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Influence of elasticity on the syneresis properties of κ-carrageenan gels

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ABSTRACT

Kappa-carrageenan hydrogels spontaneously release fluid (syneresis) under certain elasticity conditions, which depend on the temperature, the salt concentration in the gel (KCl) and the polysaccharide concentration. Strong and weak gels exhibit notably weak syneresis properties. The maximum syneresis was found at intermediate elasticity where the gel was neither strong nor weak. The variation in the gel composition indicated that the fluid is released according to the thermal retraction coefficient, which depends on the elasticity. Experiments revealed a dynamic equilibrium of the syneresis process where syneresis fluid was not withdrawn. However, once the fluid was removed from the gel surface, the release of solvent starts again if the elasticity is below the compressive pressure in the gel. Therefore, swelling of the gel is suggested as an explanation for the dynamic equilibrium of the syneresis process.

1. Introduction

Kappa-carrageenan (κ-car) belongs to the polyelectrolyte biopolymer family. This biopolymer is a sulphated polysaccharide extracted from seaweed and has a random coil conformation in aqueous solutions at high temperatures and forms a gel when the solution is cooled to the gelation temperature (T_g). The rheological properties of κ-car have been extensively studied. These investigations assessed the effects of the κ-car concentration, salt and temperature on the gel elasticity (Ciancia, Milas, & Rinaudo, 1997; Hermansson, Eriksson, & Jordansson, 1991; Meunier, Nicolai, Durand, & Parker, 1999; Morris & Chilvers, 1983). Rheological measurements of the sol–gel transition showed that T_g increases with the potassium concentration. By reducing the temperature well below T_g, κ-car gels become firm. When the temperature is increased to T_g, the gels become weak (Ciancia et al., 1997; Hermansson et al., 1991; Meunier et al., 1999; Morris & Chilvers, 1983).

κ-car Hydrogels are known to spontaneously release fluid under certain gel composition conditions (Piculell, Borgström, Chronakis, Quist, & Viebke, 1997). This process is called syneresis and is defined as the spontaneous contraction of a gel without the application of external forces, resulting in the expulsion of a liquid (Gerentes, Vachoud, Doury, & Domard, 2002; Scherer, 1989). This behaviour has attracted much attention in the past and continues to attract significant interest in the field of biomedical applications, including drug delivery systems (Daniel-da-Silva et al., 2012; Ekenseair et al., 2012; Ren, Zhu, & Haraguchi, 2011; Yoshida & Uesusuki, 2005). The precise mechanism that gives rise to syneresis in gels is not clear and still of great interest (Helbig, Hütter, & Schönholzer, 2000; Scherer, 1989; Takeshita, Kanaya, Nishida, & Kaji, 2001; Tijskens & De Baerdemaeker, 2004). Syneresis induced slippage occurs at the gel surfaces during rheological measurement (Richardson & Goycoolea, 1994). The gels are syneresing and the G' measurement shows a G'_{max} (Richardson & Goycoolea, 1994; Lai, Wong, & Lii, 2000; Hermansson, 1989; Hermansson et al., 1991). The gelation of κ-car hydrogels is thermoreversible (Piculell et al., 1997), making this sample a very interesting system to investigate the temperature dependence of syneresis by reheating and cooling the same sample to the desired temperature during rheological measurements.

Gels shrink to expel solvent; therefore, it will be more difficult for strong gels to undergo spontaneous contraction than weak gels. However, syneresis was found in strong gels (Hermansson, 1989) and not weak gels (Chen, Liao, & Dunstan, 2002; Lai et al., 2000; Meunier et al., 1999). The influence of the gel composition on syneresis has already been studied (Piculell et al., 1997; Lai et al., 2000), but there have been no investigations into the influence of the gel elasticity. The aim of the present work is to investigate the influence of elasticity on the syneresis properties of kappa-carrageenan gels by varying the potassium chloride (KCl)

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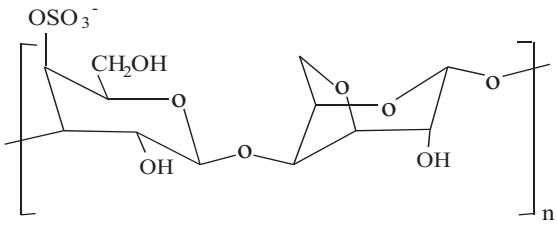

Fig. 1. The kappa-carrageenan molecular structure.

concentration, the κ-car concentration and the temperature. In this work, particular attention is given to the temperature at which the syneresis measurement is performed because the elasticity of the gels depends on the temperature.

