



# Molecular and rheological characterization of carrageenan solutions extracted from *Kappaphycus alvarezii*

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## ABSTRACT

This study evaluates and relates the molecular and rheological characteristics of native carrageenan obtained from *Kappaphycus alvarezii* seaweed. Native carrageenan was extracted by a differentiated methodology by atomization drying process, which reduces the time for obtaining carrageenan dry powder and minimizes costs and environmental damages. Rheological properties of native carrageenan were compared with a commercial carrageenan grade. Molecular properties were performed by SAXS and GPC analysis and the rheological properties by DMTA and stress relaxation tests. Molecular analysis proved a folded and compact molecular structure and indicated the presence of chains with different molecular weights for native carrageenan. The results obtained showed that the helix-coil transition occurs at temperature about 50 °C. The native and commercial grade carrageenan presented the characteristic of viscoelastic materials and their gel properties show a higher contribution from solid elastic component, and the initial force ( $F_0$ ) was higher in commercial carrageenan than native one.

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## 1. Introduction

Carrageenans are a class of sulfated galactan extracted from different species of red seaweed (*Phyllum Rhodophyta*). *Kappaphycus alvarezii*, seaweed of high commercial value, is cultivated as raw material for industrial production of  $\kappa$ -carrageenan (Estevez, Ciancia, & Cerezo, 2004). Carrageenans are extensively used in food, pharmaceutical and cosmetic industry as viscosity builders, gelling agents and stabilizers (De Ruiter & Rudolph, 1997).

The three principal carrageenan types of industrial importance are kappa, iota and lambda. These polysaccharides backbones are formed of D-galactose units (G) linked alternately with alpha-(1→3) and beta-(1→4) linkages. Their chemical structures differ according to the presence of 3,6-anhydro-D-galactose (DA) on the 1,4-linked residue and the position and number of sulfated groups, resulting in distinctive gel properties (Tojo & Prado, 2003; van de Velde, 2008). Kappa ( $\kappa$ ) and iota ( $\iota$ ) forms are gelling polymers, while lambda ( $\lambda$ ) is a non-gelling, thickening agent (De Ruiter & Rudolph, 1997).

The functionality of a natural biopolymer like carrageenan is in most cases governed by their molar mass, molar mass distribution, size, shape and viscoelastic properties. Furthermore, it may also depend on the temperature and on solvent composition as many biopolymers self-associate and aggregate in solution (Viebk

& Williams, 2000). The characterization of these parameters for a polymer in solution is thus important to understand the properties of a product (Myslabodski, Stancioff, & Heckert, 1996; Viebke & Williams, 2000).

The viscoelastic properties of carrageenan fluid gels depend on their microstructure as well as the interactions/bridging between the produced particles. If some biopolymer properties were known, these both can be modified and controlled by typical formulation/process parameters such as the rate of deformation and the rate of cooling, during the temperature quench applied to induce the conformational ordering and gelation of the biopolymer (Gabriele, Spyropoulos, & Norton, 2009).

*K. alvarezii* cultivation in Brazil started a few years ago with experimental crops in the southeastern coast with  $\kappa$ -carrageenan production (Bulboa, Paula, & Chow, 2007; Paula, Pereira, & Ohno, 1999). Nowadays, implementation of *K. alvarezii* cultivation has been studied in experimental growths in the southern region of Brazil, in Florianópolis, in Santa Catarina State (Hayashi et al., 2011).

This study was developed aiming to evaluate and relate the molecular and rheological characteristics of native carrageenan obtained from the *K. alvarezii*, extracted by a differentiated methodology by atomization drying process, which reduces the time for obtaining carrageenan dry powder and minimizes costs and environmental damages caused by the use of organic solvents. Thus, analysis by SAXS, GPC and DMTA were performed in order to characterize the molecular aggregation, the distribution of molecular weight, molecules size and shape. Through the DMTA analysis and the stress relaxation tests information about native carrageenan

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gel rheology, mechanical properties and viscoelastic behavior were obtained. These native carrageenan properties were compared with a commercial grade carrageenan from Sigma–Aldrich (C1013).

## 2. Materials and methods

### 2.1. Samples

*K. alvarezii* samples of brown tetrasporophytic strain were obtained from Biological Sciences Center (CCB) of Federal University of Santa Catarina (UFSC), which were grown in an experimental cultivation in Sambaqui Beach, in Florianópolis, Santa Catarina State, Brazil (27°29'19"S/48°32'28"W). Algae were collected in March 2010, they were air-dried for 4 days and, then, dried in the oven (60 °C) for 48 h before extraction. Commercial carrageenan pattern (type I, containing predominantly *kappa* ( $\kappa$ ) with the least amount of *lambda* ( $\lambda$ )) (C1013) was purchased from Sigma–Aldrich).

