



Gel setting of hybrid carrageenan solutions under steady shear



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ABSTRACT

We study the gel formation under steady shear and the final gel properties of hybrid-carrageenan solutions in NaCl and KCl, with a systematic comparison with kappa- and iota-carrageenan solutions. For high enough shear rates corresponding to homogeneous flow, the structural development of the gels is overall the same for the different salts and carrageenans, and shows the following features: (a) helices are formed during cooling and the onset of formation is not affected by the flow; (b) the flow-induced orientation of structures results in the shear thinning behaviour of the cooling fluids; (c) structural orientation is locked upon the gel setting which takes place immediately after flow cessation and results in a significantly weaker gel elasticity, longer gel structural build-up, a shift of the spectrum of gel relaxation times to longer times, and in the eventual birefringence of films obtained from dried gels. A new phenomenological model that contemplates all experimental results is proposed.

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1. Introduction

Kappa/iota-hybrid carrageenans (KI) are natural polysaccharides extracted from seaweeds species of the Gigartinales, Petrocelidaceae, Phylloporaceae and to some extent the Solieriaceae families (van de Velde, 2008). These phycolloids are known in the food industry as “weak gelling kappa” or “kappa-2” and find specific applications in the dairy industry (Bixler & Porse, 2011; Villanueva, Mendoza, Rodriguez, Romero, & Montañó, 2004). KI are now becoming attractive substitutes to more conventional iota-carrageenan (I) and kappa-carrageenan (K) in order to mitigate the pressure on the natural resources generated by the increasing demand for such food additives (Bixler & Porse, 2011).

Despite their industrial relevance in many applications, the gel behaviour of KI at large deformation is poorly documented (Hilliou, Wilhelm, Yamanoi, & Gonçalves, 2009; van de Velde, 2008; Villanueva et al., 2004). In contrast to this, an extensive literature on the effect of a steady simple shear on gel microstructure and final viscoelastic properties is available for other gelling food ingredients, such as for instance gelatin (Ottone, Peirotti, & Deiber, 2009; Ronsin, Caroli, & Baumberger, 2011 and references therein).

The first report (to the best of our knowledge) on the gelling and flow behaviour of KI hot solutions undergoing steady shear was given a decade ago by Paul Callaghan and Ana Gil, who used rheo-NMR to image the velocity profiles in the sheared solutions and gels by inserting a Couette cell in an NMR magnet (Callaghan & Gil, 2001). The experimental section of this report indicates that the commercial carrageenan sample was “...extracted from *Chondrus crispus* (the sea weed, Irish Moss)”. This seaweed is known to produce KI (Bixler, 1996; Chopin, Kerin, & Mazerolle, 1999) with K content ranging from 81 mol% to 30 mol% (van de Velde, 2008). Hot KI solutions submitted to small enough shear rates during cooling showed non-homogeneous velocity profiles corresponding to co-existing gel (close to the fixed wall) and solution (closed to the shearing surface) phases in the gap. For larger shear rates, homogeneous velocity profiles reminiscent from shear thinning fluids were recorded during the whole cooling. T_2 magnetic relaxation data showed that during the cooling under shear, the break-up of intermolecular junction zones between KI macromolecules favours the formation of a shear-induced fluid phase which flows together with a phase showing significantly more connectivity at the macromolecular level. However, flow curves could not be measured in-situ during the gel build-up and the effect of shear on the viscoelastic and structural properties of resulting gels was not reported.

The general objective of this paper is to expand the limited set of data available so far for the characterization of the properties of

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gelling solutions of hybrid carrageenan (HY) under shear (Hilliou & Gonçalves, 2007). HY differ from KI as they are composed of biosynthetic precursors such as μ - and ν -carrageenan, which act as kinks which hinder the gelation process (Rees, 1972), in addition to gelling blocks of I and K. HY are obtained by the non complete alkali conversion of precursors into K and I (Hilliou, Larotonda, Abreu, et al., 2006; Hilliou, Larotonda, Sereno, & Gonçalves, 2006), resulting in products exhibiting gelling properties intermediate between K and I gels. In particular, this paper aims at benchmarking the results with those obtained with sheared solutions of gelling K and I under equivalent experimental condition, at comparing the results with predictions from structural kinetics models commonly used to describe the thixotropy of structuring fluids under steady shear (Beris, Stiakakis, & Vlassopoulos, 2008; Dullaert & Mewis, 2006; Møller, Mewis, & Bonn, 2006; Ottone et al., 2009) and with the phenomenological models currently used to explain the formation of “fluid gels” (De Carvalho & Djabourov, 1997; Norton, Jarvis, & Foster, 1999). Gel formation in the presence of two different salts, namely K^+ and Na^+ , is explored because HY shows salt-dependent gelling properties which are inherent to HY chemical structure. A two-step gelling process has been found in the temperature dependence of the loss modulus G'' during the cooling of a 2 wt% HY solution in NaCl (Souza, Hilliou, Bastos, & Gonçalves, 2011). In contrast to this, the same HY in KCl solutions presents a single gelling process (Hilliou, Larotonda, Sereno, et al., 2006).