2. Materials and methods

2.1. Samples preparation

The kappa-carrageenan polysaccharide is characterised by an alternating disaccharide unit of α-(1-3)-D-galactose-4-sulfate and β-(1-4)-3,6-anhydrose-D-galactose (Fig. 1).

The kappa-carrageenan used in this study was a gift from Cargill, France and was in the pure potassium kappa-carrageenan form. The powder, consisting of 3.9% (w/w) potassium, was used without further purification. The other salts, particularly calcium and sodium, are considered to be only trace amounts.

A 10 g/L stock solution of polysaccharide concentrate (κ-car) was prepared by directly dissolving the powder in demineralised water with 200 ppm sodium azide added as bacteriostatic agent with vigorously stirring for several hours under heating in a water bath at 90 °C. The solution was filtered through 0.2 μm pore size Anotop filters before it was used to prepare all other concentrations. All samples examined were prepared by diluting the kappa-carrageenan solution at room temperature with the appropriate amount of a 400 mM KCl solution containing 200 ppm sodium azide to give the desired final concentration of polysaccharide and salt. The samples were mixed under heating in a water bath at 90 °C for approximately 15 min to give homogeneous solution. Then, 4 g of the hot sample were transferred to individual Pyrex glass tubes of approximately with diameters of 15 mm and allowed to cool to room temperature. The tubes were sealed with paraffin immediately after they were filed to avoid evaporation. Hydrogel formation was confirmed by inverting the tubes to confirm that the meniscus did not flow. To evaluate the influence of the gel composition on the syneresis, the κ-car concentrations ranged from 1 g/L to 8 g/L in the presence of 40 mM KCl, and the KCl ranged from 10 mM to 200 mM with 4 g/L of κ-car.

2.2. Syneresis

The syneresis measurements were performed at room temperature via measuring the amount of solvent release by the hydrogels after various time intervals using a digital high precision balance with a resolution of ±0.01 mg. The syneresis ratio (R_s) in percentage was calculated using the following equation:

$$R_s = \frac{w_e}{w_g} \times 100 \quad (1)$$

where w_e is the weight of solvent releases by the gel and w_g is the weight of the initial gel. w_e was obtained using two methods: pipetting (P) the solvent surrounding the gel with a micro syringe or wiping (W) the gel with filter paper after the gel was removed from the tube (Boral, Saxena, & Bohidar, 2010; Daniel-da-Silva et al., 2012; Kunitz, 1928). The first method gives access to the syneresis of weak gels because it was not possible to wipe those samples. However, this method did not allow for the removal of all of the solvent lost by the gel, and great care was exercised to recover the maximum of water without collecting any gel. The second method led to the extraction of more water than just the water surrounding the gel. To appreciate the constancy of the experimental error, both methods were used on the same gel for all samples studied in this report when it was possible. Syneresis ratios for more than ten different samples were used to establish the relation given by the following equation:

$$R_s^{(W)} = 1.2R_s^{(P)} + 5 \quad (2)$$

The reported values are averages of four sample replicates. For convenience, the pipetting method is used for the syneresis ratio measurements, and 5% is taken as the experimental error of the measurement.

Two series of experiments were performed on the same sample: the first is to quantify the syneresis when the fluid squeeze out is allowed to remain in contact with the gel (called the once removal method, ORM), and the second is to quantify the syneresis when the fluid is removed periodically (called the cumulative removal method, CRM). The results were collected at room temperature (22 ± 2 °C) and refrigerator temperature (9 °C) over approximately 21 days. A stock solution with the indicated composition was poured into several tubes and gelled at room temperature. Seven tubes were kept in the refrigerator while the other samples remained at room temperature. For the ORM experiments, the syneresis of the gel as a function of time was studied by collecting one sample after another. For the CRM experiments, the syneresis was monitored by periodically removing the fluid from the same gel.

