



TITLE:

Effect of moisture in  $\kappa$ -carrageenan films on their tensile and relaxation behavior studied by correlation between stress and birefringence

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1           **Effect of moisture in  $\kappa$ -carrageenan films on their tensile and relaxation behavior**  
2                           **studied by correlation between stress and birefringence**

3

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17 Abstract:

18 A picture on the molecular level describing the deformation and the following relaxation of  $\kappa$ -  
19 carrageenan chains has been proposed based on the three-domain structural model for  $\kappa$ -  
20 carrageenan films and on the idea of the modified stress-optical rule. The uniaxial tensile and the  
21 relaxation behavior for dry and moist  $\kappa$ -carrageenan films has been examined by using a  
22 homemade apparatus available for the simultaneous mechanical and birefringence measurements.  
23 It has been suggested that the continuous amorphous phase of  $\kappa$ -carrageenan in the dry film is  
24 deformed together with the local glass component and only the glass component relaxes in the  
25 following process. On the other hand, concerning the moist film, the crosslinks of  $\kappa$ -carrageenan  
26 aggregates in addition to the continuous phase are movable with deformation, while the following  
27 relaxation is attributed only to the unbridged  $\kappa$ -carrageenan chains in the continuous phase.

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30 Keywords:  $\kappa$ -carrageenan; gel film; birefringence; stress-optical coefficient; moisture

31

32

### 33 Introduction

34 The first-order molecular structures of polymer chains are intrinsically anisotropic, that is, the  
35 local refractive index with respect to the direction of main chain is different from that normal to  
36 it, although such local anisotropies are cancelled out in macroscopically isotropic systems, where  
37 the chain segments are randomly oriented. However, once such a system undergoes deformation,  
38 the total difference in the refractive index with respect to the direction of deformation can be  
39 detected as birefringence reflecting the global chain orientation in the system. Therefore, it is  
40 often helpful for understanding the way in which polymer chains behave against deformation to  
41 use optical techniques measuring the birefringence together with the conventional mechanical  
42 tests. To give a good example, the modified stress-optical rule (MSOR) holds well for polymer  
43 melts and solutions: Both the stress and the birefringence are considered consisting of two  
44 components, which are usually referred to as the rubber and the glass components, and the  
45 proportionality between the birefringence and the stress holds for each component. A great  
46 number of studies on the viscoelasticity and the birefringence for amorphous polymers, especially  
47 for styrene polymers, have established the proportionality, and the orientation relaxation of  
48 polymer chains has been analyzed by using MSOR so that the contribution of each component  
49 can be estimated (Inoue et al. 1991; Janeschitz-Kriegl 1983; Okamoto et al. 1992; Read 1983). In  
50 our previous study, mechanical measurement for amorphous pullulan films by the uniaxial

51 stretching has been combined with birefringence measurement, and a set of stress-optical  
52 coefficients for the rubber and the glass components of pullulan have been determined as the  
53 material constants on the basis of MSOR (Horinaka et al. 2018b).

54 Carrageenan is a group of polysaccharides consisting of repeating units of D-galactose  
55 alternating  $\beta$ -1,4- and  $\alpha$ -1,3-linkages. Among them  $\kappa$ -carrageenan is characterized in terms of the  
56 chemical structure by a 3,6-anhydro-galactose ring as well as a single sulfate group in the  
57 companion ring.  $\kappa$ -Carrageenan has been widely used as an additive in the food and cosmetic  
58 industries due to its favorable function of forming hydrogels. Regarding the network structure of  
59  $\kappa$ -carrageenan hydrogels, it should be noted that the crosslinks are very likely composed of  
60 aggregates of  $\kappa$ -carrageenan chains in the helical conformation, that is,  $\kappa$ -carrageenan hydrogels  
61 have fairly large sizes of crosslinks in comparison with ordinary chemical and physical gels (Ikeda  
62 et al. 2001; Morris et al. 1980; Viebke et al. 1994). When  $\kappa$ -carrageenan films are prepared by  
63 drying  $\kappa$ -carrageenan hydrogels, it is almost certain that there remain the large crosslinks of  
64 aggregates inside the films and that the obtained  $\kappa$ -carrageenan films do not become amorphous  
65 as a whole due to the crystal-like aggregates. This implies that MSOR cannot be applied to the  
66 correlation between the stress and the birefringence for the  $\kappa$ -carrageenan films in the same  
67 manner as the pullulan films mentioned above. Although the mechanical tests of  $\kappa$ -carrageenan  
68 hydrogels have been extensively carried out from the point of the industrial applications (Sason

69 et al. 2018; Rochas et al. 1990; Watase et al. 1986), the mechanism of the mechanical behavior  
70 has not been fully understood on the molecular level, nor is the role of the large crosslinks.