2. Experimental

2.1. Hybrid carrageenan solutions

The extraction of HY from *Mastocarpus stellatus* seaweeds has been reported in length elsewhere (Hilliou, Larotonda, Abreu, et al., 2006; Hilliou, Larotonda, Sereno, et al., 2006). Briefly, gametophytes fronds stored under conditions described elsewhere to enhance post-harvest duration storage (Hilliou et al., 2012) were submitted to an alkali treatment (40 g dried algae soaked in 4 L of 0.1 M Na_2CO_3 solution at room temperature for 70 h) prior to extraction (at pH 8 and 95 °C during 2 h). After filtration of seaweeds, concentrated carrageenan solutions were precipitated in 2 volumes of ethanol. The precipitate was then dissolved in hot water and centrifuged for further purification of the HY. HY was finally recovered as films by drying the supernatant. The extracted HY has a molecular mass of 431,000 g/mol (polydispersity index is 2.4), contains 48 mol% of K units and 32.7 mol% of I units randomly distributed in blocks of various lengths to impart gelling properties. In addition, these blocks are separated by 19.3 mol% of highly sulphated carrageenan units. Due to the extraction process, HY is recovered in the sodium form (3 wt% Na^+) and no other cation could be detected. K (lot 083K125), I (lot 121K1200), and other chemicals (KCl and NaCl, ACS reagent grades, dodecane, technical grade) were obtained from Sigma–Aldrich (Steinheim, Germany) and used as received. No other K and I lots were tested. Carrageenans were added to 0.05 M KCl or 0.1 M NaCl solutions previously prepared with distilled water, and stirred during 1 h at 75 °C to ensure complete dissolution. The chosen ionic strengths allow screening out any salt effect associated with the cations contents of the commercial products and of the HY, and bringing the gelling temperatures T_g and temperatures $T_g - 10$ °C into the experimental window of the cooling unit attached to the stress-controlled rheometer for the carrageenan concentrations studied here. Thus different gelling systems can be compared under similar temperature conditions with respect to T_g . In addition, the lower ionic strength for KCl was chosen to avoid any syneresis when forming gels with K in the range of concentrations tested.

2.2. Gel formation under steady shear and viscoelastic characterization of obtained gels

Hot carrageenan solutions were loaded in the pre-heated (at 90 °C) plate–plate geometry of a stress-controlled rotational rheometer (ARG2, TA Instruments Inc., USA), and the geometry was covered with dodecane to prevent any water loss. Carrageenan solutions were first cooled at -5 °C/min from 90 °C to a temperature located 10 °C below the gel setting temperature T_g , while a steady shear rate $\dot{\gamma}$ was continuously applied and an apparent shear viscosity η_{app} was measured each 6 s. T_g was determined in a separate cooling experiment (-5 °C/min) where small amplitude oscillatory shear (SAOS) with a strain of 0.5% at a frequency of 1 Hz was applied to determine the temperature at which the phase shift angle δ is 45°. The effect of cooling rates on the yield stress and non linear mechanical properties of sheared K gelling solutions has been reported elsewhere (Gabriele, Spyropoulos, & Norton, 2009). However, the cooling rate was kept constant in the present study to focus on the effects of shear rate, salts and the chemical structure of the carrageenan. Second, a SAOS time sweep (strain 0.5%, 1 Hz) was performed to monitor the time evolution of both shear elastic and loss moduli (G' and G'' , respectively) after the flow cessation at $T_g - 10$ °C. A characteristic time for gel structural build up, t_{build} , was computed as the time at which G' reaches 85% of its final plateau value, which determines gel equilibrium. Finally, a frequency sweep (strain 0.5%) was performed to measure the mechanical spectra of equilibrated gels and record the gel elasticity corresponding to the value of G' measured at 1 Hz.

2.3. Polarized optical microscopy (POM) and cryo-SEM

Right after the completion of the frequency sweep, gels were gently removed from the rheometer by simply sliding the shearing upper plate (previously detached from the rheometer head), and detaching the gel from the bottom plate using a razor blade. Gels formed in KCl could not be removed from the upper plate without structural damaging and thus were discarded. Recovered gel samples were dried in a vacuum oven at room temperature as to obtain solvent free films. These films were then imaged with an Olympus BH2 polarized optical microscope (Olympus America, USA) coupled to a digital camera (DFC280, Leica Camera AG, Germany). Recovered gel samples were also imaged with cryogenic scanning electron microscopy (cryo-SEM). Gel samples were cryo-fractured using an Alto 2500 cryogenic preparation chamber (Gatan Inc., CA), and further imaged using a JEOL JSM 6301F scanning electron microscope. Experimental detail on the sample preparation and SEM imaging can be found elsewhere (Hilliou et al., 2009).

3. Results and discussion

3.1. Gel formation in 0.05 M KCl

The evolution of the apparent viscosity η_{app} recorded during the cooling of carrageenan hot solutions under a representative steady shear of 100 s $^{-1}$ is displayed in Fig. 1 for two different HY concentrations, and for K and I solutions with similar carrageenan concentration. Results are qualitatively similar to those reported elsewhere (Hilliou & Gonçalves, 2007). At higher temperatures, η_{app} follows the simple thermorheological behaviour of dilute and semi-dilute non entangled polymer solutions, which includes an Arrhenius temperature dependence and a Newtonian behaviour (at least within the range of shear rates tested here). η_{app} shows a step increase when a specific temperature T_{on} is reached. The inset in Fig. 1 indicates that the applied shear rate has no effect on T_{on} which simply depends on the type of carrageenan in the solution. We thus

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