2.3. Rheology

The rheological measurements were performed using a MCR501 Anton Paar rheometer instrument with a parallel plate geometry (diameter 50 mm, gap 1 mm). A portion of the prepared hot sample solution was loaded onto the Peltier of the rheometer and set at a temperature above the gelation temperature of the sample. After loading the sample, the surface was covered with a thin layer of mineral oil to avoid evaporation. Then, the temperature was lowered to 20 °C at a cooling rate of 3 °C/min, unless otherwise specified. The elastic modulus (G') was recorded for all experiments in the linear response regime (1 Hz, 0.5% strain). The gelling temperature (T_g) was defined as the temperature at which G' began to rise up rapidly.

3. Results and discussion

3.1. Kinetic studies of syneresis: The effect of κ-car on the syneresis

Kinetic studies of the syneresis ratio (R_s) using ORM and CRM with method P have been made on gel at κ-car = 4 g/L and KCl = 40 mM at room temperature (≈22 °C) and at refrigerator temperature (≈9 °C). The time dependence of the syneresis ratio for both temperatures, 22 °C and 9 °C, were found to be the same, and for this reason, the results for 9 °C are not shown in Fig. 2a.

The first measurement of the syneresis ratio was performed after one day, so data were not available before that time. The measurements are not precise when R_s < 5% because of experimental error. R_s was examined using both ORM and CRM by pipetting the water surrounding the gel; the result is shown in Fig. 2a. The same data, but in terms of concentration of κ-car versus time, are shown in the inset to Fig. 2a. The gelling temperature for this

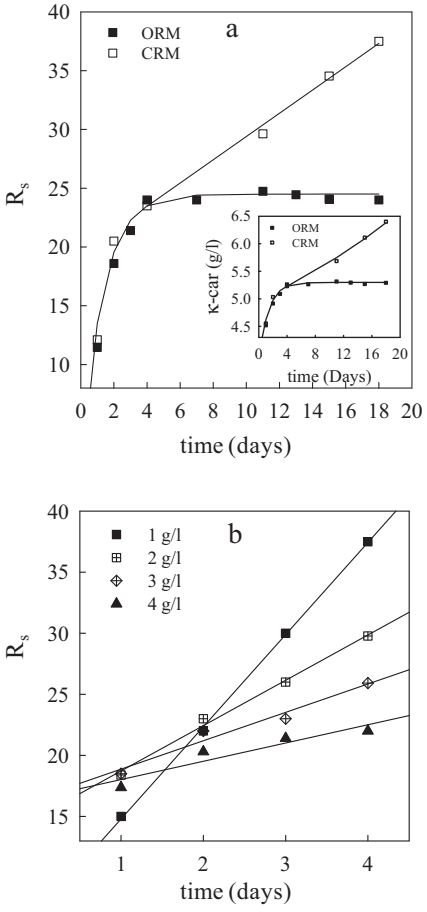

Fig. 2. (a) Syneresis at room temperature (≈22 °C) as a function of time for the gel with κ-car = 4 g/L and KCl = 40 mM; using method P. The inset shows the same data but for the concentration of κ-car versus time. The solid line is a guide to the eye. (b) Time variation of syneresis before the dynamic equilibrium using method P; for a gel containing 40 mM KCl and different amount of κ-car indicated in the Figure. The syneresis fluid was allowed to accumulate on the gel surface. The solid lines represent linear fits to the data.

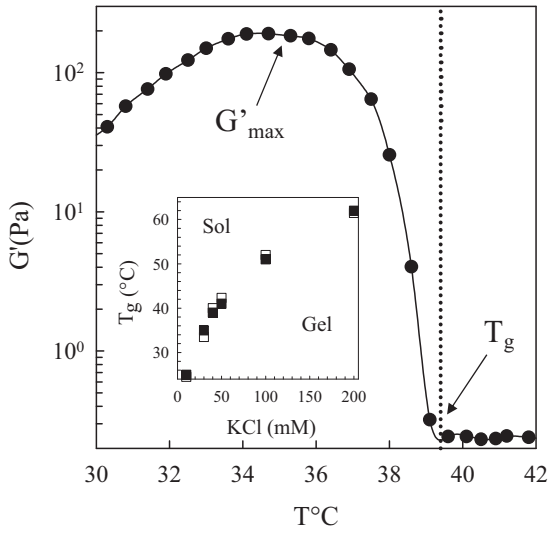

Fig. 3. Storage modulus variation during the cooling of a gel with κ-car = 4 g/L and KCl = 40 mM. The dotted line indicates the gelling temperature. The inset shows the gelation temperature as a function of the KCl concentrations before (■) and after (□) the syneresis water was removed from the gels.

composition is approximately 39 °C; therefore, at room temperature, the gels were already strong (Ciancia et al., 1997), which may explain why the syneresis ratio does not change significantly below room temperature.

