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# Effects of gelation concentration on cyclic deformation behavior of $\kappa$ -carrageenan hydrogels

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**Effects of gelation concentration on cyclic deformation behavior of  
 $\kappa$ -carrageenan hydrogels**

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## 1. Introduction

Tuning of the mechanical properties of polysaccharide hydrogels is a current topic of soft materials. Freeze-thaw and solvent-exchange with water and DMSO have been used for creation of physical hydrogels of curdlan [1]. Use of additives such as gelatin and carbon nanotubes has been proposed for  $\kappa$ -carrageenan hydrogels [2]. The viscoelastic properties and network microstructures of mixed gels of high-methoxyl pectin and  $\kappa$ -carrageenan prepared at various volume fractions has been investigated [3].

$\kappa$ -Carrageenan is a water-soluble linear polysaccharides extracted from red algae. The main chain consists of alternating  $\alpha$ -(1-3)-D-galactose-4-sulfate and  $\beta$ -(1-4)-3,6-anhydro-D-galactose units.  $\kappa$ -Carrageenan is a familiar anionic polysaccharide and has been used as gelling agents. The fact that  $\kappa$ -carrageenan forms biocompatible hydrogels at room temperature has been widely utilized for medicines, cosmetics, and foods [4-6]. Regarding the gelation mechanism on the molecular level, it has been reported that  $\kappa$ -carrageenan chains dissolved in water transform from random-coil to helical conformation on decreasing temperature and a piece of hydrogel appears successively by the aggregation of the helical chains to be crosslinks of the gel above a critical concentration [7-9]. Hence, the crosslinks of the three-dimensional network of the hydrogels are made of aggregated  $\kappa$ -carrageenan chains in the helical conformation, which are significantly different from the network structures of ordinary chemical and physical gels.

Because of the broad utilization of  $\kappa$ -carrageenan hydrogels, there have been a large number of studies on the factors that possibly affect the structure and the physical properties of the hydrogels [10-15]. Among them, the concentration of  $\kappa$ -carrageenan in the aqueous system ( $c$ ) and the cooling rate during the gelation process have been recognized as the factors that control the network structure of  $\kappa$ -carrageenan hydrogels [13,14]. Accordingly, the value of  $c$  and the cooling rate would also play vital roles in the mechanical properties of  $\kappa$ -carrageenan hydrogels, since the mechanical properties are directly related with the deformation of the network structure. However, it is difficult in practice to elucidate the respective effects on the mechanical properties. It should be noted that  $c$  seems to have a double effect on the mechanical properties: One acts on the network structure before the gelation is completed, while the other appears important after gelation for a given network structure. The after-effect can be easily understood by an example that  $\kappa$ -carrageenan hydrogels generally tend to be stiffer as  $c$  increases by evaporating the solvent water, and vice versa. However, the before-effect, that is, the relationship between the  $c$ -dependent network structure of  $\kappa$ -carrageenan hydrogels and their mechanical properties has not been examined sufficiently [15].

In this study, the before-effect on the mechanical properties has been examined by paying attention to the gelation concentration ( $c_0$ ) instead of  $c$ ; here,  $c_0$  is the concentration of  $\kappa$ -carrageenan at which the aqueous system becomes gel. Comparisons of the mechanical properties

have been made at nearly the same  $c$  between  $\kappa$ -carrageenan hydrogels prepared at different  $c_0$ . Since the cooling rate may also affect the network structure, as mentioned above, the hydrogels have been prepared just below the predetermined gelation temperature for each  $c_0$ . Mechanical properties of such  $\kappa$ -carrageenan hydrogels have been examined by means of repeating cyclic deformations consisting of a combination of uniaxial stretching and contraction.

## 2. Experimental

### 2.1 Sample preparation

$\kappa$ -Carrageenan (TCI, Japan) was used without further purification; the metal content of the  $\kappa$ -carrageenan as the counter ion was reported elsewhere [16]. The concentrations of  $\kappa$ -carrageenan in the pre-gel aqueous solutions, which corresponded to  $c_0$ , were determined by preliminary gelation tests to be  $5 \text{ gL}^{-1}$  and  $30 \text{ gL}^{-1}$ , so that the values of  $c_0$  were set apart as far as possible within available gelation conditions. Practically, a small amount of KCl (Wako, Japan) was added at  $5 \text{ mM}$  to the pre-gel solutions to obtain handleable gels. In the preliminary tests, gelation temperature ( $T_{\text{gel}}$ ) was determined as follows: The aqueous solution of  $\kappa$ -carrageenan prepared at  $80 \text{ }^\circ\text{C}$  was stored in a glass vessel at a given temperature for  $24 \text{ h}$  in a water bath and then the gelation was judged by the fluidity of the solution. The temperature of water bath was stepped down by  $1 \text{ }^\circ\text{C}$  and  $T_{\text{gel}}$  was defined as  $0.5 \text{ }^\circ\text{C}$  higher than the apparent gelation temperature on the