### 2.2. Carrageenan aqueous extraction

Previously dried algae were washed in water on order to remove salts and dirtiness. Samples of 10 g were soaked in distilled water (800 mL) for 1 h and then crushed in a mixer. This solution was placed in a water-bath (with different times and temperatures, according to the statistical design). After that, Celite (25 g) was added to this solution 15 min before the end of the process in order to help the filtration process. Separation of carrageenans (filtrate) from seaweed residue was carried out in a filtration vacuum system with qualitative paper. Then, the filtrated solution containing carrageenan was atomized in Mini Spray Dryer B-290 (BÜCHI) to obtain carrageenan powder by using the following parameters: inlet temperature 200 °C, air flow 30 mL min<sup>-1</sup>, aspiration capacity of 100% and pump capacity of 25%.

### 2.3. Small-angle X-ray scattering

The SAXS measurements for native carrageenan were performed in the Synchrotron Light National Laboratory, LNLS, in Campinas, Brazil. The experiments were made by wavelength of the photons  $\lambda = 1.76 \text{ \AA}$  and the detector distance from the sample  $d = 2.5079 \text{ m}$ . These conditions impose a limit angle of  $0.05 < \bar{q} < 1.15$ . The detection was made with a CCD camera. The samples (1.5%, w w<sup>-1</sup>) were prepared upon heating to 80 °C, and after, they were thermostated during all measurements at 25 °C. The acquisition was made with two frames (XRD patterns) of 150 s each, except when the time was adjusted according to the scattering of the sample. Liquid samples (emulsions) were injected into a sample holder with mica window. Solid samples were attached to a set of metal rings with a Kapton tape. The rings were then inserted in mica window of the previous sample holder and they were sealed with PTFE rings.

### 2.4. Gel permeation chromatography

Native carrageenan analyses by gel permeation chromatography (CPG) were performed in an instrument called TDA 302 – Triple Detector Array from Viscotek®. The sample was diluted in sodium phosphate buffer 70 mM pH 7.0 to a final concentration of approximately 2.72 mg mL<sup>-1</sup> and subjected to heat (40 °C) for approximately 10 min. After cooling down, the samples were homogenized and filtered through a Millipore filter® PVDF 0.45  $\mu\text{m}$ , and they were transferred to 2 mL vial being positioned in the autosampler rack. We made two runs of each sample to confirm the reproducibility of measurements. It was used a mobile phase of sodium phosphate buffer (70 mM pH 7.0) filtered vacuum and degasser with membrane of 0.45  $\mu\text{m}$ . It was used the column

3 × PolyAnalytik PAA 206M Aqua000125 (30 cm × 8 mm) – exclusion limit  $2 \times 10^7$ . The column temperature was 30 °C, the detector temperature was 30 °C and the pumped flow was of 1 mL min<sup>-1</sup>. The injection volume used was 100  $\mu\text{L}$  and the running time was set at 55 min. Detectors (refractive index, viscometer capillary and double-angle light scattering RALS, LALS RALS and DP) were calibrated with standard PEO 22 K in NaNO<sub>3</sub> (2.04 mg mL<sup>-1</sup>). The chromatograms were analyzed using dn/dc (refractive index increment) equal to 0.145.

### 2.5. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis was performed in carrageenan solutions (commercial and native) prepared to 3% (w w<sup>-1</sup>) diluted to 80 °C. These solutions were placed in cylindrical molds with a diameter of 11 mm and a height of 2.5 mm. Then they were cooled to 10 °C. The equipment used was a DMA from TA Instruments Q 800. The experiments were performed within the linear viscoelastic region (0.1% strain) using a geometry compression.

Two tests were performed. The first one evaluated the fusion of the gel, with a variation of temperature from –10 °C to 80 °C in a constant frequency. The second test was done in a scanning frequency of 0.1–100 Hz at a constant temperature of 10 °C.

### 2.6. Stress relaxation

The rheological analyses (stress relaxation) were carried out using a TA-XT2 Plus (Stable Micro Systems, Ltd., Surrey, UK) fitted with a 50 kg load cell and a 45 mm diameter cylindrical probe. The carrageenan gels samples (3%, w w<sup>-1</sup>, 25 mm diameter and 10 mm height) were subjected to 50% compression for 20 s at a cross-head speed of 0.5 mm s<sup>-1</sup> at 8 °C. The relaxation rate was determined by Eq. (1). The experimental results for the stress relaxation were normalized and analyzed through the empirical model proposed by Peleg (1980) as shown in Eq. (2):

$$R_{\text{RELAX}} = \frac{F(t)}{F_0} \times 100 \quad (1)$$

$$\frac{F(t)}{F_0} = 1 - \frac{c_1 \cdot t}{c_2 + t} \quad (2)$$

$F(t)$  is the force at time ( $t$ ) and  $F_0$  is the initial force.

