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Solution Properties of κ -Carrageenan and Its Interaction with Other Polysaccharides in Aqueous Media

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1. Introduction

Carrageenans are an important class of hydrophilic sulfated polysaccharides used as thickening, gelling and stabilizing agents in a great number of foods such as sauces, meats and dairy products. In frozen foods its high stability to freeze-thawing cycles is very important. They are also responsible of the smoothness, creaminess, and body of the products to which they are added. Its combination with starch allows different textures to be obtained and reductions in fat content of up to 50%. The commercially important forms are kappa (κ), iota (ι) and lambda (λ). κ -carrageenan, consists of an alternating linear chain of (1 \rightarrow 3)- β -D-galactose-4SO₃⁻-(1 \rightarrow 4)-3,6, anhydro- α -D-galactose. It is soluble in hot water (> 75 °C) and even low concentrations (0.1 to 0.5%) yield high viscosity solutions. Viscosity is stable over a wide pH range, because the semi-ester sulfates are always ionized even under strongly acidic conditions. κ -carrageenan can adopt different conformations in solution, e.g. random coil and double helix. Therefore, its rheological behavior is strongly affected by the total ionic concentration, temperature and ion content of the system.

In this chapter we review the solution properties of κ -carrageenan and its interaction with starch and non-starch polysaccharides in aqueous media. We stress the importance of the sol-gel transition and gelation mechanism of κ -carrageenan; particularly the effect of temperature, polysaccharide concentration and external counterions on the transition and the interaction of κ -carrageenan with other polysaccharides. Given the economic importance of κ -carrageenan, we also discuss its viscoelastic behavior and microstructure as well as actual and potential applications in foods.

2. Origin of carrageenans and their classification

Carrageenans are found in marine red algae of the family *Rhodophyceae* (Snoeren, 1976, Chen et al., 2002). The main source is the *Chondrus crispus*, collected along the coast of North

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America from Boston to Halifax and the *Eucheuma* species, which is obtained mainly from cultivation in shallow waters around the Philippines (Whistler & BeMiller, 1997). Carrageenans constitute from 30 to 80% of the cell wall of these algae, and their functionality depends on the species, season, and growing conditions. They are composed of linear chains of D-galactopyranosyl units linked via alternated (1→3)-β-D- and (1→4)-α-D-glucoside (Chandrasekaran, 1998), in which sugar units have one or two sulfate groups. Some units contain a 3,6-anhydro ring. This provides a sulfate content of 15 to 40% (Fennema, 2002). Depending on the amount and position of the SO₃⁻ groups carrageenans are classified as μ, ν, λ, ξ, κ, ι, and θ types (Stanley, 1987) (Figure 1). The chemical and functional properties of each type of carrageenan are different due to the presence of sulfate groups. For example, ι and κ-carrageenan do form gels in the presence of counterions, whereas λ-carrageenan does not. The commercially available carrageenans are utilized to prepare a wide variety of gels; clear or cloudy, rigid or elastic, hard or soft, thermo-stable and with or without syneresis (Whistler & BeMiller, 1997). Carrageenan gels do not require refrigeration since they do not melt at room temperature.

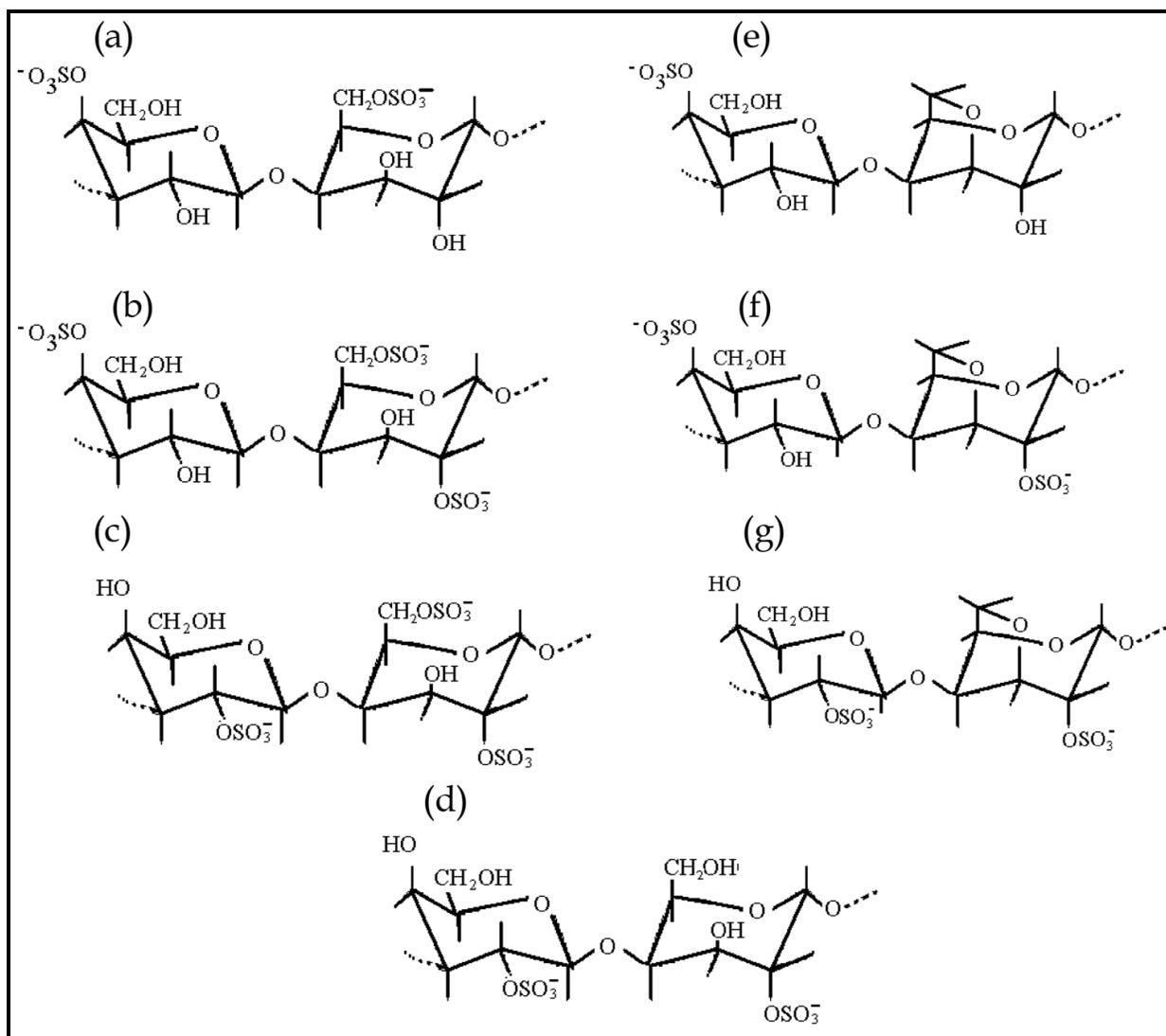


Fig. 1. Ideal repeating unit of carrageenans: (a) μ (b) ν (c) λ (d) ξ, (e) κ (f) ι and (g) θ carrageenan (adapted from Stanley, 1987).

Due to their hydrophilic nature, carrageenans are used as thickening agents (mainly λ -carrageenan), gelling agents (κ and ι -carrageenan), stabilizers or combinations of these functions in a number of food products, standardized with the necessary amounts of sucrose, glucose, salts or gelling aids, such as KCl.

3. Crystal structure

As κ -carrageenan molecules have a net negative charge, the polysaccharide is sensitive to ionic interactions with anions and cations. The interaction of κ -carrageenan with various counterions, particularly with potassium, has been studied by X-ray diffraction (Chandrasekaran, 1998). κ -carrageenan strands are less oriented and less crystalline than the salts of ι -carrageenan. However, like the iota form, κ -carrageenan adopts a double helix conformation. As shown in Figure 2, the double helices are stable parallel right-handed strands forming twisted in-phase structures so that when an anhydrous galactose residue of one strand is in front of a sulfate group of the other strand, the arrangement is stabilized by a hydrogen bond. A twist between the residues of the anhydrous galactose molecule has three hydrogen bonds that stabilize the helix (dotted lines in Figure 2). The sulfate groups are located on the periphery of the double helix, and are interacting with other ions.