The CRM experiment shows a steady increase in R_s, which contrasts with the ORM experiment, and shows a constant R_s after four or five days. Before the fifth day, both methods give almost the same variation of R_s. The ORM experiment allows the gel to stabilise in its fluid. The contrast between the ORM and CRM results reveals the complexity of the syneresis mechanism of the gel.

The syneresis of gels at different κ-car concentration was determined during the time before stabilisation (approximately 4 days). The variation of R_s during this period for a given concentration was found to be linear with time (Fig. 2b). The slope decreases when the concentration increases. Increasing the κ-car concentration decreases the syneresis rate and ratio. The ability of the gels to shrink is reduced by increasing the κ-car concentration, which increases the elasticity. Increasing the elasticity during syneresis arrests the retraction of the gel (Gerentes et al., 2002). However, the result shown in Fig. 2a contradicts this analysis because the gel is surrounded by its syneresis solvent at the plateau and shrinks when the solvent is removed. When the syneresis of the gel with 1 g/L reaches the plateau as a function of time (when its syneresis fluid is not removed), the concentration of the gel under the fluid was approximately 1.6 g/L, while gels with more than 2 g/L exhibits syneresis. The study reported in Fig. 2 reveals that the syneresis was arrested by another phenomenon when the gel was allowed to remain in contact with its fluid (Butler, Clark, & Adams, 2006; Ren et al., 2011). The gel and its syneresis solvent at the plateau are considered to be in dynamic equilibrium.

Swelling is made possible by allowing the solvent to accumulate on the gel surfaces (Butler et al., 2006; Northrop, 1927; Piculell et al., 1997), although it is not clear why a fraction of this solvent return to the gel when the tendency of the gel is to drive out solvent. If the solvent is removed, the gel restarts expelling fluid. Based on this observation, a *swelling* process is suggested, assuming that the retraction and swelling proceed continuously in the gel, but the retraction rate is faster than that of the swelling at the beginning. The kinetics of the syneresis slow with time because of the increase in the polysaccharide concentration in the gel during the syneresis. When the retraction kinetics equal that of swelling, the syneresis ratio remains constant in time (Northrop, 1927).

3.2. Rheological measurement of syneresis and gelling temperature

The temperature dependence of the storage modulus during the cooling of the sample with κ-car = 4 g/L and KCl = 40 mM has been investigated. Fig. 3 shows that G' increased steeply to a maximum. The maximum observed in the evolution of G' is due to the syneresis as reported in the literature (Lai et al., 2000; Richardson & Goycoolea, 1994): the gels are syneresing, and the measurements below G'_{max} are due to slipping. Richardson and co-worker have shown that, if the syneresis is eliminated during the measurements, its value does not deviate significantly from G'_{max}; therefore, G'_{max} will be considered to study the relationship between syneresis and elasticity. The gelling temperature T_g is defined here as the temperature at which G' begins to increase. The insert in Fig. 3 shows the dependence of the gelling temperature on the salt (KCl) concentration before and after the syneresis fluid has been removed. It is known that T_g is independent of the biopolymer concentration if the contribution from the counter ion is negligible in the presence of added KCl (Snoeren & Payens, 1976), which is shown in the results in the inset to Fig. 3, and means that the fluid expelled from the gel contains almost the same concentration of salt as the initial sample. The gelation temperatures recorded for different salt

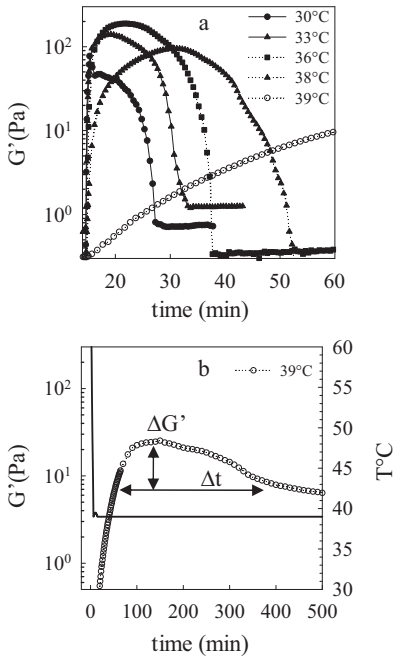

Fig. 4. (a) Time variation of the storage modulus at different temperatures indicated in figure. (b) Time variation of the storage modulus at the gelling temperature. The temperature variation is indicated by the solid line. The vertical arrow indicates the height of the storage modulus variation from the maximum to the reference. The horizontal arrow indicates the width at the reference.