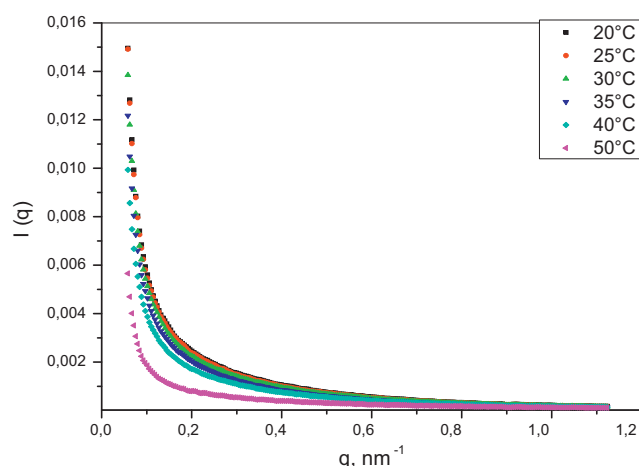
Parameters  $c_1$  and  $c_2$  were estimated by non-linear regression using STATISTICA 6.0 software. In this model,  $1 - c_1$  and  $c_1/c_2$  provide information about the material viscoelastic characteristics. The value of  $(1 - c_1)$  can be seen as a “degree of solidity”, while the ratio  $c_1/c_2$  represents the initial rate of the stress decay. The “degree of solidity” is associated with the global behavior of the material, thus all the experimental data were considered. In order to obtain a precise estimation of the initial decay the rate data were adjusted by using the first 20 experimental points from the relaxation curve, without dimension through the ratio  $F(t)/F_0$  versus time as suggested by Müller, Laurindo, and Yamashita (2009) and Fritzen-Freire, Müller, Laurindo, and Prudêncio (2010).

## 3. Results

### 3.1. Small-angle X-ray scattering

Small-angle X-ray scattering measurements were used to investigate the aggregation formation. Fig. 1 shows the scattering intensity increases while native carrageenan (1.5%, w v<sup>-1</sup>) solution temperature decreases.

The SAXS intensity solutions can also be interpreted by the Guinier formalism, described in Eq. (1). According to this approach,



**Fig. 1.** Small-angle X-ray scattering for the native carrageenan at different temperatures.

**Table 1**

Radius of gyration obtained from the different temperatures estimated through small-angle X-ray scattering measurements for native carrageenan.

Temperature (°C)	Radius of gyration (nm)	Error (nm)
20	24.42	1.62
25	23.52	1.39
30	23.98	1.60
35	23.31	1.24
40	22.65	1.35
50	25.61	1.53

it is possible to obtain the radius of gyration  $R_g$  from the slope of the linear section slope of the SAXS curves in the limit  $q \rightarrow 0$  on the Guinier graph. In other words,  $\ln(I(q))$  versus  $q^2$ . Table 1 show the radius of gyration values at different carrageenan solution temperatures at 1.5%. The values for the radius of gyration ranged from 22.65 nm (40 °C) to 25.61 nm (50 °C). On the temperature of 50 °C, the radius of gyration presented the highest value, probably due to the expansion of the particles on the sol state:

$$\ln I = \ln I_0 - q^2 \left( \frac{R_g^2}{3} \right) \quad (3)$$

### 3.2. Gel permeation chromatography

An important aspect of the polymer structure is the polymerization degree or molecular weight. Table 2 shows the data obtained for native carrageenan molecular characteristics.

Table 3 below shows a relationship between some  $\rho$ -ratio values and their associated topology.

The radius of gyration, found by X-ray scattering at low angles (Table 1) was 24 nm, and the hydrodynamic radius was 21.83 nm (Table 2). The  $\rho$ -ratio obtained for the native carrageenan sample was 1.10, similar to a related hollow sphere that is 1.00 (Table 3).

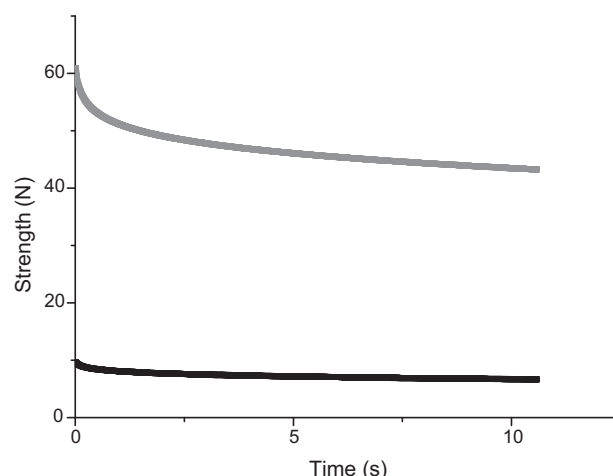
### 3.3. Stress–relaxation tests

The stress–relaxation curves (Fig. 2) present the characteristic shape of viscoelastic materials, with a residual stress decreasing to

**Table 2**

Z-Average molecular weight, the number-average molecular weight, the weight-average molecular weight, the polydispersity index and the hydrodynamic radius of native carrageenan.