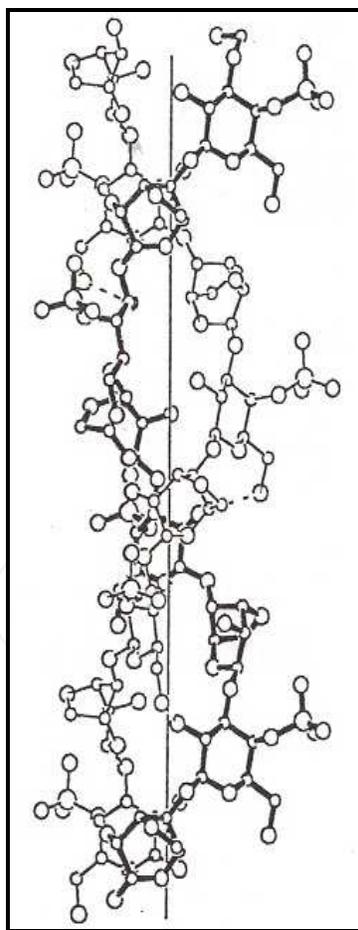


Fig. 2. Crystal structure of κ -carrageenan. One strand is clear and the other dark to distinguish them from each other. The dotted lines represent hydrogen bonds (adapted from Chandrasekaran, 1998).

4. Conformation in solution in the presence of counterions

The type of external counterions plays an important role in the solution properties of κ -carrageenan as a result of the decrease in the effective charge density of the polysaccharide (Takemesa & Nishinari, 2004). In sodium chloride solutions, κ -carrageenan adopts a disordered conformation (Snoeren, 1976) while in sodium iodide solutions the polysaccharide adopts an ordered helical conformation (Slootmaekers et al., 1988) at 25 °C in both cases. In the disordered state κ -carrageenan exists as a random coil, expanded as a result of the effect of the excluded volume and electrostatic repulsions between chain segments (Snoeren, 1976; Vreeman et al., 1980) with a high water absorption capacity (Harding et al., 1996). In this conformation, the chains are flexible and sensitive to the presence of ions. For some time, there was controversy on whether the ordered helical conformation consisted of one or two helices (Slootmaekers et al., 1988), however, light diffraction observations showed that the ordered conformation has twice the molecular mass of a random coil, a fact that is interpreted as the adoption of a double helix conformation (Viebke et al., 1995). Thus, the transition of κ -carrageenan is described from a disordered state to an ordered state as 2 random coils \leftrightarrow 1 double helix.

Meunier et al. (2001) showed that formation of double helices does not yield exactly twice the molecular mass of a random coil and that the relationship between the molecular masses and radii of gyration between the two conformations depends on the range of molecular mass of the random coils. Studies of κ -carrageenan in sodium iodide solution show that the ordered state is a rigid structure (Chronakis et al., 2000) with a high charge density (Takemesa & Nishinari, 2004). The disorder-order transition of κ -carrageenan occurs at a given temperature called the transition temperature, T_{d-o} (Rochas, 1982). This temperature depends on the nature of the counterion and the total ionic concentration. The same behavior is shown by other polyelectrolytes, e.g. gellan (Milas et al., 1990) and ι -carrageenan (van de Velde et al., 2002).

κ -carrageenan has different affinities for some ions. Considering the ability to stabilize the ordered conformation, determined from measured values of T_{o-d} , the decreasing order of affinity is (Rochas, 1982):

- monovalent cations: $Rb^+ > Cs^+ > K^+ > NH_4^+ > (CH_3)_4N^+ > Na^+ > Li^+$
- divalent cations: $Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+} > Zn^{2+} > Co^{2+}$

According to this sequence, the monovalent cations Rb^+ , Cs^+ and K^+ induce the transition at lower temperatures. Unlike other polyelectrolytes, the disorder-order transition of κ -carrageenan is also sensitive to the presence of iodide as a result of electrostatic repulsion between the anion and the sulfate group of κ -carrageenan without aggregation of double helices to form a gel network. Because of this particular feature, the iodide ion has been used to study the mechanism of gelation of this polysaccharide (Slootmaekers et al., 1988; Viebke et al., 1995, 1998; Meunier et al., 2001; Takemesa & Nishinari, 2004).

5. The sol-gel transition diagram

Rochas (1982) obtained the sol-gel transition diagram of the potassium salt of κ -carrageenan using polarimetry and ionic conductivity during heating and cooling treatments. The diagram shows the relationship between the total ionic concentration and the inverse of the

absolute temperature of transition (Figure 3). κ -carrageenan gels are thermoreversible, i.e. they can be formed upon cooling hot solutions and melted upon heating. Above a critical concentration C_{crit} the melting temperature (T_{melt}) is higher than the gelling temperature (T_{gel}). This phenomenon, known as thermal hysteresis, is a consequence of aggregation of the helical structures during gel formation. Below the critical concentration, which for the potassium salt of κ -carrageenan is about 0.007 mmol/dm^3 (Figure 3), thermal hysteresis does not exist. The total ionic concentration, C_T , is given by:

$$C_T = C_S + \gamma C_P \quad (1)$$

where C_S is the concentration of added salt, C_P is the concentration of charged groups in the polysaccharide and γ is the average activity coefficient; 0.55 for the potassium salt of κ -carrageenan.

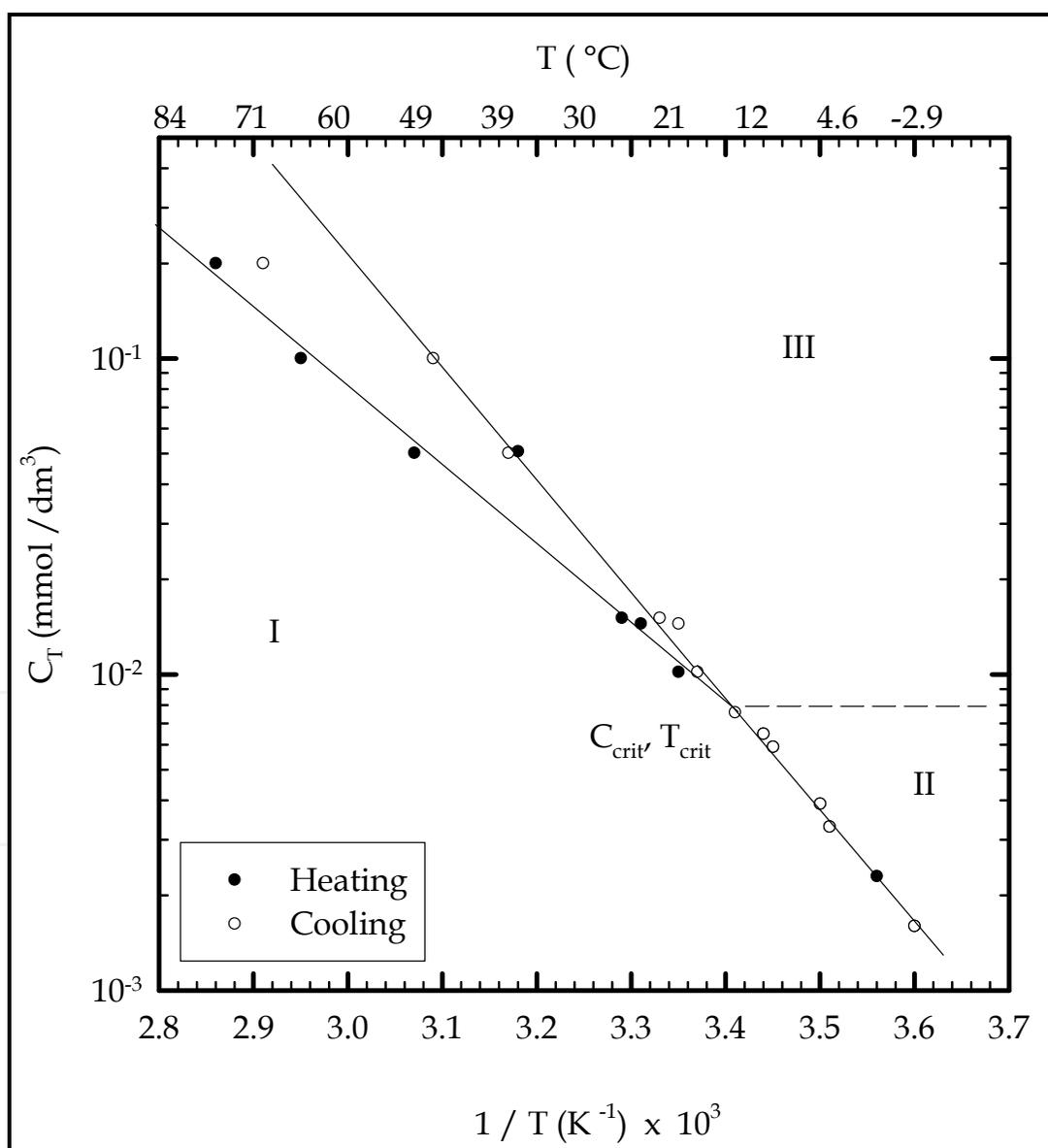


Fig. 3. Sol-gel transition diagram of the potassium salt of κ -carrageenan (adapted from Rochas & Rinaudo, 1982). The dotted line represents the division between zone I and II.