fluidity basis. The obtained values of  $T_{\text{gel}}$  at  $5 \text{ gL}^{-1}$  and  $30 \text{ gL}^{-1}$  were  $11.5 \text{ }^\circ\text{C}$  and  $51.5 \text{ }^\circ\text{C}$ , respectively.  $\kappa$ -Carrageenan hydrogels used for mechanical measurements were prepared commonly as follows. Each pre-gel solution of  $c_0 = 5 \text{ gL}^{-1}$  or  $30 \text{ gL}^{-1}$  was stuffed in a rectangular mold made of metal and Teflon and then the mold was stored at  $5 \text{ }^\circ\text{C}$  below  $T_{\text{gel}}$  for 24 h. The formed hydrogels were placed on a Teflon plate and the solvent water was evaporated until the  $\kappa$ -carrageenan concentration in the hydrogels, namely  $c$ , reached about  $50 \text{ gL}^{-1}$  regardless of  $c_0$ . The prepared gels were cut into rectangular pieces of  $5 \text{ mm} \times 30 \text{ mm}$ . In fact,  $c$  was calculated from the gel volume and the weight of dried-out sample measured after the mechanical measurement. Hereafter the gel samples prepared at  $c_0 = 5 \text{ gL}^{-1}$  and  $30 \text{ gL}^{-1}$  are referred to as C05 and C30, respectively. In addition, to examine the effect of gel-preparation temperature, another kind of  $\kappa$ -carrageenan hydrogel was prepared from a pre-gel aqueous solution of  $c_0 = 5 \text{ gL}^{-1}$  containing KCl at  $50 \text{ mM}$ . The value of  $T_{\text{gel}}$  for this pre-gel solution was  $43.5 \text{ }^\circ\text{C}$ , and therefore the gel, hereafter coded as C05K50, was prepared by being stored at  $38.5 \text{ }^\circ\text{C}$ .

## 2.2 Measurement

Mechanical measurements were carried out with a commercial tensile machine (TENSILON RTM-500, Orientec Corp., Japan). The measurement temperature was  $25 \text{ }^\circ\text{C}$ . The hydrogel samples were uniaxially deformed between cramps at a constant speed of  $1$  or  $10 \text{ mm/min}$  up to

the nominal strain ( $\varepsilon$ ) of 1 or 4 – 6 %. The initial length between the cramps was around 15 mm. The stress ( $\sigma$ ) obtained in this study was the nominal tensile stress calculated from the force and the initial cross section of the gel sample. The first cyclic deformation (run 1) was conducted by stretching the sample up to the target  $\varepsilon$  and immediately returning to  $\sigma = 0$ . The subsequent cyclic deformations, run 2 – run 4, started right after the former cycle unless otherwise mentioned. Actually, a preliminary cyclic deformation was applied before every run 1 under the same conditions and it takes a finite time less than 1 s to manually change the deformation direction in each cycle. The reproducibility was confirmed by testing three gels of each prepared independently.

The specific rotation ( $[\alpha]$ ) for C05 and C30 was estimated to compare the helical content of the gels. The values of optical rotation ( $\alpha$ ) for the  $\kappa$ -carrageenan hydrogels as well as dilute aqueous solutions of  $\kappa$ -carrageenan were measured at 632.8 nm using a homemade apparatus based on the polarization modulation method. Details of the homemade apparatus and the principles of the optical rotation measurement were described in the previous papers [17,18]. In this study, a quartz cell with the path length of 100 mm was used for the aqueous solutions. The measurement temperature was 25 °C.