	$M_z$ (g mol <sup>-1</sup> )	$M_w$ (g mol <sup>-1</sup> )	$M_n$ (g mol <sup>-1</sup> )	$M_w/M_n$	$R_h$ (nm)
Native carrageenan	489.063	259.882	81.667	3.18	21.83



**Fig. 2.** Experimental stress–relaxation curves from (○) commercial grade  $\kappa$ -carrageenan and (●) native carrageenan from *K. alvarezii* (3%, w w<sup>-1</sup>).

**Table 3**

Relation between  $\rho$ -ratio for the most-typical particle morphologies.

Topology	$\rho$ -Ratio
Homogeneous sphere	0.775
Hollow sphere	1
Ellipsoid	0.775–4
Random polymer coil	1.505

Source: Adapted from Scharl (2007).

an asymptotic value. The values of gels relaxation ratios ( $R_{RELAX}$ ), parameters  $c_1$  and  $c_2$  of the Peleg's model, determined from the relaxation curves are shown in Table 4.

### 3.4. Dynamic mechanical thermal analysis

Figs. 3 and 4 show the commercial and native carrageenan behavior 3% (w w<sup>-1</sup>) when they are subjected to a dynamic mechanical thermal analysis.

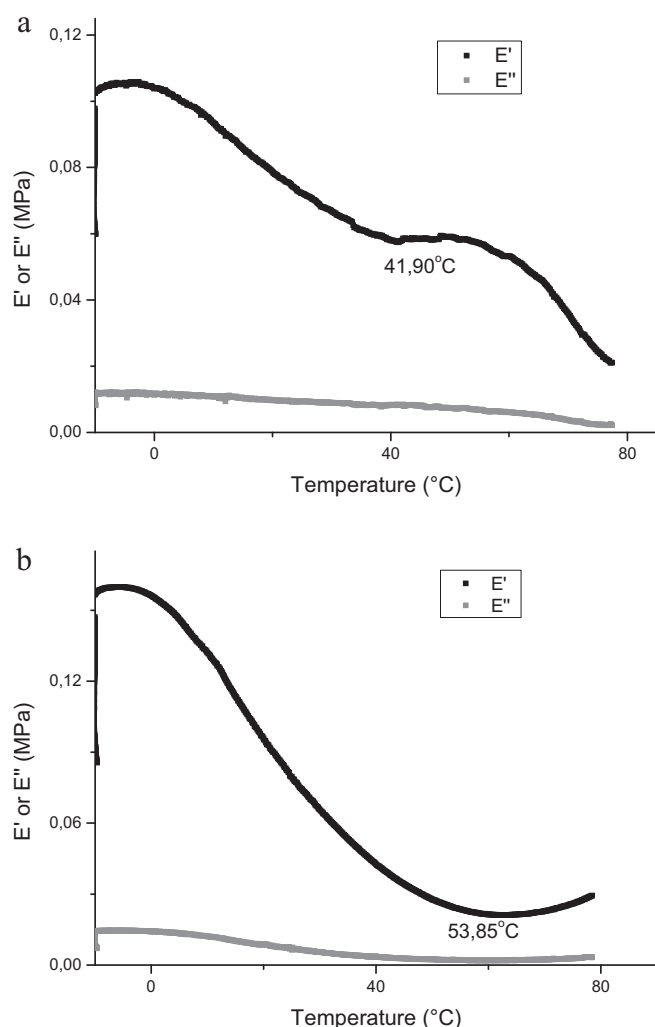
Fig. 3 shows the reduction of the modules (elastic and viscous) while the temperature increases. The ratio between viscous module ( $E''$ ) and elastic modulus ( $E'$ ), or tangent  $\delta$  ( $\tan \delta$ ), defines the gel as more or less strong. A higher ratio can be observed at temperatures lower than 0 °C, in which the gel is stronger. As the temperature increases  $E'$  gets closer to  $E''$ , characterizing the slow occurrence of the gel–sol transition. There is an inflection in the curve of the elastic modulus for the commercial carrageenan sample at a temperature of 41.90 °C, while this same inflection occurred for the native carrageenan sample in 53.85 °C, these inflections correspond to sol–gel transition.

**Table 4**

Rheological properties of gel samples.