According to the sol-gel transition diagram, gels can be obtained from low concentrations of κ -carrageenan and high concentrations of potassium ion and viceversa; these gels have, however, different rheological behaviors.

Three regions can be identified on the transition diagram (Rochas, 1982). In each one of these regions κ -carrageenan adopts different conformations. The boundary between regions II and III is only approximate (Fig. 3). In region I, the polysaccharide exists as a random coil for temperatures above T_{melt} . In region II, dimers are formed without aggregation for temperatures below T_{gel} and C_T lower than C_{crit} . In region III, helical conformation exists and aggregation leads to a three-dimensional network for C_T greater than C_{crit} and T lower than T_{gel} . Therefore, it is possible to maintain conditions leading to the formation of double helices without aggregation. When the polysaccharide chains are in this condition, formation of double helices does not depend on polysaccharide concentration (Mangione et al., 2003), as long as C_T is lower than C_{crit} . In this type of polysaccharides, the transition is characterized by a linear relationship between the inverse of T_{gel} and $\log C_T$ (Rinaudo, 2001), but it is particular to each polysaccharide and the salt added to promote gelation. The diagram is very useful to set the conditions for a specific application.

6. Mechanism of gelation

The mechanism of gelation of κ -carrageenan is reported as a process divided into several stages (Figure 4). Starting from the random coil conformation, the polysaccharide is in solution at a concentration below C_{crit} and at a temperature above T_{melt} (**a** in Figure 4); this corresponds to region I in the sol-gel transition diagram (Figure 3). A decrease in temperature below T_{gel} keeping a constant concentration or an increase in concentration at constant temperature leads to the formation of a helical dimer (**c** in Figure 4); this corresponds to region II in Figure 3. For a given temperature, increasing C_T above C_{crit} leads to aggregation of helical dimers (**d** in Figure 4) and formation of a three-dimensional network (**e** in Figure 4) with possible dependence on time (Rochas, 1982; Chen et al., 2002; Takemasa & Chiba, 2001; Yuguchi et al., 2002). This condition corresponds to region III in Figure 3. It is possible to change from this condition to one in which a three-dimensional network does not exist, instead a semi diluted solution of random coil is present (**b** in Figure 4); it is necessary to increase the temperature or to decrease the concentration provided that it is kept above C_{crit} . Thus, a further decrease in C_T will lead to the starting point (**a** in Figure 4).

According to Bayley (1955) (cited by Rochas, 1982) the $-\text{SO}_3^-$ of κ -carrageenan interacts with K^+ through ionic bonds. Specifically, the potassium ion interacts simultaneously with two $-\text{SO}_3^-$ groups of anhydrous galactose.

In recent years, the development of new equipments and techniques has allowed the mechanism of gelation of natural polymers to be studied. In the case of κ -carrageenan, the transition from random coil to double helix has been studied by techniques including rheology (Takemasa & Chiba, 2001, Chen et al., 2002; Nishinari & Takahashi, 2003, Mangione et al., 2003), polarimetry (Mangione et al., 2003), light scattering (Mangione et al., 2003), photon transmission (Kara et al., 2003), spectrophotometry (MacArtain et al., 2003), low amplitude X-ray scattering (Yuguchi et al., 2002, 2003), differential scanning calorimetry (Nayouf, 2003) and laser dispersion during deformation (Takemasa & Chiba, 2001). All these

techniques have confirmed the association of two linear κ -carrageenan strands to form a double helix during gelation, reaffirming the mechanism proposed by Rochas (1982). The transition from random coil to double helices is extremely fast (Norton et al., 1983), whereas subsequent aggregation of double helices into small domains to form a three dimensional network (Mangione et al., 2003) is slower. Gel cure experiments monitoring the change with time of the storage modulus, G' , have revealed that the time for complete gel formation, i.e. aggregation of κ -carrageenan is between 12 (Meunier et al., 1999) to 15 hours (Tecante & Doublier, 1999).

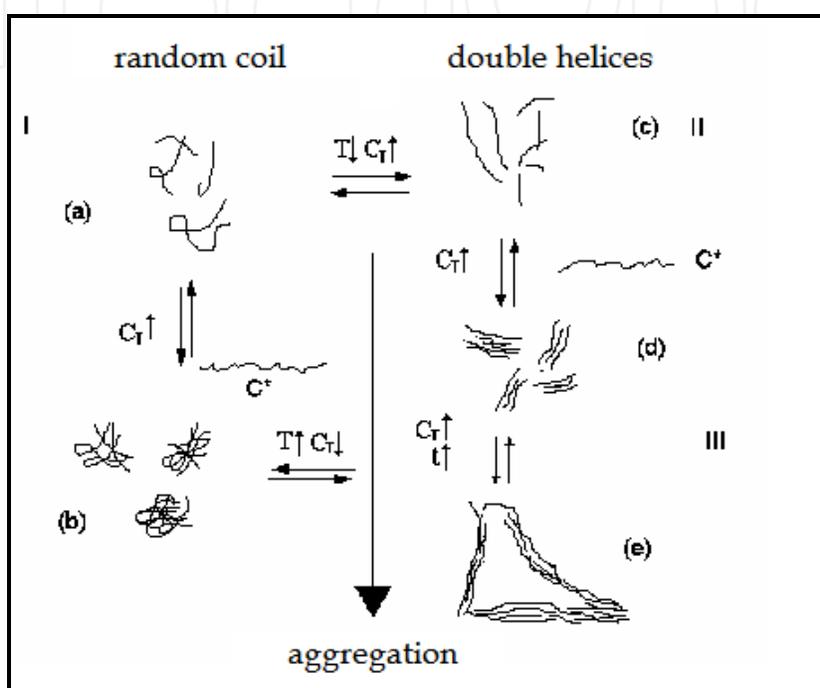


Fig. 4. Gelation model of κ -carrageenan (Rochas, 1982).

7. Rheological behavior of κ -carrageenan solutions

Like other polyelectrolytes in solution, e.g. gellan (Miyoshi & Nishinari, 1999), κ -carrageenan in the disordered conformation exhibits high sensitivity to counterions (Núñez-Santiago & Tecante, 2007; Núñez-Santiago et al., 2011). The viscoelastic behavior at 40 °C for 0.5% κ -carrageenan solutions with 0 - 30 mmol/dm³ KCl is shown in Figure 5. As shown in Fig. 5a, the loss modulus, G'' , was greater than the storage modulus, G' , and the dependence of both moduli with frequency ($G' \propto \omega^{1.7}$, $G'' \propto \omega^{0.93}$) approached that of a viscoelastic liquid ($G' \propto \omega^2$, $G'' \propto \omega^1$) (Ferry, 1980). Over the range of frequency, G'' decreased with the increase in KCl concentration. The viscoelastic behavior was governed by the viscous component. The complex viscosity of the solutions, Fig. 5b, exhibited a plateau followed by a decrease at high frequencies.

The variation of the plateau value of the complex viscosity, i.e. the zero-shear complex viscosity, $|\eta^*|_0$, as a function of KCl concentration at 40 °C is shown in Fig. 6. Addition of KCl reduced the complex viscosity from about 14.7 to 9.7 mPa s from 5 to 15 mmol/dm³ KCl and then slightly increased to about 13.7 mPa s. Therefore, κ -carrageenan is in the sol

state over the KCl concentration range of 0-15 mmol/dm³ at 40 °C. When the total ionic concentration approaches the sol-gel transition at 40 °C, incipient gelation probably occurs and consequently the zero-shear complex viscosity rises as shown. Addition of KCl reduced $|\eta^*|_0$; however, when the total ionic concentration approaches the sol-gel transition at 40°C, incipient gelation probably occurs and consequently the zero-shear complex viscosity rises as observed in Fig. 6. In polyelectrolytes, counterions shield the electrostatic repulsions between polymer chains and coil dimensions decrease as the counterions concentration increases. This shielding effect is well documented in the literature on the basis of viscosity measurements in dilute solution. The intrinsic viscosity decreases as the counterion concentration increases and a linear relationship between the intrinsic viscosity and the reciprocal of the ionic strength is generally reported; the slope depends on the rigidity of the polymer chain.