### 3. Results and Discussion

Fig. 1 shows the stress-strain curves for (a) C30 and (b) C05 measured at the deformation speed ( $v$ ) of 1 mm/min up to  $\varepsilon = 1\%$ . The upper curve of each cycle corresponds to the stretching process, as guided with the arrows. It is seen that the four cyclic curves for C30 are almost the same and each cycle returns to the origin. The curves also illustrate a linear-like relation between  $\sigma$  and  $\varepsilon$ , so that the difference between the stretching and contraction curves are quite small. On the other hand, the cyclic curves for C05 obviously shift toward larger  $\varepsilon$  as the run proceeds due to a residual strain appearing in each cycle and there is a significant difference between the stretching and contraction curves compared to those for C30. Here, the residual strain means the difference in  $\varepsilon$  between the beginning and the end points at  $\sigma = 0$  of the same run. It can be also realized that Young's modulus ( $E$ ) defined as the initial slope of the stretching curve for C30 ( $1.4 \times 10^5$  Pa) is smaller than that for C05 ( $2.0 \times 10^5$  Pa), and  $E$  for both C30 and C05 seems to remain unchanged during the four runs within the experimental error. The energy loss during a given run can be estimated from the area surrounded by the stretching and contraction curves. The ratio of the energy loss to the elastic energy obtained during the stretching process is negligibly small for C30, while about 20 % of the energy loss occurs for C05. The noticeable differences in the cyclic deformation behavior described above would be attributed to the effect of  $c_0$  on the network structures of the gels, which is relevant to the deformation mechanism.



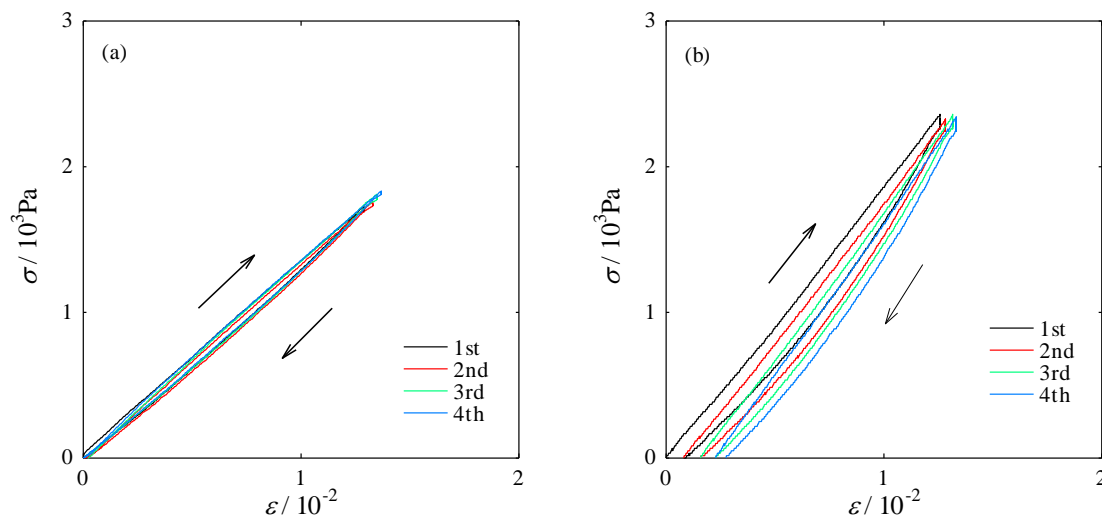


Fig. 1 Stress-strain curves of four cyclic deformations for (a) C30 and (b) C05 measured at  $v = 1$  mm/min up to  $\varepsilon = 1$  %. Upper and lower curves of each cycle corresponds to stretching and contraction processes respectively, as guided with the arrows.

The stress-strain curves for C30 up to  $\varepsilon = 6$  % measured at  $v = 1$  mm/min were drawn by solid lines in Fig. 2. The four cyclic curves follow the same route without any residual strain, indicating that the elastic deformation behavior of C30 does not depend on  $\varepsilon$  within the experimental condition. The broken lines in Fig. 2 illustrate the stress-strain relation for C30 measured under the faster deformation  $v = 10$  mm/min. Although the stress at a given run and a given  $\varepsilon$  is slightly larger than that at  $v = 1$  mm/min probably due to less stress relaxation during stretching, the cyclic deformation behavior of C30 having no residual strain is a common feature being independent of  $v$ . The estimated values of  $E$  at  $v = 1$  and 10 mm/min are  $1.6 \times 10^5$  and  $1.9 \times 10^5$  Pa respectively. These results obtained for C30 imply that the network structure is similar to that of ideal rubber in principle, where each crosslink consisting of helical  $\kappa$ -carrageenan chains

can be assumed a permanent junction point and the elastic force results from the entropy of  $\kappa$ -carrageenan chains between the crosslinks.

