12) and 2.4 ($\pm$0.11), respectively. This behaviour demonstrates that water uptake capacity of the mixture is three times higher than gel formed only by YAM, at 25 °C.

As starch gels generally comprise of a complex system of partly gelatinized granules in a matrix of amylose, the observed rheology is dependent on the (i) origin of the starch, (ii) characteristics of the degraded granule, and (iii) the proportions of interacting constituents. We have now shown that iota-carrageenan does not have any effect incompatible with any of

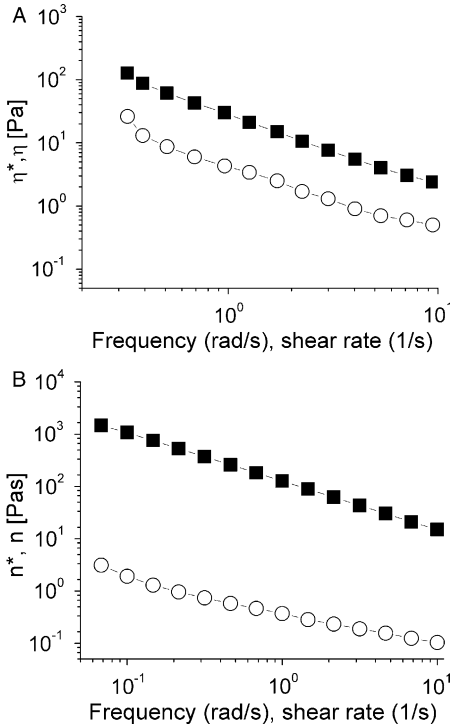

Fig. 8. Cox-Merz plot of YS alone (25 g l^{-1}) (A) and ι-CAR (5 g l^{-1})–YS (20 g l^{-1}) (B). (■) dynamic viscosity, (○) absolute viscosity.

the examined starches, since the rheological properties of the mixtures was similar to those observed with starch alone.

Our experiments demonstrated that the characteristics of all mixtures were dependent on the heating. In the systems with CS and MS softer and more stable gels were obtained, over the range of temperature of 45–85 °C, while the elastic modulus was less dependent on temperature in this range. Better characteristics were obtained with WS, during cooling, and which were maintained on re-heating (not shown). This better interaction could reflect that most homogeneous systems could be obtained after a heating process and a high polysaccharide concentration could be present in the continuous phase, which would facilitate interaction of the both carrageenan and starch helices.

On examination of CS and YS, which have similar amylose content, an improvement of strength of gel was observed only in the system between ι-CAR and YS. One possible explanation for this greater interaction is the presence of distinct characteristics of amylopectin in the YS starch, where less branch points are present and the amylopectin chains have a low molar mass (Mali, Karam, & Grossmann, 2004), compared to amylopectin presents in CS. In this way, YS with its fewer branch points and more linear structure can improve the interaction with ι-CAR.

The coupling action between starch and carrageenan involve the interaction between carrageenan (helix) with leached amylose (helix) by hydrogen bonds producing a viscosity increase via sinergism. This is similar to the interaction process of starch with xanthan gum (model B) (Abdulmola, Hember, Richardson, & Morris, 1996).

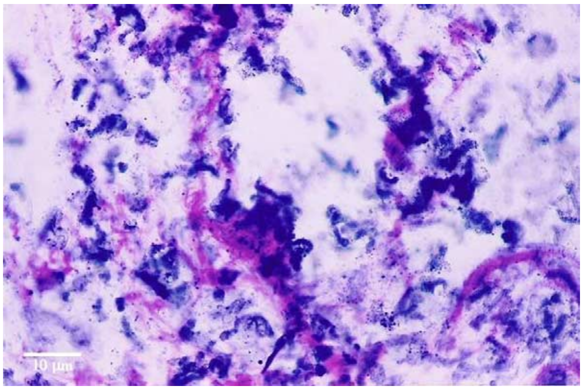

Fig. 9. Optic microscopy of mixture ι-CAR (5 g l^{-1})–YS (20 g l^{-1}); bar, 10 µm. Dyes methylene blue and iodine solutions (For interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

The microscopic analysis (Fig. 9) showed that there is ordered regions, and that the starch was found throughout the solution, confirming the model B, as observed to mixture starch–CMC (Shi & BeMiller, 2002). The region of interaction between helices originated strong gel and improved swelling capacity of the mixtures. The conformation to both polymers in which there is the same orientation in the helix (right-handed) (Picullel, 1995; Wu & Sarko, 1978a,b) can contribute to this specific interaction between helices, after cooling process.

4. Conclusions

Rheological measurements showed that in the starch (2.0%) and carrageenan (0.5%) systems analysed, the percentage of branching (amylopectin) could apparently influence the interaction or solubilisation of both polysaccharides. Considering the two-phase picture, one important fact is that the rheological properties of these systems are determined by both concentration and the rheological behaviour of dispersed continuous phase. The rheological properties and influence of temperatures in the viscoelastic behaviour of the mixtures showed that the gel characteristics are mainly governed by the polysaccharide concentrations in the continuous phase.

Considering the structural characteristics of the starches, such as proportions of amylose/amylopectin, a greater interaction between carrageenan and the starch with more linear structure (YS), originated more expanded chains, which occupy a greater hydrodynamic volume. In this way its chains are enabling better interaction.

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