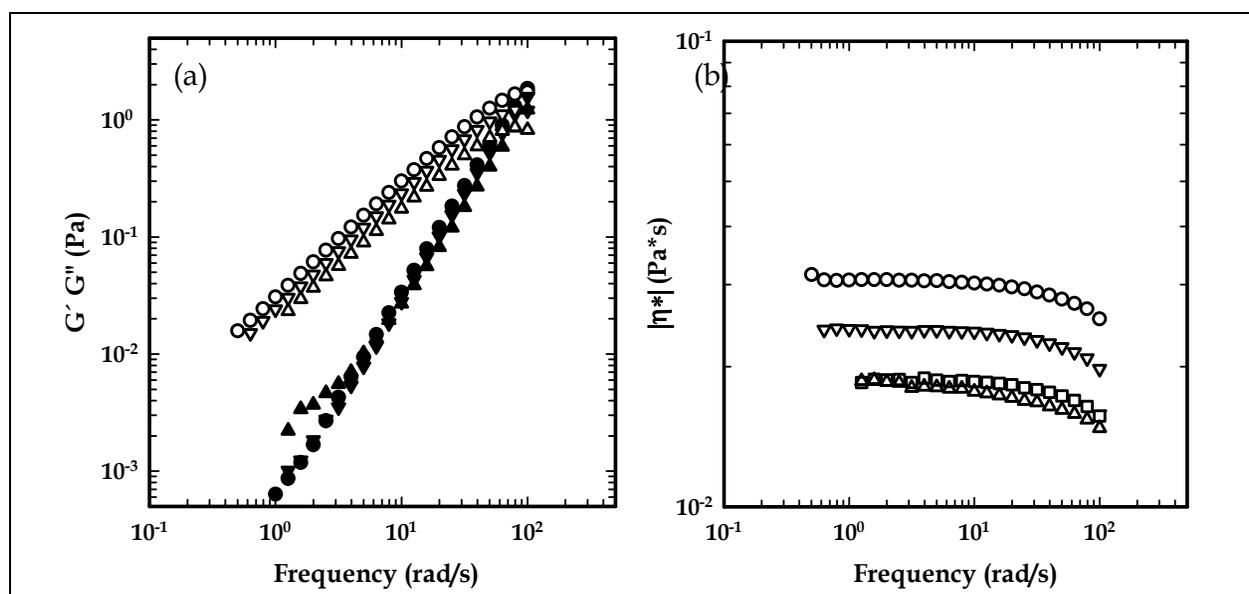


Fig. 5. Variation of G' (black symbols), G'' (white symbols) and $|\eta^*|$ with angular frequency at 40 °C for 0.5% κ -carrageenan with different KCl concentrations (mmol/dm³): (a) 0 (circles), 5 (inverted triangles), 15 (square) and 30 (triangles). Experimental conditions correspond to region I in Fig. 3.

This effect has been investigated for κ -carrageenan and values of rigidity have been determined (Snoeren, 1976; Vreeman et al., 1980). The present results (Fig 5.) for higher carrageenan concentrations can be interpreted by the same shielding effect. However, as the total ionic concentration approximates that for the sol-gel transition to occur, formation and possibly incipient aggregation of helical chains is promoted, increasing the number of junction zones driving the chains to network formation.

κ -carrageenan not only interacts with cations. In the presence of I⁻, repulsion between negative charges compel κ -carrageenan to form intermolecular associations by adopting an ordered double helix conformation (Takemesa & Nishinari, 2004). "Weak gels" are formed when κ -carrageenan is used in high concentrations (> 0.9%) in the presence of I⁻ (Chronakis et al., 1996). This condition is characterized by the predominance of G' over G'' , with both moduli depending on frequency (Chen et al., 2002). However, additional creep tests

(Chronakis et al., 2000) and monitoring of dynamic moduli with temperature (Ikeda & Nishinari, 2001) shows that it is not a “weak gel” but a concentrated polysaccharide solution with low relaxation rates.

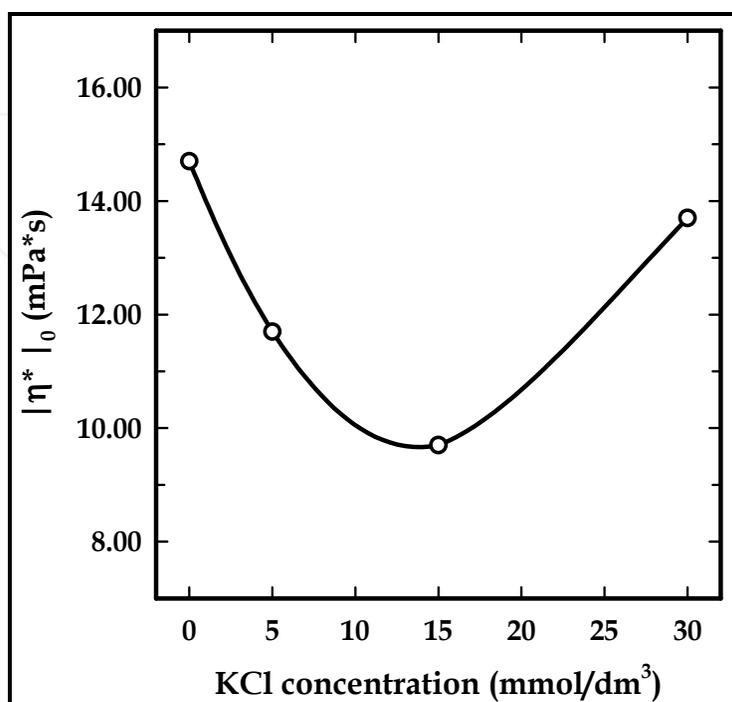


Fig. 6. Variations of the zero-shear complex viscosity with potassium chloride concentration at 40 °C. Experimental conditions correspond to zone I in Fig. 3.

Rheological and calorimetric studies of κ -carrageenan for conditions in which double helices do not aggregate in the presence of K^+ (region II in Figure 3) have been made (Núñez-Santiago et al., 2001). Figure 7a shows the DSC thermograms and the evolution of dynamic moduli with temperature for 0.3% κ -carrageenan ($C_T = 4.3 \text{ mmol/dm}^3$) without KCl; for this condition, $C_T < C_{\text{crit}}$ ($C_{\text{crit}} \approx 7 \text{ mmol/dm}^3$). The change in temperature crosses the transition line. As a result, one “exo” and one “endo” peaks are observed on cooling and heating, respectively, with a difference between them of less than 2 °C. This confirms that helical chains formed upon cooling are not aggregated and hence do not form a three-dimensional network. The variations of G' and G'' with temperature illustrate the effect of the disorder-order on cooling and the order-disorder transition on heating although gelation does not occur as shown by the signals of G' and G'' . The dynamic moduli do not over-cross on cooling and thermal hysteresis is not observed on cooling or heating. These results show that by monitoring the change in dynamic moduli with temperature one can determine the order-disorder transition temperature either rheologically or with micro-DSC. Unlike gelation, the order-disorder transition is rapid, is time-independent and the transition enthalpy does not change with polysaccharide concentration as a consequence of the lack of aggregation of helical chains.

Fig. 7b shows the rheological behavior of 0.3% κ -carrageenan at 9 °C without KCl. The loss modulus is greater than the storage modulus over most of the frequency window and both depend on frequency ($G' \propto \omega^{0.96}$; $G'' \propto \omega^{0.74}$). This overall viscoelastic behavior reveals the

fluid-like character of the system with the viscous character predominating over the elastic one. At 9 °C κ -carrageenan molecules are in the ordered state but neither aggregation nor gelation takes place. Moreover, κ -carrageenan molecules being in the ordered state are obviously stiffer than in the disordered one.

A decrease in the intrinsic viscosity, $[\eta]$, with ionic strength is the classical behavior of a polyelectrolyte. In the ordered state, κ -carrageenan at 9 °C, for $C_T = 1.4$ mmol/dm³ ($C_T < C_{crit}$ and $T < T_{crit}$, region I in Fig. 3), $[\eta] = 45.5$ dL/g. This value is particularly high and corresponds to a highly expanded coil because the salt concentration is so low that polysaccharide chains are not sufficiently shielded. For C_T values of 2.9, 3.6 and 4.3 mmol/dm³ ($C_T < C_{crit}$ and $T < T_{crit}$, region II in Fig. 3), $[\eta]$ was about 30 dL/g, indicating the presence of more compact chains in which aggregation is not likely to occur (Núñez-Santiago et al., 2011). The value abruptly decreases to 23 dL/g when C_T increases to 5.8 mmol/dm³. A further slight decrease down to 20 dL/g is noticed when C_T reaches values in region III ($C_T < C_{crit}$). Moreover, for the two latter C_T values the Huggins coefficients ($k_1 \approx 0.8$) are relatively high indicating a tendency to aggregation (Núñez-Santiago et al., 2011). It is noteworthy that the $[\eta]$ values are more than twice higher than those obtained in NaCl (0.1 mol/dm³) for this sample: 10.5 dL/g.