71 In this study, mechanical measurement for  $\kappa$ -carrageenan films during the uniaxial stretching  
72 and subsequent stress relaxation has been performed simultaneously with birefringence  
73 measurement using the polarization modulation method. The stiffness of the films has been  
74 changed by adding small amount of water to the thoroughly dried state. The correlation between  
75 the stress and the birefringence for the  $\kappa$ -carrageenan films with and without the moisture has  
76 been examined by partly using the idea of MSOR, and the difference in the tensile and the  
77 relaxation behavior of the  $\kappa$ -carrageenan films due to the moisture has been clarified.

78

## 79 **Experimental**

### 80 Sample preparation

81 In order to use  $\kappa$ -carrageenan films for birefringence measurement, we needed to prepare  
82 transparent and isotropic samples, so that the intrinsic birefringence of the samples at the as-  
83 prepared states ( $\Delta n_0$ ) could be neglected. However, the preliminary test showed that  $\kappa$ -  
84 carrageenan films prepared just by drying  $\kappa$ -carrageenan hydrogels on a flat plate exhibited  
85 substantial birefringence. This matter was finally settled by using a monosaccharide as an additive  
86 to the film. Practically, isotropic  $\kappa$ -carrageenan films used in this study, which had  $\Delta n_0 < 10^{-6}$ ,

87 were prepared in the following manner. Powdery  $\kappa$ -carrageenan (TCI, Japan) and a  
88 monosaccharide fructose (Wako, Japan) were dissolved in distilled water. The concentrations of  
89 the  $\kappa$ -carrageenan and the monosaccharide were fixed at 10 g/L and 30 g/L, respectively. The  
90 mixture was stirred at 80 °C for 3 h and the obtained aqueous solution was spread on a Teflon  
91 plate at 80 °C. Then evaporation of the solvent water was allowed for several hours until a  
92 transparent film formed on the plate. The film that was in the roughly dried state was cut into  
93 rectangular pieces and each one was dried further under vacuum at 80 °C for more than 6 h to be  
94 a constant weight. The dimensions of the thoroughly dried film were 10 mm × 30 mm × 0.1 mm.  
95 The addition of moisture was performed by leaving the thoroughly dried films in a moist  
96 atmosphere for more than 24 h. It was impossible to prepare moist films at arbitrary water contents.  
97 The water content of the moisturized films was estimated from the weight reduction in the re-  
98 drying process executed after the measurement described below.

99

## 100 Measurement

101 Simultaneous measurement of the stress and the birefringence for the  $\kappa$ -carrageenan films was  
102 carried out using a homemade apparatus for the birefringence coupled with a commercial tensile  
103 machine (TENSILON RTM-500, Orientec Corp., Japan). Details of the homemade apparatus and  
104 the principles of the birefringence measurement using the polarization modulation method were

105 described in our previous manuscript (Horinaka et al., 2018b). First the film sample was uniaxially  
 106 stretched between cramps at a constant speed of 5 mm/min up to a nominal tensile strain ( $\varepsilon$ ) so  
 107 that the measurement could be performed in the linear viscoelasticity region. The initial length  
 108 between the cramps was around 15 mm. Then the birefringence ( $\Delta n$ ) as well as the stress ( $\sigma$ ) was  
 109 monitored during the following relaxation process with time ( $t$ ) until  $t = 3000$  s at the longest with  
 110  $\varepsilon$  fixed. Actually,  $\sigma$  was calculated from the force with the cross section of the film measured  
 111 before stretching; hence,  $\sigma$  obtained in this study was the nominal tensile stress. The measurement  
 112 temperature was 25 °C.