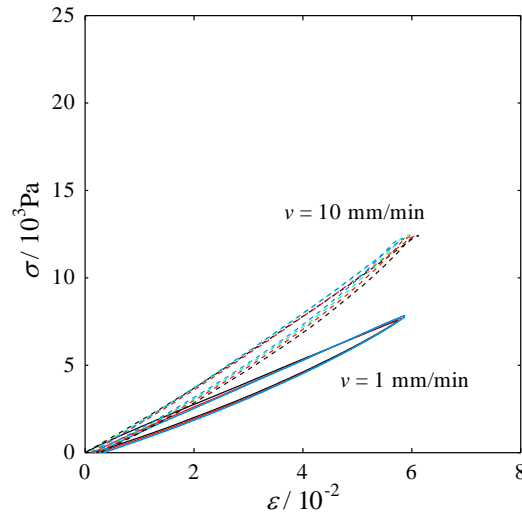


Fig. 2 Stress-strain curves for C30 up to  $\varepsilon = 6\%$ . Solid and broken lines represent cyclic deformation at  $v = 1$  and  $10 \text{ mm/min}$  respectively.

The solid lines in Fig. 3 shows the stress-strain curves for C05 deformed up to  $\varepsilon = 4\%$  at  $v = 1 \text{ mm/min}$ . The line colors indicating runs 1 – 4 are identical to those in Fig. 1. Compared to Fig. 1(b), it is noticed that the residual strain appears similarly but more clearly; in fact, the ratio of the energy loss increases to about 30%. The variable residual strain for C05 indicates that there is a mechanism of the plastic deformation in the network structure of C05 in addition to the main elastic deformation. Then the larger target  $\varepsilon$  takes more time and generates more stress for the cyclic deformation, so that the plastic deformation increases with  $\varepsilon$  and the residual strain appears

more clearly. The broken lines in Fig. 3 illustrate the stress-strain curves for the deformation at  $v = 10$  mm/min. Compared to the slower deformation drawn by the solid lines, it is noteworthy that  $E$  increases significantly from  $2.1 \times 10^5$  Pa to  $5.2 \times 10^5$  Pa with increasing  $v$  and that the residual strain after each run becomes slightly smaller. Although the stress increases with  $v$ , the residual strain is likely to be influenced more by the shorter time of deformation owing to larger  $v$  within the experimental conditions.

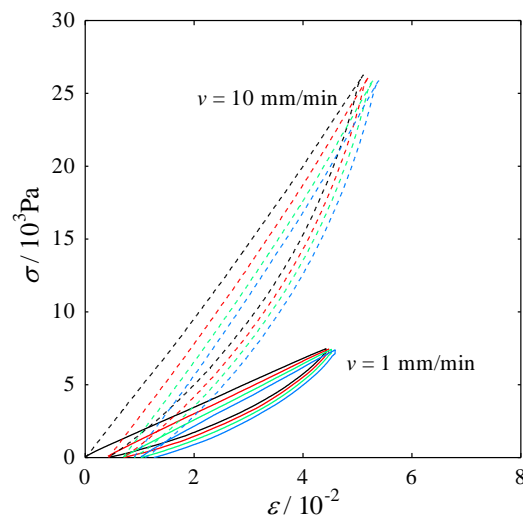


Fig. 3 Stress-strain curves for C05 up to  $\varepsilon = 4\%$ . Line colors indicating runs 1 – 4 are identical to those in Fig. 1. Solid and broken lines represent cyclic deformation at  $v = 1$  and 10 mm/min respectively.

Fig. 4 shows the cyclic deformation behavior for C05K50 examined at  $v = 1$  (solid lines) and 10 mm/min (broken lines) up to  $\varepsilon = 4\%$ . It is seen that residual strain appears after each run regardless of  $v$ , which is similar to that for C05 shown in Fig. 3, although the extent of the residual strain seems to be slightly smaller when comparing under the same deformation conditions. Moreover, the difference in the stress at a given run and a given  $\varepsilon$  between  $v = 1$  and 10 mm/min clearly exists in the deformation curves like in those for C05. The observed similarities between C05K50 and C05 demonstrate that the gel-preparation temperature, which differs by 32 °C due to the salt concentration, is not influential in determining the cyclic deformation behavior of  $\kappa$ -carrageenan hydrogels. In other words, the difference regarding the existence of residual strain between C30 and C05 described above can be simply attributed to  $c_0$ .