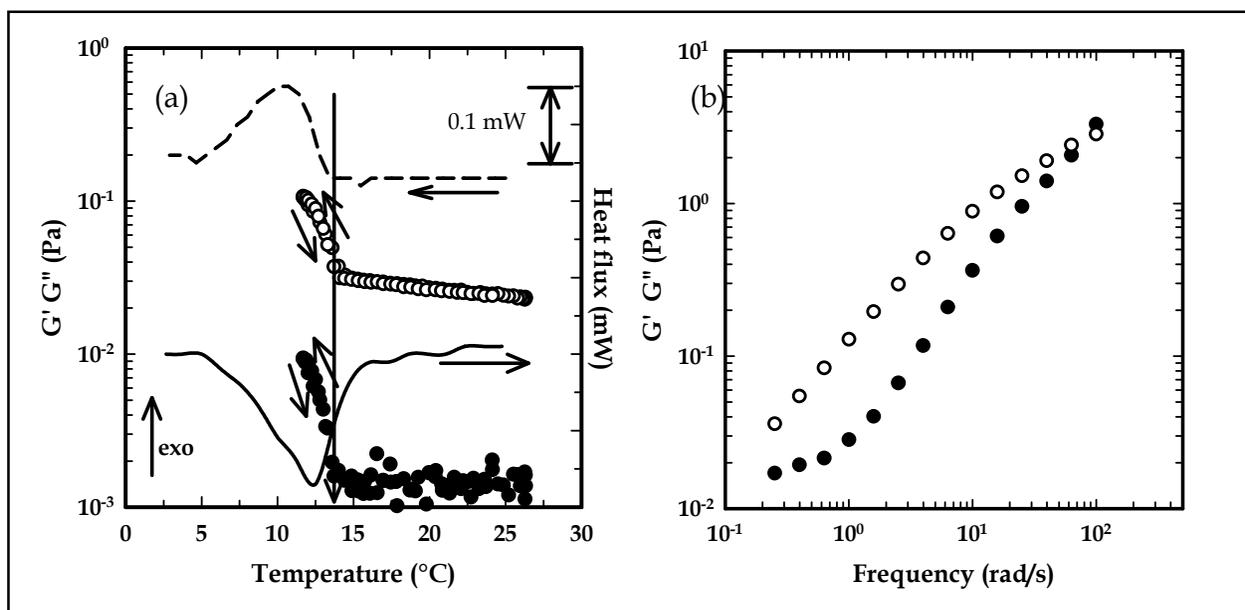


Fig. 7. (a) DSC thermograms for cooling (dotted lines) and heating (continuous lines) and variations of G' (black symbols) and G'' (white symbols) with temperature for 0.3% κ -carrageenan, without KCl. The vertical arrow indicates T_{onset} for the transition. Frequency = 1 rad/s and strain = 50% (b) Variation of G' (black symbols) and G'' (white symbols) with frequency for 0.3% κ -carrageenan without KCl at 9 °C for 50% strain. Experimental conditions correspond to region II in Fig. 3. Adapted from Núñez-Santiago et al. (2011).

8. Rheological behavior of κ -carrageenan gels

The solid character of κ -carrageenan gels arises from the formation of a three-dimensional network, which extends continuously through the entire volume and entraps the dispersed

medium within its structure. The three-dimensional network is formed by non-covalent bonds, which have low energy and a finite lifetime. The interactions include van der Waals forces, hydrogen bonds, charge transference, ionic, hydrophilic and hydrophobic. Consequently, κ -carrageenan gels are considered physical gels as they are not formed by chemical cross-linking. The non-covalent bonds can be one or more of those mentioned above, combined with specific and complex mechanisms involving interaction zones (Kavanagh & Ross-Murphy 1998; Morris, 1990). Counterions play an important role in the gelation of polyelectrolytes. Among the monovalent cations that induce gelation of κ -carrageenan are K^+ , Rb^+ , Cs^+ and high concentrations of Na^+ and Li^+ (MacArtain et al., 2003). However, the gels formed with K^+ are the strongest and most stable (Chen et al., 2002).

Figure 8 shows the effect of the K^+ ion on the viscoelastic behavior of κ -carrageenan (1%) gels under conditions corresponding to region III in Figure 3. From 5 to 80 mmol/dm³ KCl, the behavior is characteristic of a gel (Ferry, 1980) with both moduli independent of frequency (i.e. $G' \propto \omega^{0.03}$) in the range of 0.1 to 100 rad/s and $G' \gg G''$. In general, the rigidity of the gels, expressed by G' , increases with addition of potassium chloride. For concentrations below 80 mmol/dm³ KCl, Fig. 8a, addition of the salt yields a rapid increase in gel rigidity, whereas for concentrations above 80 mmol/dm³, such increase is limited as shown in Fig. 8b. Once a limiting concentration is reached, further addition of KCl does not increase gel rigidity. Additionally, the limiting gel rigidity depends on κ -carrageenan concentration (Núñez-Santiago & Tecante, 2007). The existence of a limiting salt concentration beyond which the rigidity of the gels reaches a constant value suggests that the polysaccharide is oversaturated with potassium ions reaching a maximum aggregation of helical chains in which no more space is available for further interactions.

Divalent cations such as Ca^{2+} and Cu^{2+} also have the ability to induce gelation of κ -carrageenan with the resulting gels having the same level of rigidity than those of monovalent cations (Michel et al., 1997). In such systems the calcium ion to sulfate group ratio is one to one (MacArtain et al., 2003). Regarding the effect of concentration of cations on the stiffness of gels, rheological (Chronakis et al., 1996, Chen et al., 2002) and uniaxial compression tests (MacArtain et al., 2003) show a progressive increase of the moduli with increasing salt concentration. The increased stiffness of the gels results from neutralization of the electrostatic charges of the polysaccharide chains which promotes their association. However, the reverse effect also exists when there is a high concentration of ions, as in the case of Ca^{2+} (Lai et al., 2000). This decrease is attributed to the fact that Ca^{2+} induces a large increase in the number of branches formed by the aggregates during gelation of κ -carrageenan, resulting in long aggregates and precipitation, which may explain the decrease of moduli when the concentration of the external ion in the medium increases (MacArtain et al., 2003).

In general, rheological studies of κ -carrageenan have been conducted with high concentrations of polysaccharide (0.5 to 2%) and concentrations of K^+ sufficiently high to ensure gel formation (> 10 mmol/dm³ KCl). However, rheological studies of κ -carrageenan in moderate concentrations (0.7 to 1.4%) in the absence of ions show that "weak gels" can be formed; their stiffness depends on temperature (Chen et al., 2002). Although these gels do not withstand their own weight (Chen et al., 2002) they are able to recover their structure

when they are re-cooled. Under these conditions, although $G' > G''$, both moduli depend on frequency. Thus, the term "weak gel" is used in various systems invariably when $G' > G''$ without making or including additional tests to define this type of gels, for example, the analysis of the dependence of the phase angle with frequency. On the other hand, a larger amount of κ -carrageenan produces strong gels due to the presence of a larger proportion of aggregated helices (Núñez-Santiago et al 2011). However, it is possible that in spite of the presence of a sufficient amount of κ -carrageenan to induce gelation, potassium ions are necessary to aggregate the polymer.

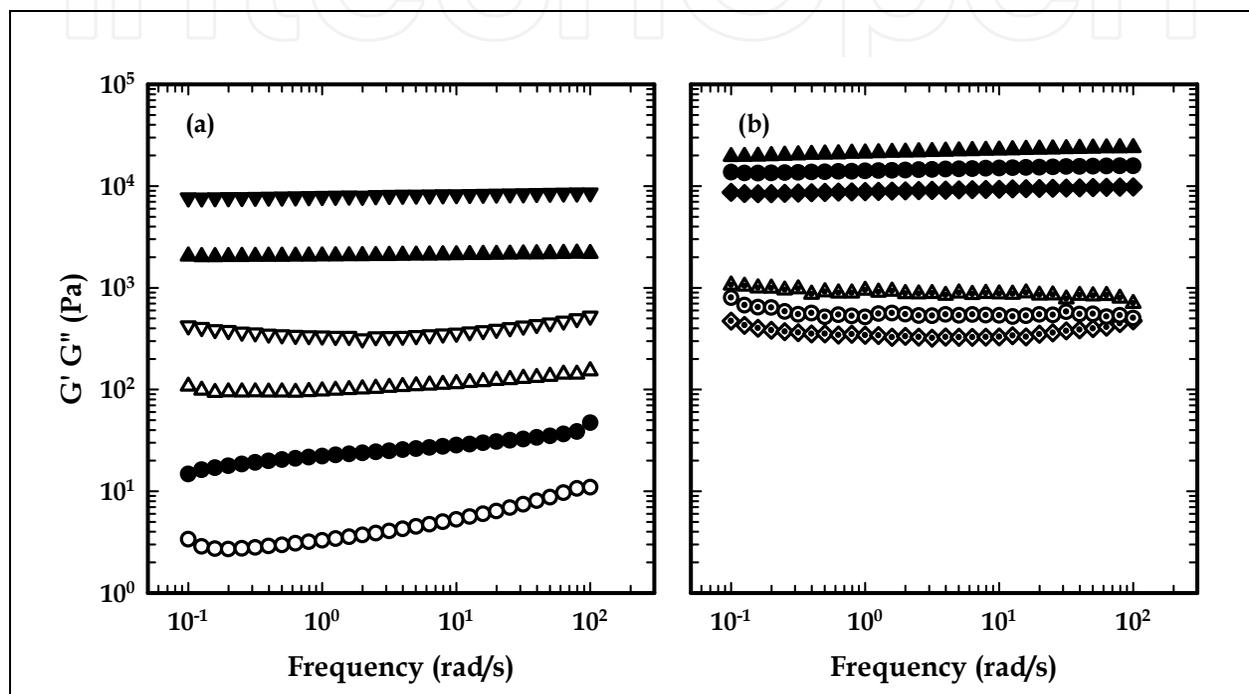


Fig. 8. Variation of G' (black symbols) and G'' (white symbols) with angular frequency for different KCl concentrations (mmol/dm^3) for 1.0% κ -carrageenan gels at 25 °C. (a) 5 (circles), 40 (triangles), 80 (inverted triangles). (b) 90 (diamonds), 100 (dotted circles) and 200 (dotted triangles). Experimental conditions correspond to region III in Fig. 3.