Carrageenan	$(1 - c_1)$	$(c_1/c_2)$ (s)	$F_0$ (N)	$R_{RELAX}$ (%)
Commercial	$0.63^a \pm 0.01$	$0.74^a \pm 0.09$	$9.22^a \pm 0.7$	$63.50^a \pm 1.05$
Native	$0.66^b \pm 0.01$	$0.76^a \pm 0.02$	$60.96^b \pm 2.68$	$66.48^b \pm 1.08$

Within a column, different superscript lowercase letters denote significant difference ( $p < 0.05$ ) among gels samples.



**Fig. 3.** Dynamic mechanical thermal behavior with  $E'$  and  $E''$  at temperatures ranging from  $-10^{\circ}\text{C}$  to  $80^{\circ}\text{C}$  (a) commercial carrageenan and (b) native carrageenan – ( $\blacksquare$   $E'$  and  $\bullet$   $E''$ ) at constant frequency of 1 Hz.

Fig. 4 shows the behavior of  $E'$  and  $E''$  modules of commercial and native carrageenan (3%, w w $^{-1}$ ) when subjected to a frequency sweep at a constant temperature of  $10^{\circ}\text{C}$ .

The modules  $E'$  and  $E''$  are higher for commercial carrageenan in relation to native carrageenan (Fig. 4), which shows that the commercial carrageenan is more resistant to increased frequency of the applied strength, demonstrating the highest level of commercial carrageenan aggregation. The curves show that at  $10^{\circ}\text{C}$ , on this range of frequency sweep test, the samples have no changes in their physical structure, and these remained a gel behavior, with strong solid component, which is predominant in relation to viscous behavior. The difference between  $E'$  and  $E''$  at high frequencies is reduced, particularly when samples are subjected to high temperatures (Chen, Liao, & Dunstan, 2002).

The gel strength, which can be seen through the elastic modulus ( $E'$ ), is higher for commercial carrageenan. The elastic modulus increases with polymer concentration and varies with the type of carrageenan ( $\kappa$  >  $\iota$  >  $\lambda$ ) (Daniel-da-Silva et al., 2008).

#### 4. Discussion

The increase in intensity at low scattering angles (Fig. 1) expresses the presence of a structure in large-scale network. In other words, it means a high degree of intermolecular

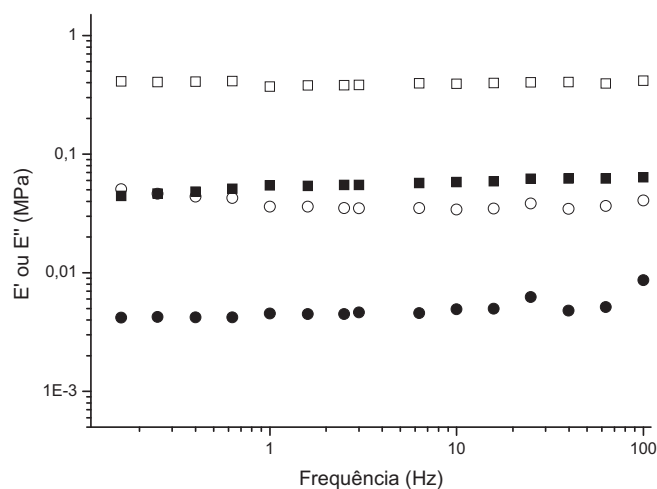
aggregation (Tomsic, Prossnigg, & Glatter, 2008). The higher the temperature the lower the intensity of scattering, until a rapid drop in scattering intensity occurs at  $50^{\circ}\text{C}$ . At this specific temperature, there is a sol–gel transition. This gradual decrease of the scattering intensity in a temperature range reflects a decrease in the intermolecular interactions and in the weakening of the gel network. That is, when the intermolecular bonds begin to break down, the network structure begins to weaken and the molecules lose their structure and the network organization disappears. During this process of merging network, there are still regions of intermolecular bonds remaining which still yield a slight increase in the scattering intensity at low angles, but these bonds are rapidly disappearing with the temperature increasing.

All these results are in agreement with the gelation mechanism described in previous works, where the first conformational change of carrageenan molecules from ropes to helices occurs and is followed by the aggregation of these helices to form a large network structure (Kara, Arda, Kavzak, & Perkan, 2006; Kara, Tamerler, Bermek, & Peckan, 2003; Iijima, Hatakeyama, Takahashi, & Hatakeyama, 2007; Yuguchi, 2009).

Mechanical and gelling properties of pure  $\kappa$ -carrageenan gels are a function of the polysaccharide molecular mass  $M_w$  (Rochas, Rinaudo, & Landry, 1990; Souza, Hilliou, Bastos, & Gonçalves, 2011). When polysaccharide molecular mass is under a critical molecular mass of  $M_{ck} = 3 \times 10^4 \text{ g mol}^{-1}$  no  $\kappa$ -carrageenan gel is formed. However, gel elastic properties are independent of  $M_w$ , as soon as the latter is above  $180,000 \text{ g mol}^{-1}$  (Rochas et al., 1990). In addition, values for carrageenan molecular molar weight below  $50,000 \text{ g mol}^{-1}$  are related to degraded carrageenan, which can cause damage to health (European Scientific Committee on Food – SCF, 2003).