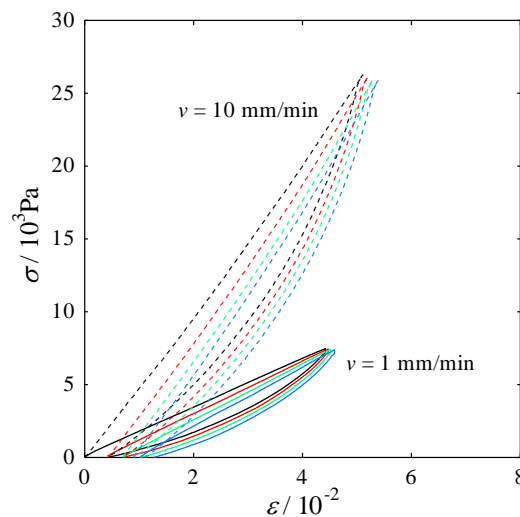


Fig. 4 Stress-strain curves for C05K50 up to  $\varepsilon = 4\%$ . Line colors indicating runs 1 – 4 are identical to those in Fig. 1. Solid and broken lines represent cyclic deformation at  $v = 1$  and 10 mm/min respectively.

The residual strain observed for C05 has been examined further. Fig. 5 shows the time course of  $\varepsilon$  during which two cyclic deformations up to  $\varepsilon = 4\%$  has been carried out at  $v = 1$  mm/min with observation of the reduction in the residual strain in between. After the first cyclic deformation drawn by the black line,  $\varepsilon$  decreases very slowly to zero with maintaining  $\sigma = 0$ , as demonstrated by the blue line. The stepwise reduction in  $\varepsilon$  results from the manual operation of the tensile machine with visual observation of  $\sigma$ ; the least contraction motion has been repeated against gradual increases in  $\sigma$  after the first cycle. Then the following profile of the second cyclic deformation is very similar to the first cycle, as represented by the red line. The black and red lines in Fig. 5 are replotted as the stress-strain relation in Fig. 6. The two cyclic solid lines appear almost the same. It is interesting that C05 seems to hold memories of the original network structure even after the plastic deformation. By contrast, the broken lines in Fig. 6 indicate the first and second cyclic deformations up to  $\varepsilon = 10\%$  between which the reduction in the residual strain has been observed for 500 s in a similar manner. The residual strain has reduced by half and become constant after 500 s (data not shown). It seems that the memory effect cannot bring the network structure into the original state against such a large strain.

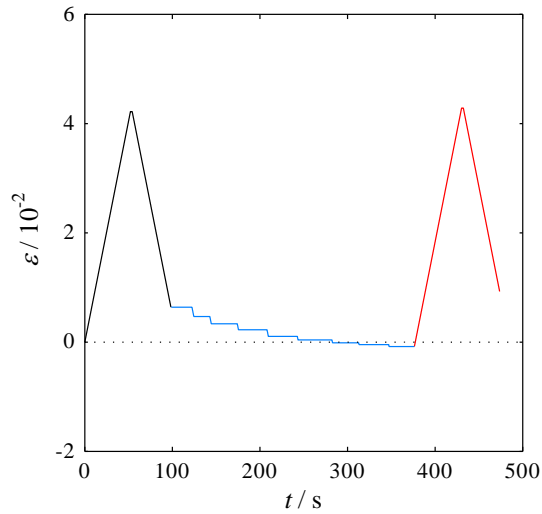


Fig. 5 Time course of  $\varepsilon$  of two cyclic deformations up to  $\varepsilon = 4\%$  at  $v = 1$  mm/min and observation of the reduction in the residual strain maintaining  $\sigma = 0$ . First and second cyclic deformations are drawn by black and red lines respectively and decrease in  $\varepsilon$  between the two deformations is indicated by blue line.

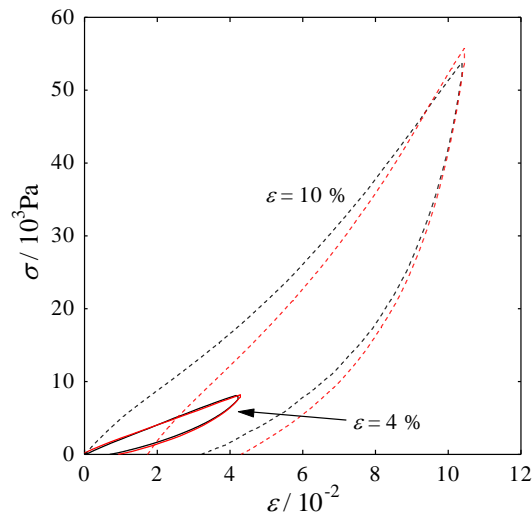


Fig. 6 Stress-strain relation of the first (black) and second (red) cyclic deformations up to  $\varepsilon = 4\%$  shown in Fig. 5. Broken lines represent the first (black) and second (red) cyclic deformations up to  $\varepsilon = 10\%$  between which the reduction in the residual strain has been observed for 500 s.