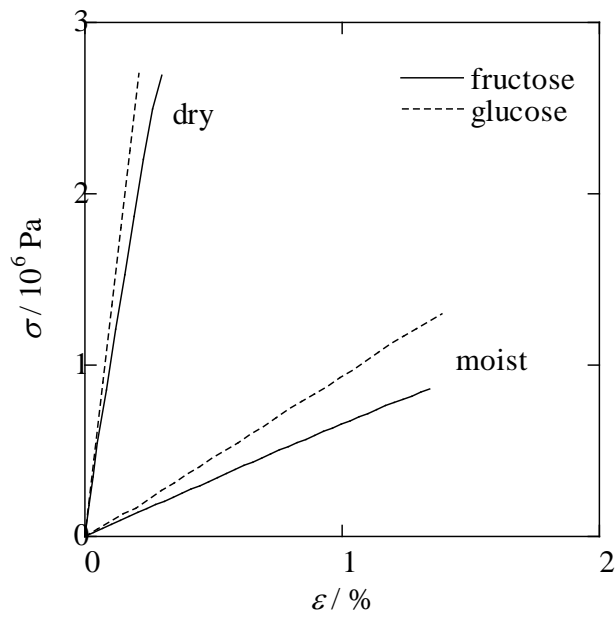
113

## 114 **Results and discussion**

115 Figure 1 shows the stress-strain curves for the dry and moist  $\kappa$ -carrageenan films with fructose.  
 116 To check the effect of species of the monosaccharide additive, the stress-strain curves for  $\kappa$ -  
 117 carrageenan films with glucose of the same content are also given in the figure. The weight  
 118 fraction of moisture has been estimated to be 19 % for the film with fructose and 16 % for the  
 119 film with glucose. It is seen that the stress-strain behavior is independent of the species of the  
 120 monosaccharide additive within the experimental error and is significantly affected by the  
 121 moisture; each stress-strain curve appears almost linear within the  $\varepsilon$ -range examined but the slope  
 122 of the curve, which is defined as the Young's modulus ( $E$ ), greatly decreases as the moisture is