GPC revealed a molecular mass variable for native carrageenan as it was found by Villanueva, Mendoza, Rodriguez, Romero, and Montañó (2004) when they analyzed carrageenan samples. The  $M_w$  value found in this study was approximately  $259,882 \text{ g mol}^{-1}$  (Table 2).

Hayashi et al. (2007) compared the molecular weights of carrageenans extracted from *K. alvarezii* (farmed on Brazilian coast) by a natural and alkaline method against a commercial carrageenan and found higher values than the ones obtained in this experiment. The molecular weight values found by these researches were between  $1.2 \times 10^6$  and  $1.8 \times 10^6 \text{ g mol}^{-1}$  to the carrageenan extracted by the natural method, from  $1.8 \times 10^6$  to  $2.75 \times 10^6 \text{ g mol}^{-1}$  to the carrageenan extracted by alkaline



**Fig. 4.** Frequency sweeps of the commercial and native carrageenan samples at  $10^{\circ}\text{C}$ : squares,  $E'$ ; circles,  $E''$ ; hollow symbols, commercial; filled symbols, native carrageenan.



method, and between  $4.8 \times 10^5$  and  $5.4 \times 10^5 \text{ g mol}^{-1}$  to a commercial carrageenan.

The polydispersity index obtained for native carrageenan (Table 2) agreed with the results from a study realized by Hilliou et al. (2006), who worked with seaweed *Mastocarpus stellatus* (predominantly  $\kappa$ -carrageenan) in alkaline condition in different time (0.5, 1, 2, 4 and 6 h) and temperature conditions (80, 95 and 110 °C), and they found, by molecular exclusion chromatography, polydispersity indices ranging from 2.4 to 4.0.

The ratio between radius of gyration ( $R_g$ ) and hydrodynamic radius ( $R_h$ ), called  $\rho$ -ratio, is an experimental value derived from a combination of the particle size. The  $\rho$ -ratio provides an indication of the particle topology, especially for comparatively small particles (between 10 and 100 nm), according to Scharl (2007).

The value obtained for molecular weight of native carrageenan was lower than the previous studies (Hilliou et al., 2006; Hayashi et al., 2007). This variation may be due to the different sources of carrageenan and different extraction methods used in different studies (van de Velde et al., 2005). However, the molecular mass of native carrageenan is above  $M_{ck}$  and  $180,000 \text{ g mol}^{-1}$ , and the elastic properties of the gel, which characterize the stiffness of the polymer, are independent of molecular weight. Therefore, the difference in the elastic behavior analyzed ( $E'$ , Figs. 3 and 4) between both carrageenan is probably due to the degree of molecular aggregation related to the presence of sulfate groups acting as counterions.

It can be seen from the molecular weight and polydispersity analysis (Table 2) that the native carrageenan sample is very polydisperse. Thus, the contribution of chains with small molecular weight is more significant. In addition, the high concentration of potassium ions ( $K^+$ ) acting as counter ions of the carrageenan sulfate groups reduces the electrostatic repulsion of the polymer chains, making it more folded and compact, which translates into a  $\rho$ -ratio close to 1 (Table 3).

The results given in Table 4 show that both gels (commercial grade  $\kappa$ -carrageenan and native carrageenan) presented a higher contribution from solid elastic component. However, the commercial  $\kappa$ -carrageenan showed a higher degree of solidity. The initial force ( $F_0$ ) was higher in the commercial  $\kappa$ -carrageenan than in the native (Fig. 2). The initial rate of stress decay was the same for both gels. According to Peleg (1979),  $(1 - c_1)$  can be seen as degree of solidity, while  $(c_1/c_2)$  is the initial stress decay rate. When  $(1 - c_1)$  goes to 1, the material behaves as an elastic solid, and when  $(1 - c_1)$  goes to zero, the material behavior is controlled by the viscous component.

The viscoelastic properties analysis results, reported in Fig. 3, show that for both samples the elastic modulus ( $E'$ ) had a higher variation than the viscous module ( $E''$ ), being  $E'$  higher than  $E''$ , as expected for viscoelastic materials with a predominance of solid behavior. The values of the elastic and viscous modules are very different for the two samples, because they depend on the ionic composition, although they do not depend on the ionic strength (Mangione et al., 2007).