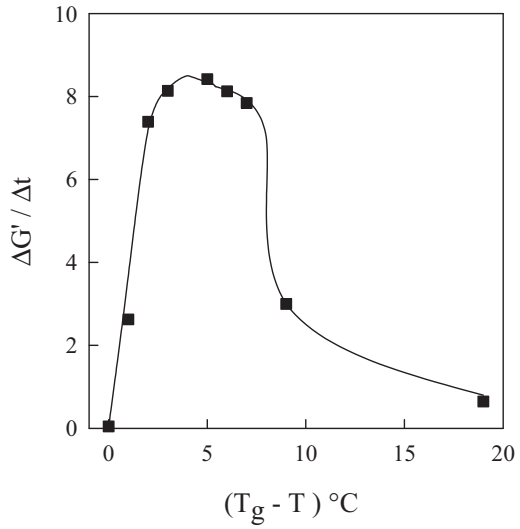

Fig. 5. Syneresis of the gel with κ-car = 4 g/L and KCl = 40 mM as a function of the temperature from the analysis of the storage modulus variation in time at different temperatures (Fig. 4a). The solid line is a guide to the eye.

concentrations are in agreement with the literature (Ciancia et al., 1997; Hermansson, 1989).

The temperature dependence of G' reveals a maximum at a specific temperature (T_{syn}). The available results report the variation in G' as function of time at temperatures below T_{syn} (Hermansson, 1989). The variation in G' with time for sample with κ-car = 4 g/L and KCl = 40 mM is studied at different temperatures (below and above T_{syn}), and the results are shown in Fig. 4a. Heating and cooling were repeated on the same sample several times to ensure that the measurement was reproducible for a given temperature. The sample was heated above 65 °C to melt it completely and cooled to the desired temperature. G' increases to G'_{max} and decreases from G'_{max} because of the syneresis. The decrease in G' with time may be influenced by the syneresis rate; therefore, the influence of the temperature should be quantified by the way G' decreases with time. When the temperature is reduced to 36 °C, G'_{max} increases, and decreases below 36 °C, while the width (Δt) of the plot decreases. At the gelling temperature (39 °C), a slow increases and decreases in G' with time towards a constant G' has been observed, leading to a broader curve, see Fig. 4b. The measurements were recorded at 39 °C for more than 1 h before G' reached the maximum ($G'_{max} \approx 25$ Pa), and the total measurement took 10 h.

It is a difficult task to evaluate the syneresis of a gel when the syneresis ratio is too weak ($R_s \ll 5\%$). Rheological measurements appear to resolve this difficulty. To study the influences of the temperature on the syneresis, the reference values of the storage modulus (G'_{ref}) are chosen considering the limit of G' at 39 °C to determine the width, Δt, represented by the horizontal arrow and the height, $\Delta G' = G'_{max} - G'_{ref}$, represented by the vertical arrow (Fig. 4b). The ratio between $\Delta G'$ and Δt is a first approach for syneresis characterisation using rheological measurements and is considered a study of the temperature dependence of syneresis. For low syneresis samples, Δt will be broad and $\Delta G'$ narrow, while for high syneresis samples, Δt will be narrow and $\Delta G'$ will be high.

Plot of $\Delta G'/\Delta t$ as a function of $(T_g - T)$ is illustrated in Fig. 5 where $T_g = 39$ °C and T is the temperature at which the syneresis experiment is performed. The ratio $\Delta G'/\Delta t$ may be correlated to the syneresis of the gels at different temperatures. The results show two domains; in the first domain, the syneresis increases, and in the second domain, it decreases. These observations suggest that the two domains, $T_g - T < 3$ °C and $T_g - T > 6$ °C, are, respectively, a weak gel and a strong gel. The transition between the domains occurs in the range of 3 °C to 6 °C where syneresis is important. This study shows that the syneresis effect is present in both the weak and strong gels, but its amplitude is reduced by the strengthening and softening of the gel. The syneresis decreases strongly in the strong gel domain ($T < 33$ °C or $T_g - T > 6$ °C) towards a stabilised state, which is found for this sample to be approximately 20 °C ($T_g - T = 19$ °C). This result shows that the syneresis of a gel containing 40 mM KCl at temperatures below 22 °C will not give a significantly different syneresis ratio, which is the result observed when the gels with κ-car = 4 g/L and KCl = 40 mM are cured at refrigerator temperature (≈9 °C) and at room temperature (≈22 °C).