9. Microstructure of κ -carrageenan

Microscopy is one of the best tools to understand the rheological behavior of polysaccharides and materials in general. Various techniques, such as scanning electronic microscopy (SEM) and atomic force microscopy (AFM) allow the microstructure of materials to be observed. Other techniques, such as confocal laser scanning microscopy, CLSM, allow the ultrastructure and internal structure to be observed without breaking the material. On the other hand, most foods are mixtures of several components. Therefore, microscopic examination of the structural arrangement of the different components helps to understand the possible interactions among them. Sample preparation is the main problem to observe foodstuffs (Heertje & Pâkes, 1995). In SEM, there are physical and chemical methods to prepare the samples. Chemical methods are used to dehydrate and solidify liquid or semi-liquid samples through the use of chemical agents that can induce changes in

the structures of the sample. Physical methods are used to solidify the samples by freezing and there is always the possibility of formation of small crystals that can break down their structure.

AFM has been used to study individual molecules and their interactions, particularly polysaccharides of complex structures. For example, the effect of salts on κ -carrageenan gelation (Ikeda et al., 2001). The images corresponding to an ionic concentration high enough for κ -carrageenan to form gels (100 mg/mL of κ -carrageenan in 100 mmol/dm³ KCl), show the existence of local networks composed of faint filaments with some degree of branching resulting presumably from side to side aggregation of the helices, or by a thick bundle of aggregated helices, known as "supercritical spiral concentration". Ikeda et al. (2001) suggest that κ -carrageenan in the presence of NaI can form a local network without side to side aggregation of helices, however, this network is not as solid nor as rigid as the one formed in the presence of added salts.

In the case of CLSM, fluorescent staining is necessary to observe the materials under study. κ -carrageenan has been covalently labeled with rhodamine B isothiocyanate (RITC, excitation/emission wavelengths 543/575 - 640 nm) (Núñez-Santiago et al., 2011) and examined at 25 °C. The CLSM images of gels formed with 40 mmol/dm³ KCl are shown in Fig. 9. With this amount of salt, 0.5% κ -carrageenan forms gels with a dense three-dimensional network and a homogeneous distribution of the polysaccharide as can be seen in Fig. 9a. As the polysaccharide concentration decreases to 0.25, and 0.01, Fig. 9b and 9c respectively, the network is still continuous but with perceptible dark zones of about 10-20 μ m, Fig. 9d, the lack of continuity of the network becomes apparent in spite of a certain degree of aggregation. The three-dimensional images in CLSM confirm the presence of a three-dimensional network for polymer concentrations as low as 0.05%.

However, when polysaccharide concentration is very low, even though κ -carrageenan exists as aggregated helical chains, such aggregates are not enough to occupy all the volume and one obtains a salt solution in which short and fragmented κ -carrageenan networks are dispersed in the continuous phase.

As mentioned previously, κ -carrageenan has the ability to form a three-dimensional network in the presence of monovalent and divalent ions. However, the analysis of the structural conformation in the presence of two different cations, K⁺ and Ca²⁺, shows that the network structure is different. Figure 10a shows the image of κ -carrageenan in the presence of 10 mmol/dm³ KCl (Dunstan et al., 2001) and Figure 10b is the image of κ -carrageenan in the presence of Ca²⁺ in a molar calcium to sulfate ratio of one to one (MacArtain et al., 2003). In both SEM images, the concentration of polysaccharide is 1.0%. The image with K⁺ shows a dense structure, similar to the cross section of various tubular structures in the gel with a characteristic diameter of the spaces between 10 and 20 μ m. The network with Ca²⁺ is fine with thin filaments of κ -carrageenan linked together to form a continuous network. The images are useful to understand that the gels formed with K⁺ are stronger because they have denser and more continuous structures than those formed with Ca²⁺.

Roh & Shin (2006) used SEM to observe the structure of mixtures, to analyze the replacement of alginate by κ -carrageenan and the effect of two agents to crosslink the

polysaccharides. The images show that association between the two polysaccharides occurs by interpenetration between the two structures. Contrary to what happens with locust bean gum, replacing alginate with κ -carrageenan produces a structure with smaller pore sizes in relation to the network of alginate alone, which results in improved mechanical properties of the network. A similar behavior is observed in alginate-gellan mixtures, in which interpenetration occurs and the rheological behavior is governed by the polysaccharide present in higher concentration (Amici et al., 2001).

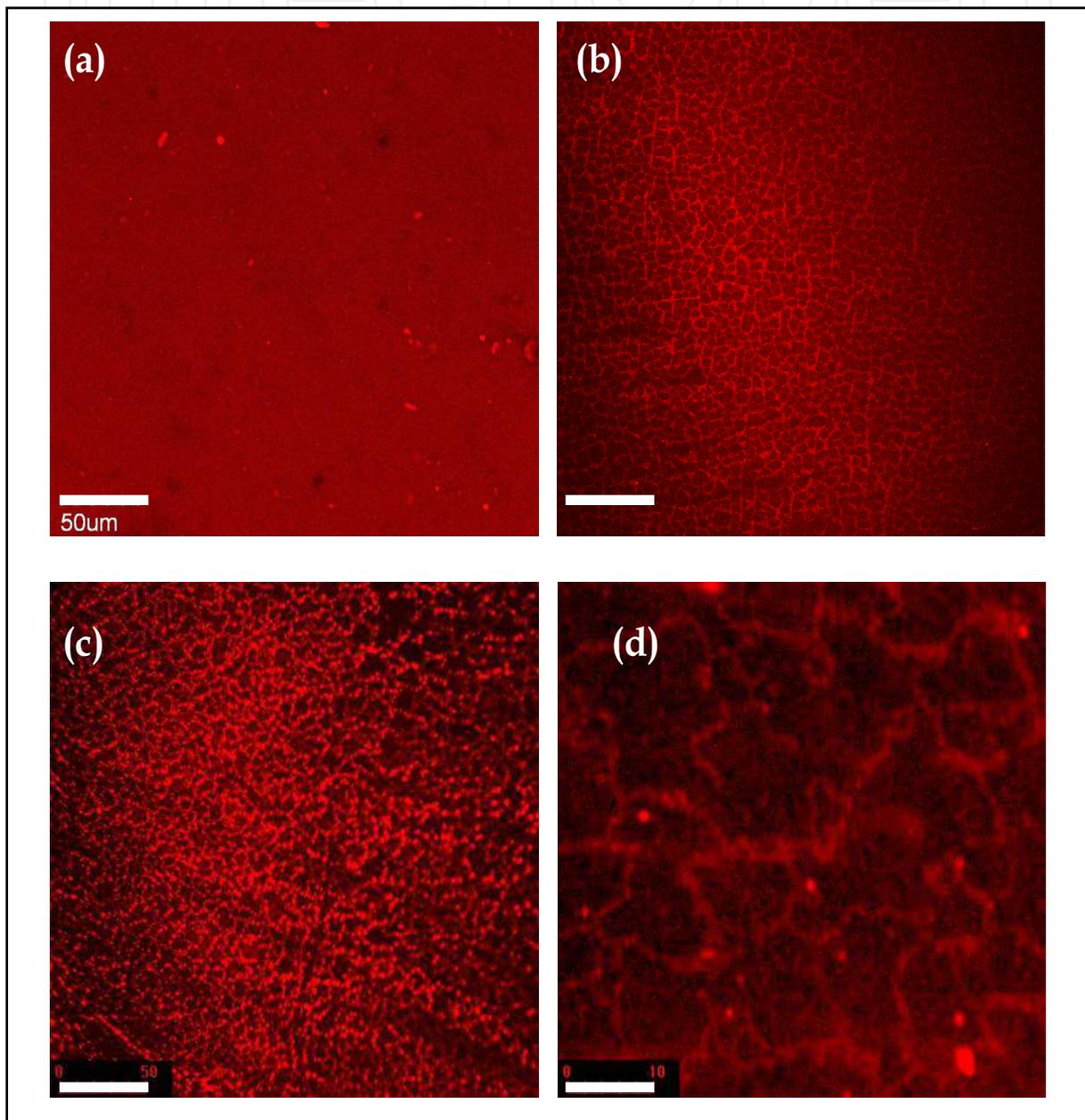


Fig. 9. CLSM images of covalently-labeled κ -carrageenan in the presence of 40 mmol/dm^3 KCl at $\lambda = 580 \text{ nm}$ for concentrations (%) of: 0.5 (a), 0.25 (b), 0.1 (c) and 0.05 (d). The scale bar is $50 \mu\text{m}$ in (a), (b) and (c), and $10 \mu\text{m}$ in (d).