The greater elasticity (strength) of the gel in commercial carrageenan (Figs. 2–4 and Table 4) can be explained by its lower number of sulfate groups (data not shown), which are a direct measure of the amount of not gelling units in the polysaccharide structure. The increasing elasticity with the reduction of sulfate groups is well documented in the literature (Nilsson & Picullel, 1991) for homopolymers  $\kappa$ - and  $\iota$ -carrageenan and is explained by the fact that biological precursors sulfated stopped the stereochemistry regularly at the site (gelling process is interrupted by non-gelling monomers) restricting the conformational transition of polysaccharide from rope to aggregate helices aggregate (Hilliou et al., 2006).

## 5. Conclusion

Molecular characterization of native carrageenan showed a compact molecular structure and the presence of chains with different molecular weight; with a large contribution of low molecular weight ones. As a consequence, the  $M_w$  of native carrageenan was lower when compared to the values described in the literature for carrageenan.

The rheological properties were affected by the distribution of molecular weight and molecular aggregation. Native carrageenan from *K. alvarezii* showed similar degree of solidity when compared with a commercial grade  $\kappa$ -carrageenan. However, native carrageenan presented lower initial force in stress relaxation curve, lower gel strength and lower resistance to applied force in DMTA analysis. These results suggest a higher molecular weight and higher degree of aggregation of commercial carrageenan. Probably, the differences between commercial and native carrageenans are due to the extraction and to the drying process, once the present work used a hot extraction and spray drying, an innovative process which did not involve any organic solvent (alcohol). However, both carrageenans showed viscoelastic materials behavior with a predominance of solid behavior.

There are a number of thickeners and gels on the market which have multiple uses, particularly in the food industry. Their physicochemical properties depend on the specific chemical nature and each one is more adequate for certain uses. Carrageenan gel properties extracted from *K. alvarezii* showed potential application in the food and pharmaceutical industry. In addition, mariculture of this species holds the potential for rural production and/or industrial scale use in the future, and could contribute to an additional income source for (local) people of Santa Catarina Island.

## References

- Bulboa, C. R., Paula, E. J., & Chow, F. (2007). Laboratory germination and sea out-planting of tetraspore progeny from *Kappaphycus striatum* (Rhodophyta) in subtropical Waters of Brazil. *Journal of Applied Phycology*, 19, 357–363.
- Chen, Y., Liao, M.-L., & Dunstan, D. E. (2002). The rheology of  $K^+$ - $\kappa$ -carrageenan as a weak gel. *Carbohydrate Polymers*, 50, 109–116.
- Daniel-da-Silva, A. L., Lóio, R., Lopes-da-Silva, J. A., Trindade, T., Goodfellow, B. J., & Gil, A. M. (2008). Effects of magnetite nanoparticles on the thermorheological properties of carrageenan hydrogels. *Journal of Colloid Interface Science*, 324, 205–211.
- De Ruiter, G. A., & Rudolph, B. (1997). Carrageenan biotechnology. *Trends in Food Science and Technology*, 8, 389–395.
- Estevez, J. M., Ciancia, M., & Cerezo, A. S. (2004). The system of galactans of the red seaweed *Kappaphycus alvarezii*, with emphasis on its minor constituents. *Carbohydrate Research*, 339, 2575–2592.
- Fritzen-Freire, C. B., Müller, C. M. O., Laurindo, J. B., & Prudêncio, E. (2010). The influence of Bifidobacterium BB-12 and lactic acid incorporation on the properties of Minas Frescal cheese. *Journal of Food Engineering*, 96, 621–627.
- Gabriele, A., Spyropoulos, F., & Norton, I. T. (2009). Kinetic study of fluid gel formation and viscoelastic response with kappa-carrageenan. *Food Hydrocolloids*, 23, 2054–2061.
- Hayashi, L., Oliveira, E. C., Bleicher-Lhonné, G., Boulenguer, P., Pereira, R. T. L., Von Seckendorff, R., et al. (2007). The effects of selected cultivation conditions on the carrageenan characteristics of *Kappaphycus alvarezii* (Rhodophyta, Solieriaceae) in Ubatuba bay, São Paulo, Brazil. *Journal of Applied Phycology*, 19, 505–511.
- Hayashi, L., Santos, A. A., Faria, G. S. M., Nunes, B. G., Souza, M. S., Fonseca, A. L. D., et al. (2011). *Kappaphycus alvarezii* (Rhodophyta, Areschougaceae) cultivated in subtropical waters in Southern Brazil. *Journal of Applied Phycology*, 23, 337–343.
- Hilliou, L., Larotonda, F. D. S., Abreu, P., Ramos, A. M., Sereno, A. M., & Gonçalves, M. P. (2006). Effect of extraction parameters on the chemical structure and gel properties of  $\kappa/\iota$ -hybrid carrageenans obtained from *Mastocarpus stellatus*. *Biomolecular Engineering*, 23, 201–208.
- Iijima, M., Hatakeyama, T., Takahashi, M., & Hatakeyama, H. (2007). Effect of thermal history on kappa-carrageenan hydrogelation by differential scanning calorimetry. *Thermochimica Acta*, 452, 53–58.
- Kara, S., Arda, E., Kavzak, B., & Perkan, O. (2006). Phase transitions of  $\kappa$ -carrageenan gels in various types of salts. *Journal of Applied Polymer Science*, 102, 3008–3016.