3.3. Effect of KCl on the syneresis

The syneresis of gels containing κ-car = 4 g/L and KCl between 10 and 200 mM was studied. The gels were set at room temperature until equilibrium between the gel and its syneresis fluid was achieved. The dependence of the syneresis on the KCl concentration shows a pronounced peak (Fig. 6a), indicating that gels with low and high salt concentration, i.e., weak gels and strong gels, respectively, lead to weak syneresis. The maximum syneresis corresponds to intermediate gels. Studies of the influence of K^+ on the internal structure of κ-car gels investigated using static light scattering (SLS) and optical rotation (OR) have shown that K^+ ions promote the formation of an ordered matrix composed of double helix aggregates (Mangione et al., 2005). The concentration of potassium ions used in this study is above the critical concentration for coil-helix transition at 20 °C. The structure of the κ-car gels for a given polysaccharide concentration is composed of fine strands and coarse strands that varied proportion as a function of the concentration of potassium (Hermansson, 1989). The syneresis originates from the coil-helix transition and aggregation of helices to generate fine strands, superstrands, and rigid-rod-like bundles, which can associate to form dense and ordered domains (Piculell et al., 1997). Basically, the structure of the κ-car gel is described as the alignment and aggregation of helical dimmers to form a continuous

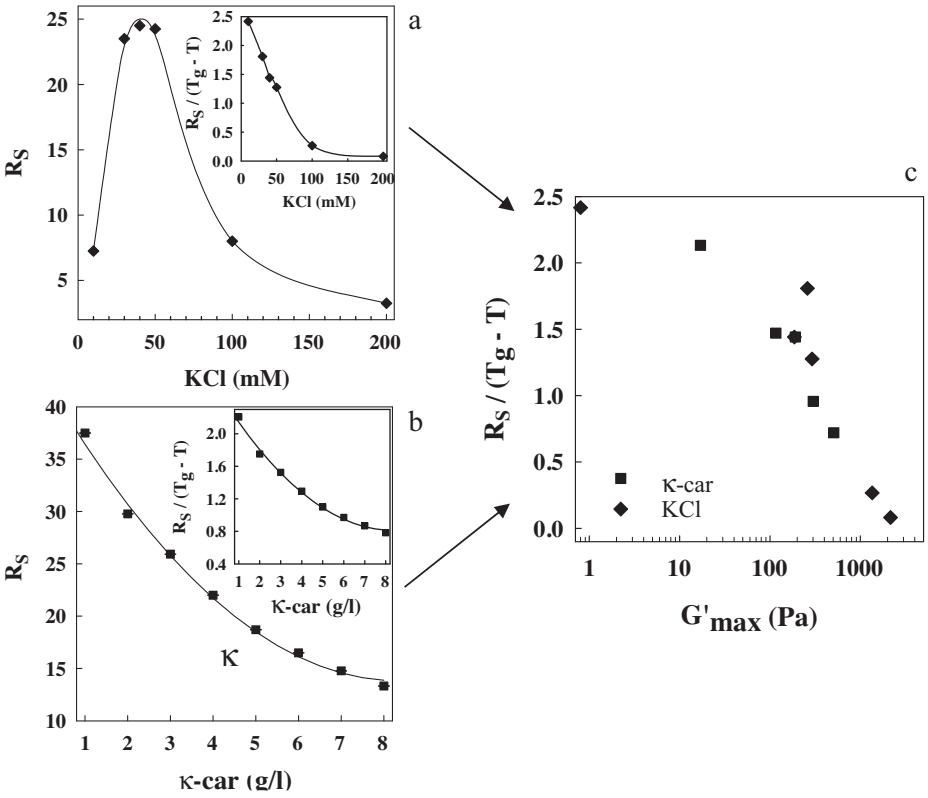

Fig. 6. (a) Syneresis as a function of KCl at 4 g/L κ-car. The inset represents the coefficient of thermal retraction as a function of KCl. (b) Syneresis as a function of the κ-car concentration in the presence of 40 mM KCl. (c) Lin-log representation of the thermal retraction coefficient versus the storage modulus of the gels by varying the KCl and κ-car concentration. Syneresis was performed at room temperature (≈22 °C) using method P. The solid line is a guide to the eye. Here, the syneresis fluid was allowed to accumulate on the gel surface.