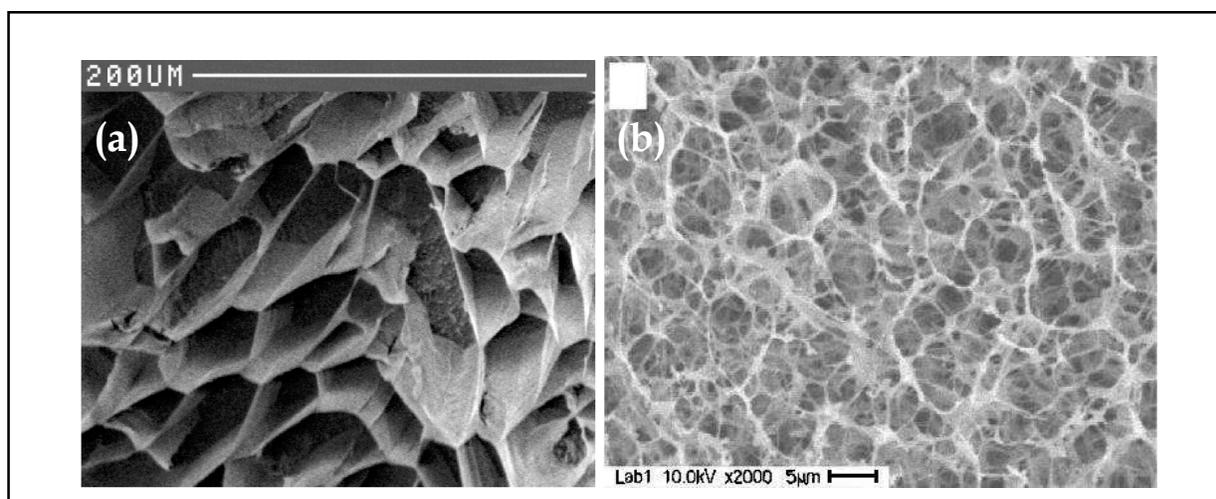


Fig. 10. SEM images of 1.0% κ -carrageenan networks. (a) with 10 mmol/dm³ KCl (Reprinted from Dunstan, et al., (2001), with permission from Elsevier), (b) with Ca²⁺ in a 1:1 ratio (Reprinted from MacArtain et al., (2003), with permission from Elsevier).

10. Interaction between κ -carrageenan and other macromolecules

In industrial applications polysaccharides are not generally used alone because blends extend the range of possible different rheological and textural properties and improve the properties of the systems. Some binary mixtures of gelling hydrocolloids produce more resilient gels than the individual components or gels with the same resistance but with lower total concentrations, with an obvious economic advantage. Therefore, this has increased the interest in the study of mixtures of κ -carrageenan with starch, other non-starch polysaccharides or proteins in addition to systems containing only κ -carrageenan.

10.1 Non-starch polysaccharides

The simplest mixtures are those of two components. One of them can be a gelling agent such as κ -carrageenan, whereas the other a non-gelling macromolecule. These blends produce stronger gels with reduced syneresis and fragility. In this context, several rheological studies using oscillatory shear tests have shown increases in the storage modulus, G' , due to the presence of galactomannans such as locust bean gum (Stading & Hermansson, 1993; Lundin & Hermansson, 1997; Dunstan et al., 2001; Chen et al., 2001), or an increase in the maximum fracture stress of the gels (Dunstan et al., 2001). Other mixtures studied include κ -carrageenan-guar gum (Damasio et al., 1990) and κ -carrageenan-cactus mucilage (Medina-Torres et al., 2003). However, this phenomenon, sometimes called rheological synergy, occurs only under very specific conditions. Examination of the viscoelastic behavior (Stading & Hermansson, 1993) of systems containing potassium, sodium or calcium salt of κ -carrageenan and replacing the carrageenan with guar to a total polysaccharide concentration of 1.0%, shows that only the potassium salt of κ -carrageenan produces a synergistic effect in 100 mmol/dm³ KCl. Compression and deformation tests (Chen et al., 2001) suggests more an "interaction" than a synergistic effect in mixtures of calcium salt of κ -carrageenan - locust bean gum. The synergistic effect between κ -carrageenan and locust bean gum can be reversed for high concentrations of the galactomannan, leading to lower

stiffness from certain concentrations or ratios between the polysaccharides in the mixture. Dunstan et al. (2001) kept a constant total polymer concentration (1.0%) and gradually replaced κ -carrageenan with locust bean gum. They found a maximum value of rupture stress in compression tests for locust bean gum to κ -carrageenan ratios of 30/70 and 40/60. Medina-Torres et al. (2003) report on a synergistic effect with cactus mucilage observed in compression tests. They used a total concentration of 2.0% and found a fracture stress of 50 kPa in gels with a ratio of mucilage to κ -carrageenan of 80/20 with 120 mmol/dm³ KCl.

Rheological or mechanical synergy has been observed but there is not a general criterion to explain it from a physicochemical point of view. One possible explanation is based on the presence of the volume exclusion effect between the polysaccharides that causes an increase in their effective concentration, as well as the presence of electrostatic interactions between the polymers in solution. Another possible explanation is based on the existence of interactions between the components in the network causing a synergistic effect due to the association of locust bean gum with the double helices stabilizing the “rods” of stiff κ -carrageenan in the presence of ions Na⁺ and Ca²⁺ (Lundin & Hermanson, 1997). An important factor in the existence of synergy between these macromolecules is the presence of sulfate groups in κ -carrageenan, the type of salt of the κ -carrageenan (potassium, sodium or calcium), the ratio of galactomannans when they are present, presence of external ions, temperature, the ionic contribution of the other polysaccharide, the water absorption capacity and the molecular mass.

Another type of mixture is that of κ -carrageenan with another gelling agent. The mixture of κ -carrageenan with alginate improves the structure of films formed with alginate- κ -carrageenan ratios from 6 to 4, respectively, resulting in smaller gaps, which in turn improve the mechanical properties and stability of the network (Roh & Shin, 2006). In such systems, the synergistic effect has been attributed to interpenetration between the two polysaccharides, such as in agar-gellan (Amici et al., 2001), in which the network of one macromolecule passes through the other at a minimum scale, comparable to its interstitial size, reinforcing the three-dimensional network; this results in G' values higher than the individual components.

10.2 Starch

In their blends with starches, a synergistic effect on the rheological properties of the pastes and gels exist (Loisel et al., 2000; Verbeken et al., 2004). Starch pastes and gels are considered a biphasic system with the continuous phase consisting of the solvent and dissolved starch during gelatinization and a disperse phase consisting of swollen granules (Doublier, 1981; Bagley & Christianson, 1982; Doublier, 1987). This viewpoint emphasizes the presence of swollen particles in starch suspensions. The swollen granules are not only deformable, but also compressible and elastic.

Mixtures of cross-linked waxy corn starch and κ -carrageenan have been also studied (Tecante & Doublier, 1999). This type of starch is practically free of amylose and starch granules are rigid enough to produce a suspension of swollen particles in a continuous medium. The biphasic model proposed for starch dispersions (Doublier, 1981) and gels can be applied. In these mixtures, addition of κ -carrageenan to starch pastes increases the apparent viscosity and the median diameter, $D [v, 0.5]$, compared with individual starch pastes at 60 °C. However, the

presence of K^+ (20 mmol/dm^3) produces an important decrease in the apparent viscosity of the mixture. One possible explanation for this phenomenon is that as the median diameter increases, the apparent viscosity increases and hence the nominal volume fraction of the disperse phase (Rao & Tattiyakul, 1999; Loisel et al., 2000; Paterson et al., 2001) producing mixtures with high viscosities; the addition of K^+ produced a shielding effect over the κ -carrageenan. The elastic character of these mixtures decreases with the decrease of starch concentration (2.0%) and the presence of K^+ (20 mmol/dm^3) (Tecante & Doublier, 1999). The evolution with time of G' at 25°C in mixtures with 20 mmol/dm^3 KCl and 0.5% κ -carrageenan with 2.0 to 4.0% cross-linked waxy maize starch, show that more rigid gels are produced upon increasing the concentration of starch. These gels can be considered as composites of swollen particles embedded in a macromolecular network (Tecante & Doublier, 1999). Thus, the rheological behavior of starch/carrageenan is governed by the volume fraction of the disperse phase and the viscosity of the continuous phase.