- Kara, S., Tamerler, C., Bermek, H., & Peckan, O. (2003). Hysteresis during sol–gel and gel–sol phase transitions of  $\kappa$ -carrageenan: A photon transmission study. *Journal of Bioactive and Compatible Polymers*, 18, 33–44.
- Mangione, M. R., Giacomazza, D., Cavallaro, G., Bulone, D., Martorana, V., & San Biagio, P. L. (2007). Relation between structural and release properties in a polysaccharide gel system. *Biophysical Chemistry*, 129, 18–22.
- Müller, C. M. O., Laurindo, J. B., & Yamashita, F. (2009). Effect of cellulose fibers on the crystallinity and mechanical properties. *Carbohydrate Polymers*, 77, 293–299.
- Myslabodski, D. E., Stancioff, D., & Heckert, R. A. (1996). Effect of acid hydrolysis on the molecular weight of kappa carrageenan by GPC-LS. *Carbohydrate Polymers*, 31, 81–92.
- Nilsson, S., & Picullel, L. (1991). Helix-coil transitions of ionic polysaccharides analyzed within the Poisson–Boltzmann cell model. 4. Effects of site-specific counterion binding. *Macromolecules*, 24, 3804–3811.
- Paula, E. J., Pereira, R. T. L., & Ohno, M. (1999). Strain selection in *Kappaphycus alvarezii* var. *alvarezii* (Solieriaceae, Rhodophyta) using tetraspore progeny. *Journal of Applied Phycology*, 11, 111–121.
- Peleg, M. (1979). Characterization of the stress relaxation curves of solid foods. *Journal of Food Science*, 44, 277–281.
- Peleg, M. (1980). Linearization of relaxation and creep curves of solid biological materials. *Journal of Rheology*, 24, 451–463.
- Rochas, C., Rinaudo, M., & Landry, S. (1990). Role of molecular weight on the mechanical properties of kappa carrageenan gels. *Carbohydrate Polymers*, 12, 255–266.
- SCF. (2003). *Opinion of the scientific committee on food on carrageenan, opinion expressed on 5 March 2003*. Brussels, Bélgica: European Commission Health and Consumer Protection Directorate General.
- Schartl, W. (2007). *Light scattering from polymer solutions and nanoparticle dispersions*. Berlin: Springer.
- Souza, H. K. S., Hilliou, L., Bastos, M., & Gonçalves, M. P. (2011). Effect of molecular weight and chemical structure on thermal and rheological properties of gelling  $\kappa/\iota$ -hybrid carrageenan solutions. *Carbohydrate Polymers*, 85, 429–438.
- Tojo, E., & Prado, J. (2003). Chemical composition of carrageenan blends determined by IR spectroscopy combined with a PLS multivariate calibration method. *Carbohydrate Research*, 338, 1309–1312.
- Tomsic, M., Prossnigg, F., & Glatter, O. (2008). A thermoreversible double gel: characterization of a methylcellulose and  $\kappa$ -carrageenan mixed system in water by SAXS, DSC and rheology. *Journal of Colloid and Interface Science*, 332, 41–50.
- van de Velde, F., Antipova, A. S., Rollema, H. S., Burova, T. V., Grinberg, N. V., Pereira, L., et al. (2005). The structure of  $\kappa/\iota$ -hybrid carrageenans. II. Coil-helix transition as a function of chain composition. *Carbohydrate Research*, 340, 1113–1129.
- van de Velde, F. (2008). Structure and function of hybrid carrageenan. *Food Hydrocolloids*, 22, 727–734.
- Viebkke, C., & Williams, P. A. (2000). Determination of molecular mass distribution of  $\kappa$ -carrageenan and xanthan using asymmetrical flow field-flow fractionation. *Food Hydrocolloids*, 14, 265–270.
- Villanueva, R. D., Mendoza, W. G., Rodriguez, M. R. C., Romero, J. B., & Montaña, M. N. E. (2004). Structure and functional performance of gigartinacean  $\kappa/\iota$ -hybrid carrageenan and solieriacean  $\kappa$ - $\iota$  carrageenan blends. *Food Hydrocolloids*, 18, 283–292.
- Yuguchi, Y. (2009). Nano-structure analysis of sugar chains by small angle X-ray scattering. *Trends in Glycoscience and Glycotechnology*, 21, 1–12.