network spanning the entire sample (Hermansson, 1989; Viebke, Piculell, & Nilssont, 1994). The network is formed rapidly in the presence of high K^+ ion concentrations at the gelling temperature, as shown by the rheological measurement. Syneresis is decreased or stopped depending on the strength of the network. The network is strengthened by aggregation of the strands. This process takes time to reach equilibrium (Meunier, Nicolai, & Durand, 2000; Meunier et al., 1999) without inducing more syneresis.

In the presence of small amounts of K^+ ions (slightly above that necessary for the coil–helix transition), the gel is soft and the microstructure is a fine network structure in which some superstrands or helices are partly aggregated and dispersed (Hermansson, 1989; Piculell et al., 1997). The swelling originates from the weak association of chains, coarse strand zones and the presence of biopolymers in a random coiled state in the structure of the gel. All of these behaviours form a disordered domain, creating an osmotic stress (Northrop, 1927). The syneresis is weakened by the osmotic stress that keeps the soft network in a swollen state. It has been shown elsewhere that Na^+ ions promote disordered domains (Mangione et al., 2005), which may explain why syneresis was not found in gels made with sodium chloride. One can assume that sodium chloride can induce a quite similar syneresis behaviour but only for very high concentrations because Na^+ ions have a weak effect on the elasticity of the gel compared to K^+ ions (Ciancia et al., 1997; Meunier et al., 1999).

Because changes in the salt concentration lead to variations in the gelation temperature, one should be careful not to draw rapid conclusions about the causal relationship between the syneresis and the potassium concentration. The gelling temperature for KCl = 10 mM was approximately 25 °C, very close to room temperature (22 °C ± 2 °C); thus, gels made with 10 mM KCl are fluid-like and exhibit weak syneresis. For 200 mM KCl, the gelling temperature was found to be approximately 62 °C, well above room temperature, and the gels are strong and retract much less, also resulting in weak syneresis.

Investigations of the syneresis of κ-car gels made with different concentrations of potassium at a given temperature may lead to an understanding of the effect of the temperature on the syneresis of κ-car gels. One should consider the thermal deviation $\Delta T = T_g - T$. ΔT can vary when increasing T_g by varying the salt concentration at constant T or changing T by cooling the samples. It was found that the syneresis of a gel with κ-car = 4 g/L and KCl = 40 mM evolves at refrigerator temperature (ΔT = 30 °C) and, at room temperature (ΔT = 17 °C), gives the same result. At the same time, ΔT = 17 °C, induced by 40 mM KCl salt, gives greater syneresis than ΔT = 30 °C, induced by 100 mM KCl salt at room temperature. It is clear from this result that varying T_g has a greater influence on the syneresis than changing T. The influence of salt may not be reduced to that of the temperature only, although the temperature dependence of the syneresis is intrinsic connected to the salt dependence.

One should take into account the influence of the thermal deviation ($T_g - T$) in the syneresis properties. To reflect the systematic temperature deviation on the syneresis, the *coefficient of thermal retraction* (R_T) is considered and expressed by Eq. (3):

$$R_T = \frac{R_S}{T_g - T} \tag{3}$$

The inset to Fig. 6a shows the thermal contraction coefficient versus the potassium concentration, and the results reveal a monotonic decrease towards a constant value corresponding to strong gels or a high salt concentration at room temperature. R_T seems to be relevant to the study of the relationship between

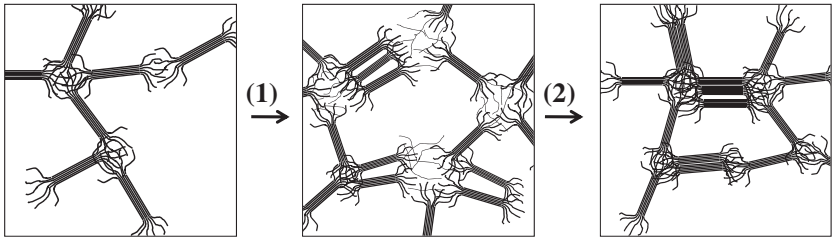

Fig. 7. Qualitative representation of the swelling and deswelling behaviour of the κ-car gels during the syneresis process. The lines indicate κ-car chains in the helix conformation. Aggregation of the helices is represented by the parallel stacking of the lines. Coarse domains are represented by the end-to-end random coil chains between aggregates. (1) Syneresis water is not removed, and (2) syneresis water is removed.

syneresis and the elasticity of the κ-car gels by varying the salt concentration.