Other studies on starch with non-starch polysaccharides mixtures have focused on changes in mixture properties during starch gelatinization (Nagano et al., 2008; Techawipharat et al., 2008). These investigations have revealed that the presence of the non-starch component decreases the gelatinization temperature of starch, probably due to a decrease in the amount of free water that the non-starch polysaccharide leaves to starch gelatinization, however, it also has been found that retrogradation decreases.

It is also possible to observe incompatibility between κ -carrageenan and other polysaccharides. In this context, Lai et al. (1999) studied the effect of incorporating κ -carrageenan to starch during cooking and gelation, through the rheological properties, the degree of gelatinization, swelling and solubility of starch granules. These authors conclude that the type of interaction between κ -carrageenan and starch is governed by the excluded effect of the swollen granules and the incompatibility existing in the gel matrix formed by κ -carrageenan and amylose. In a mixture of the calcium salt of κ -carrageenan with high amylose (70%) starch, Lai et al. (1999) found that for low concentrations of κ -carrageenan (0.3%) G' increases due to the presence of amylose, but with high concentrations of κ -carrageenan (1.0%) the rheological properties do not change, which shows that at high concentrations of κ -carrageenan, this polysaccharide prevailed over starch and governed the rheological behavior.

These results are consistent with those obtained by Tecante & Doublier (2002), who by measuring the change in turbidity and G' with time during gelation of amylose and κ -carrageenan mixtures, observed the presence of phase inversion between them. This phenomenon depends on the proportion of both polysaccharides; for concentrations of κ -carrageenan below 0.3%, amylose forms the continuous phase and carrageenan the disperse phase. For concentrations higher than 0.5% κ -carrageenan, the continuous phase is made up of κ -carrageenan and the disperse phase of amylose. κ -carrageenan behaves as a macromolecular solution when KCl is not present and forms three-dimensional networks when this salt is added.

11. Industrial applications in foods

κ -carrageenan is one of the most abundant polysaccharides in nature that can be used in prepared foods and cosmetics as a gelling, stabilizing and thickening agent due to its biocompatibility, biodegradability, high capacity of water retention and mechanical strength

of its gels. According to the sol-gel transition diagram, κ -carrageenan can adopt three different conformations: random coil, double helix and double helix aggregated forming a three-dimensional network. The dependence of the rheological properties of κ -carrageenan on external factors, such as temperature, counterion and polysaccharide concentration permits to control the way in which the functionality of the polysaccharide is desired for a given product.

For example, when the product is to be kept at room temperature or when the low concentration of κ -carrageenan and counterions permit the polysaccharide to be in the random coil conformation ($C_T < C_{crit}$ and $T > T_{crit}$). Under these conditions κ -carrageenan can be used as a thickening agent and as a stabilizer in products such as chocolate drinks (Prakash et al, 2010) in which the polysaccharide provides creaminess to milk and maintains cocoa in suspension for a long time. The polysaccharide can be used also as a foam stabilizer in cream of whipped milk (Kováčová et al., 2010) due to the increase in viscosity. Thus, κ -carrageenan used in low concentrations stabilizes dairy products as a result of its interaction with casein micelles, for this reason it can be used in other products as soy and condensed milks.

On the other hand, when the products are liquid and refrigerated (4 °C), the low concentrations of κ -carrageenan (< 0.5%) permit to have the macromolecule in an ordered state without forming aggregates. Some examples are yoghurt, flans, jellies, fruit filling for puddings, cold coffee beverages, among others. However, it is important to consider the concentration of Ca^{+2} in these systems, because in the presence of this ion, κ -carrageenan can form gels (Dunstan et al., 2001; MacArtain et al., 2003).

Due to its property of forming gels, κ -carrageenan has been used to increase the hardness of starch gels (Huang et al., 2007; Tecgawipharat et al., 2008), to prepare low-calorie products, such as turkey sausages (Ayadi et al., 2009), ham and cold meat in general, where the appearance is enhanced but the flavor is not modified. Another alternative widely studied is its use in diet desserts (Descamps et al., 1986) in which fats are substituted by starches and carrageenan obtaining a decrease of up to 50% in the amount of fats. In desserts like custards the matrix is formed by starches, sugars and milk (Depypere et al., 2009). In some cases the custard is flavored with aromatic compounds. Therefore, addition of κ -carrageenan permits to have a synergistic effect in the texture of the dessert because of the interactions with starch and milk proteins (Cayot, 2006); besides, its polymeric matrix permits to preserve the aromatic compounds and flavoring agents (Seuvre et al. 2008). In this case, mixtures of one polysaccharide as a primary stabilizer and κ -carrageenan as a secondary stabilizer are used as a cryo-protective agent, giving excellent results in the preservation of ice cream (Soukoulis et al., 2008).

Another use of κ -carrageenan is in the preparation of biodegradable and edible films to increase the shelf-life of strawberries (Ribeiro et al., 2007), storage of cheese (Kampf & Nussinovitch, 2000) and antimicrobial films (Choi et al., 2005). κ -carrageenan microgels allow foods and aromas in fruit preparation to be preserved (Savary et al., 2007; Hambleton, et al., 2009; Marcuzzo et al., 2010; Hambleton et al., 2011; Fabra et al., 2011), drugs to be released over extended periods to the desired dosage when microgels are spherical particles (Cha et al., 2002, 2003; Bonferoni et al., 2004; Karbowiak et al., 2007; Hu et al., 2009; Nessem et al., 2011) and extended release of nutraceutical products (Ellis et al., 2009). In this context,

κ -carrageenan is considered an excellent alternative for active compounds release in the intestinal tract and not in the first stages of digestion.

One of the new applications of κ -carrageenan is in copolymerization. One example is the copolymerization of κ -carrageenan with acrylic acid with further acidification to convert the sulfate groups into sulfuric groups. This copolymer has been used as a catalyst during the hydrolysis of sucrose to glucose and fructose (El-Mohdy & Rehim, 2008).

12. Conclusions

The existence of a given conformation, random coil, non-aggregated helical chains and three-dimensional networks (gels), depends on the total ionic concentration and temperature and determines the functionality of κ -carrageenan. Conditions that promote the presence of random coils result in viscoelastic behaviors typical of macromolecular solutions. Below a critical ionic concentration and its corresponding temperature, the functionality is determined by the existence of helices without aggregation. The viscoelastic behavior of this state is similar to the random coil condition at high and low temperatures. Therefore, the functionality of the polysaccharide is not expected to change drastically by a change in temperature. Above the critical conditions and low temperature, 25 °C, κ -carrageenan forms three-dimensional structures of different degrees of aggregation that result in very rigid gels. However, this rigidity remains practically unchanged above a limiting salt concentration. In making gels of this polysaccharide, it is important to bear in mind that the amount of κ -carrageenan and added KCl must be enough to form a continuous three-dimensional network over the entire aqueous medium.

13. References

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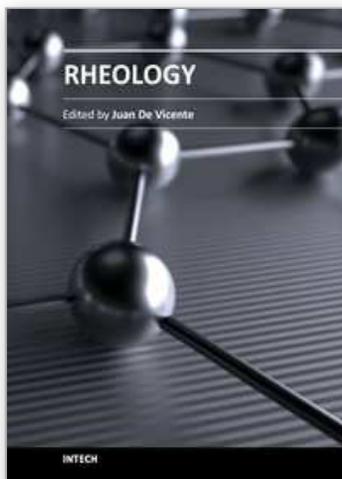
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Rheology

Edited by Dr. Juan De Vicente

ISBN 978-953-51-0187-1

Hard cover, 350 pages

Publisher InTech

Published online 07, March, 2012

Published in print edition March, 2012

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How to reference

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Alberto Tecante and María del Carmen Núñez Santiago (2012). Solution Properties of κ -Carrageenan and Its Interaction with Other Polysaccharides in Aqueous Media, Rheology, Dr. Juan De Vicente (Ed.), ISBN: 978-953-51-0187-1, InTech, Available from: <http://www.intechopen.com/books/rheology/solution-properties-of-k-carrageenan-and-its-interaction-with-other-polysaccharides-in-aqueous-media>

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