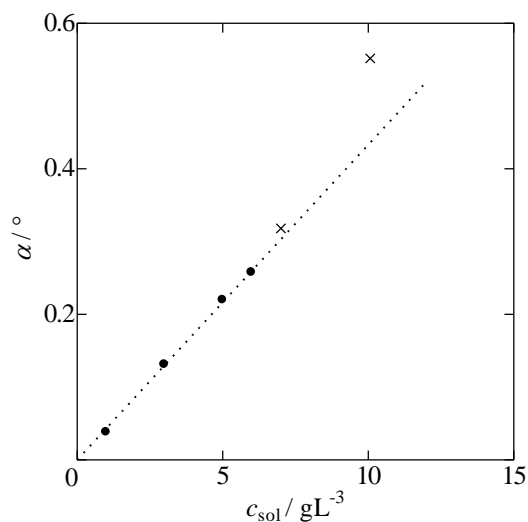


Fig. 7  $c_{\text{sol}}$ -dependence of  $\alpha$  for dilute aqueous solutions of  $\kappa$ -carrageenan at 25 °C. Dotted line is drawn as the best fit for filled circles indicating the proportionality between  $\alpha$  and  $c_{\text{sol}}$ , which gives  $[\alpha] = +43^\circ$ .  $\alpha$  at  $c_{\text{sol}} > 7 \text{ gL}^{-1}$  deviates upward from the dotted line as indicated by cross symbols.

Fig. 7 shows the solution concentration ( $c_{\text{sol}}$ ) dependence of  $\alpha$  for the dilute aqueous solutions of  $\kappa$ -carrageenan, where gelation does not occur at the measurement temperature of 25 °C. It is seen that  $\alpha$  increases proportionally with  $c_{\text{sol}}$  up to  $6 \text{ gL}^{-1}$ , as represented by filled circles and a dotted line; the slope of the dotted line gives a common  $[\alpha]$  of  $+43^\circ$ , which is consistent with the reported values [19]. This optical rotation is very likely to originate from asymmetric carbons of  $\kappa$ -carrageenan. On the other hand, the cross symbols which corresponds to  $c_{\text{sol}} = 7$  and  $10 \text{ gL}^{-1}$  deviate upward from the dotted line. This deviation should be attributed to the coil-to-helix transformation of  $\kappa$ -carrageenan chains precedent to gelation; actually, each sample has remained in the solution state as a whole. The upward deviation implies that  $[\alpha]$  for  $\kappa$ -carrageenan aqueous

systems increases with increasing the helix content, which agrees with trends reported in literature [19,20]. Regarding the gel samples, values of  $[\alpha]$  for C05 and C30 have been estimated to be  $+154^\circ$  and  $+108^\circ$  respectively, suggesting that the helix content of C05 is higher than that of C30. This difference in the helix content depending on  $c_0$  directly explains the higher values of  $E$  for C05 compared to those for C30 at the same deformation conditions, which has been described above. Generally speaking, the number density of the crosslinks made of helical  $\kappa$ -carrageenan chains would increase with the helix content, and the number of chains between crosslinks responsible for the elastic modulus would rise accordingly. On the other hand, judging from the fact that the residual strain is observed only for C05, the stiffness of the crosslinks seems to be reduced at the high helix content. Here we would attribute the residual strain of C05 to local viscoelastic deformations of the less stiff crosslinks in the network structure. In contrast to C30, where the crosslinks are assumed to be stable junction points, the helical  $\kappa$ -carrageenan chains of C05 might aggregate rather loosely and some of the crosslinks might change the shape against the stress of stretching. A possible idea at the present stage is that the length of helix involved in the aggregation is responsible for the stability of the resultant aggregates, namely the stiffness of the crosslinks. Aggregation of long helices is achieved by simultaneous interaction between a large number of attractive sites and therefore becomes stable against a given stress. The helices generated in C05 might be relatively shorter than those in C30. In this context, the apparent