3.4. Relation between the elasticity and syneresis

The elasticity of the κ-car gels can vary from low G'_{max} (fluid-like gel) to high G'_{max} (solid gel) by increasing the KCl or κ-car concentrations. In contrast to the salt, change in the κ-car concentration do not change the gelling temperature (Snoeren & Payens, 1976). Fig. 6b shows the variation of R_s versus κ-car gel concentration in the range 1–8 g/L κ-car with KCl = 40 mM. The inset to Fig. 6b shows the κ-car dependence of the coefficient of thermal retraction. The results show a monotonic decrease in R_T with increasing κ-car concentration towards a constant value corresponding to high G'_{max}. Gels with the same elasticity can be obtained by tuning the KCl and κ-car concentrations (high KCl and low k-car concentration or low KCl and high κ-car concentration). To plot the salt and κ-car concentration dependences of the syneresis on the same graph, R_T is plotted as a function of elasticity (G'_{max}) recorded for different KCl and κ-car concentrations, see the result in Fig. 6c. From low G'_{max} to high G'_{max}, the results show two regimes for the thermal contraction coefficient. R_T decreases slowly in the first regime and steeply in the second regime. Increasing the salt or polysaccharide concentration promotes the formation of physical cross-linking, and interactions between the polysaccharides are expected to dominate, leading to an increases in the gel elasticity (Piculell et al., 1997; Viebke et al., 1994). Therefore, in the second regime, the relative local deformation of a network may be almost the same as the relative deformation imposed on the entire network (Pines & Prins, 1973). It may be said that gel deformation in this regime is quasi-elastic.

Syneresis acts as tridimensional *internal compressive* pressure, which is balanced by the gel elasticity, although other forces seem to be involved in the syneresis processes. A portion of the energy of the compressive forces is lost when interactions between the polysaccharides are diminished by rising the temperature close to T_g or lowering the κ-car or salt concentrations. The slow decreases in R_T in the first regime may explain some inelastic deformation behaviour and may be the result of the fact that the smaller the number of physical bonds that are created in the gel, the greater the portion of the energy of the compressive forces that is lost in the course of inelastic deformation. When the shrinking rate is superior to that of swelling, the fluid is driven out of the gel until the rates are equal and the osmotic pressure is equal to that of the compressive pressure. At that time, syneresis reaches a dynamic equilibrium. The evolution of the gel towards more cross linking is arrested or damped because the gel is allowed to remain in contact with its fluid. Otherwise, the gel will evolve from the first regime to the second regime regardless of the gel composition if the fluid is removed periodically.

The syneresis is completely arrested (steady state) when the elasticity equals the compressive pressure. An increase in the elasticity from the first regime to the second regime is allowed if the concentration of polysaccharides increases by periodically removing the fluid accumulated at the gel surfaces. Swelling-induced dynamic equilibrium during syneresis is under investigation. A qualitative description of the syneresis behaviour is suggested in Fig. 7.

4. Conclusions

This paper presents the influence of the elastic modulus of κ-car hydrogels on the spontaneous release of solvent (syneresis) at room temperature and discusses two experimental situations. In the situation in which the syneresis fluid is periodically removed, the gel continuously releases its solvent until reaching the steady state. Increasing the elasticity reduces the rate of syneresis, but elasticity is not the only parameter that leads to dynamic equilibrium where solvent is allowed to accumulate on the gel surfaces. It is suggested in this study that swelling allowed the gel to reach equilibrium with its syneresis solvent, but it is not clear what fraction of the released solvent returns to the gel during the syneresis process. It is shown in this study that the main parameter controlling the syneresis properties of the gel is the elasticity rather than the polysaccharide or salt composition. Weak and strong gels have shown small volume changes; the maximum volume change was found at intermediate elasticities. The relationship between syneresis and elasticity described in this paper provides interesting information for potential application of kappa-carrageenan hydrogels by targeting the elasticity rather than the composition.

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