memory of C05 shown with the blue line in Fig. 5 should correspond to the reverse change of such loosely-aggregated crosslinks. Although the inner mechanism is unknown, the crosslinks of C05 seem to be reversible and exhibit slight viscoelastic feature against small deformations up to  $\varepsilon = 4\%$ , so that the reverse process, that is the reduction in  $\varepsilon$ , proceeds gradually even at seemingly  $\sigma = 0$ . The disappearance of the memory effect against large deformation up to  $\varepsilon = 10\%$  (broken lines in Fig. 6) can be attributed to breakdown and rearrangement of some of the crosslinks. It has been reported that doubly crosslinked gels prepared under stretching during the second gelation process show residual strains, which can be explained by the balance of strain energy between the first and second networks [21]. The breakdown and rearrangement mentioned above might correspond to the second networking.

#### 4. Conclusion

The effect of  $c_0$  on the cyclic deformation behavior was examined by comparing C30 and C05. C30 showed elastic responses regardless of  $\nu$  and  $\varepsilon$ , where each cycle returns to the origin and the difference between the stretching and contraction curves are quite small. On the other hand, C05 demonstrated plastic behavior having substantial residual strains in the cyclic curves. The values of  $E$  compared at the same deformation conditions were larger for C05. These differences in the deformation behavior can be simply attributed to the effect of  $c_0$ . The  $c_0$ -dependence of the

specific rotation implied that C05 have higher helix content compared to C30. The residual strain as well as the higher  $E$  for C05 was explained by local viscoelastic deformations of the less-stable crosslinks formed at the high helix content. It was also proposed that there exists the reverse deformation of the crosslinks which is responsible for the reduction in the residual strain. As a biocompatible material made of natural polymers, the distinctive feature of C05 disclosed in this study might be applied to a covering material or a damper for medical use in the human body.

## References

- [1] M. Wu, X. Chen, J. Xu, H. Zhang, Freeze-thaw and solvent-exchange strategy to generate physically cross-linked organogels and hydrogels of curdlan with tunable mechanical properties, *Carbohydr. Polym.* 278 (2022) 119003.
- [2] A. T. Gubaidullin, A. O. Makarova, S. R. Derkach, N. G. Voron'ko, A. I. Kadyirov, S. A. Ziganshina, V. V. Salnikov, O. S. Zueva, Y. F. Zuev, Modulation of molecular structure and mechanical properties of  $\kappa$ -carrageenan-gelatin hydrogel with multi-walled carbon nanotubes, *Polymers* 14 (2022) 2346.
- [3] A. M. Roque, D. Montinola, L. Geonzon, S. Matsukawa, C. F. Y. Lobarbio, E. B. Taboada, R. G. Bacabac, Rheological elucidation of the viscoelastic properties and network interaction of mixed high-methoxyl pectin and kappa-carrageenan gels, *Food Hydrocolloids*, 129 (2022)

107647.

- [4] D. Qureshi, S. K. Nayak, S. Maji, D. Kim, I. Banerjee, K. Pal, Carrageenan: a wonder polymer from marine algae for potential drug delivery applications, *Current Pharma. Design* 25 (2019) 1172-1186.
- [5] C. Valenta, K. Schultz, Influence of carrageenan on the rheology and skin permeation of microemulsion formulations, *J. Controlled Release* 95 (2004) 257-265.
- [6] N. Yang, Y. Feng, C. Su, Q. Wang, Y. Zhang, Y. Wei, M. Zhao, K. Nishinari, Y. Fang, Structure and tribology of  $\kappa$ -carrageenan gels filled with natural oil bodies, *Food Hydrocolloids* 107 (2020) 105945.
- [7] S. Ikeda, V. J. Morris, K. Nishinari, Microstructure of aggregated and nonaggregated kappa-carrageenan helices visualized by atomic force microscopy, *Biomacromolecules* 2 (2001) 1331-1337.
- [8] E. R. Morris, D. A. Rees, G. Robinson, Cation-specific aggregation of carrageenan helices – domain model of polymer gel structure, *J. Mol. Biol.* 138 (1980) 349-362.
- [9] C. Viebke, L. Piculell, S. Nilsson, On the mechanism of gelation of helix-forming biopolymers, *Macromolecules* 27 (1994) 4160-4166.
- [10] C. Rochas, M. Rinaudo, S. Landry, Role of the molecular weight on the mechanical properties of kappa-carrageenan gels, *Carbohydr. Polym.* 12 (1990) 255-266.

- [11] G. Sason, A. Nussinovitch, Characterization of  $\kappa$ -carrageenan gels immersed in ethanol solutions, *Food Hydrocolloids* 79 (2018) 136-144.
- [12] M. Watase, K. Nishinari, Rheological and thermal properties of agarose and kappa-carrageenan gels containing urea, guanidine hydrochloride or formamide, *Food Hydrocolloids* 1 (1986) 25-36.
- [13] M. Iijima, T. Hatakeyama, M. Takahashi, H. Hatakeyama, Effect of thermal history on kappa-carrageenan hydrogelation by differential scanning calorimetry, *Thermochimica Acta* 452 (2007) 53-58.
- [14] B. Walther, N. Lore'n, M. Nyde'n, A. M. Hermansson, Influence of  $\kappa$ -carrageenan gel structures on the diffusion of probe molecules determined by transmission electron microscopy and NMR diffusometry, *Langmuir* 22 (2006) 8221-8228.
- [15] J. Horinaka, K. Yamamoto, T. Takigawa, Effect of gelation concentration on tensile and stress relaxation behavior of  $\kappa$ -carrageenan hydrogels, *Zairyo* 70 (2021) 1-4.
- [16] J. Horinaka, M. Tanaka, T. Takigawa, Plasticizing effect of saccharides on uniaxial tensile behavior of  $\kappa$ -carrageenan films, *Nihon Reoroji Gakkaishi* 45 (2017) 13-18.
- [17] H. P. Jensen, J. A. Schellman, T. Troxell, Modulation techniques in polarization spectroscopy, *Appl. Spectrosc.* 32 (1978) 192-200.
- [18] J. Horinaka, Y. Hashimoto, T. Takigawa, Optical and mechanical properties of pullulan films

studied by uniaxial stretching, *Int. J. Biol. Macromol.* 118 (2018) 584-587.

[19] M. R. Mangione, D. Giacomazza, D. Bulone, V. Martorana, P. L. San Biagio,

Thermoreversible gelation of  $\kappa$ -carrageenan: relation between conformational transition and aggregation, *Biophys. Chem.* 104 (2003) 95-105.

[20] M. Ciancia, M. Milas, M. Rinaudo, On the specific role of coions and counterions on  $\kappa$ -carrageenan conformation, *Int. J. Biol. Macromol.* 20 (1997) 35-41.

[21] T. Katashima, U. Chung, T. Sakai, Mechanical properties of doubly crosslinked gels, *Polym. J.* 51 (2019) 851-859.

## Corrigendum

### Corrigendum to Effects of gelation concentration on cyclic deformation behavior of $\kappa$ -carrageenan hydrogels

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The figure for Fig. 3 must be replaced as shown below.

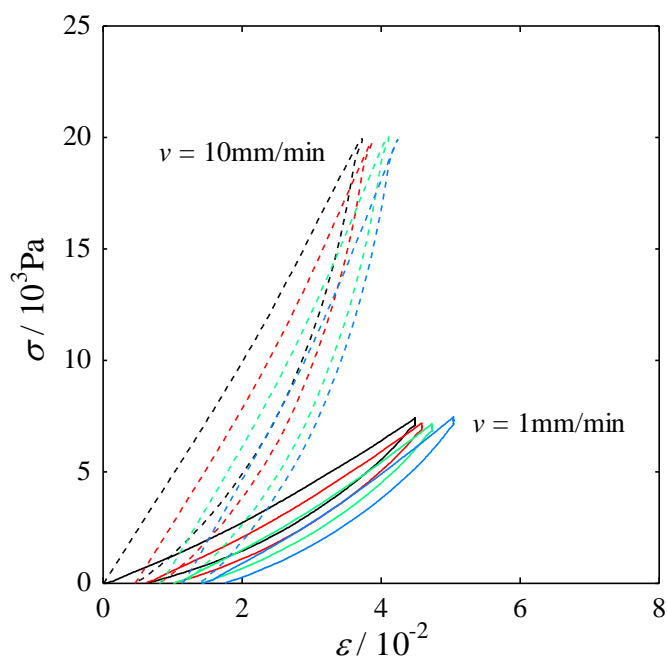


Fig. 3 Stress-strain curves for C05 up to  $\varepsilon = 4\%$ . Line colors indicating runs 1 – 4 are identical to those in Fig. 1. Solid and broken lines represent cyclic deformation at  $v = 1$  and  $10 \text{ mm/min}$  respectively.

The wrong figure used as Fig. 3 in the published paper is identical to Fig. 4. We apologize for any inconvenience caused by our careless mistake.