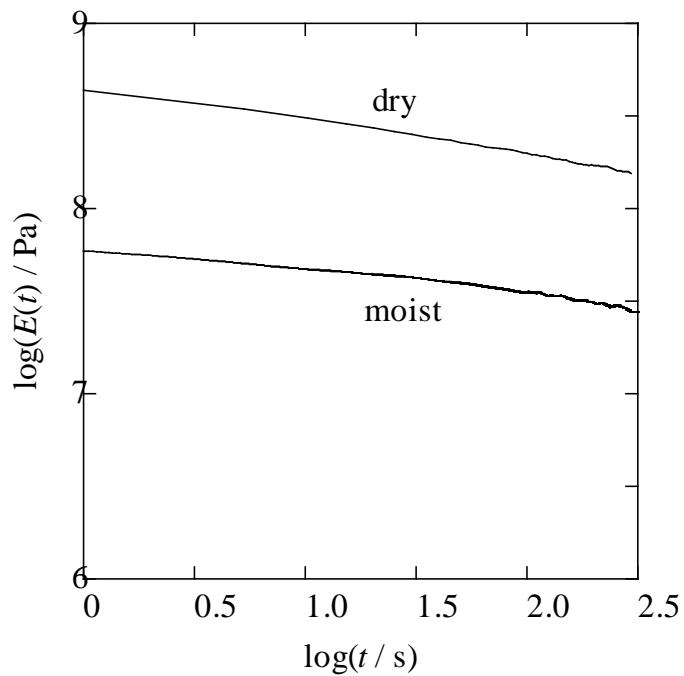


123 added. In fact, the values of  $E$  for the dry and moist films with fructose estimated from Fig. 1 are  
124  $7.4 \times 10^8$  and  $6.6 \times 10^7$  Pa, respectively. We have previously examined plasticizing effects of  
125 saccharides and alditols on the uniaxial tensile behavior of  $\kappa$ -carrageenan films (Horinaka et al.  
126 2017). Although the measurement temperature in this study is slightly lower and the procedure of  
127 sample preparation is different compared to the previous study,  $E$  for the dry film with fructose  
128 coincides well with our previous value for the film of the same content;  $E$  of the order of  $10^8$  Pa  
129 indicates that this film is under the “physical” plasticizing effect which can be explained by the  
130 blending law for immiscible blends (Dekkers et al. 2016; Katopo et al. 2012; Takayanagi et al.  
131 1963). It has been proposed that the  $\kappa$ -carrageenan film has three domains; namely, crosslinks of  
132 helical  $\kappa$ -carrageenan aggregates, continuous phase of amorphous  $\kappa$ -carrageenan, and voids  
133 without  $\kappa$ -carrageenan (Horinaka et al. 2017, 2018a, 2019). Then the additive is situated in the  
134 voids as an assembly of micro-granules having very low modulus compared with the  $\kappa$ -  
135 carrageenan matrix, which decreases  $E$  as a whole. On the other hand,  $E$  of the order of  $10^7$  Pa  
136 estimated for the moist film is close to those obtained in our previous study for the  $\kappa$ -carrageenan  
137 films under the conventional plasticization, as it were, the “chemical” effect; the additive has a  
138 good miscibility with  $\kappa$ -carrageenan and swells continuous phase of amorphous  $\kappa$ -carrageenan to  
139 soften the network (Horinaka et al. 2017). Regarding the moist film examined in this study, water  
140 from the moisture very probably works as the additive miscible with  $\kappa$ -carrageenan.



141

142 Fig. 1 Stress-strain curves for dry and moist  $\kappa$ -carrageenan films with fructose or glucose.



143

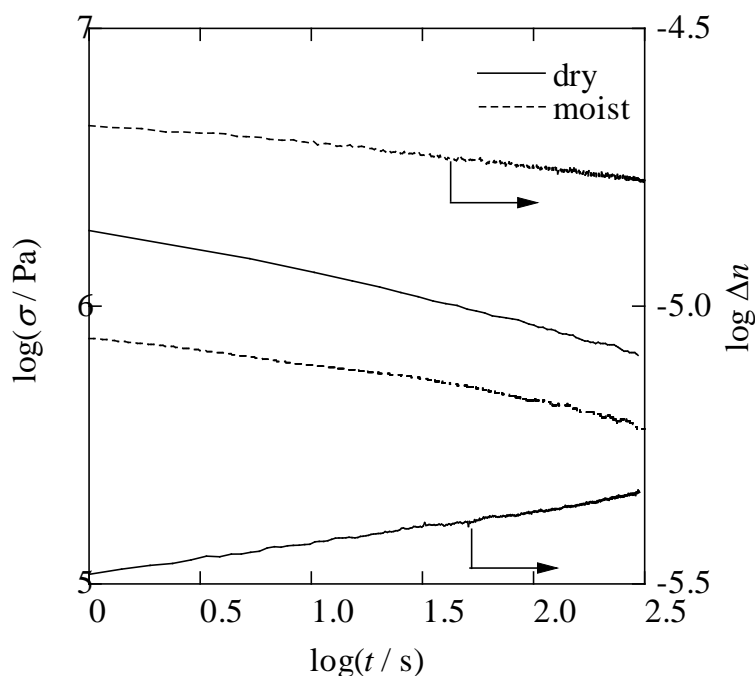
144 Fig. 2 Young's relaxation modulus for the dry and moist  $\kappa$ -carrageenan films with fructose after  
145 uniaxial stretching.

146

147 Figure 2 shows the Young's relaxation modulus ( $E(t)$ ) for the dry and moist films with fructose  
 148 after uniaxial stretching of  $\varepsilon = 0.4\%$  and  $1.3\%$  respectively. Here the duration of stretching is  
 149 less than 2 s and therefore an instant deformation is assumed in the analysis described below. It  
 150 is obvious that both  $E(t)$  curves decrease with  $t$  very slowly and remain at the same order of  $E(t)$   
 151 within the experimental condition. Now, we must remind that the  $\kappa$ -carrageenan films used in this  
 152 study have been prepared by drying  $\kappa$ -carrageenan hydrogels and basically have network  
 153 structures due to the crosslinks of  $\kappa$ -carrageenan aggregates inside, as described above. It is  
 154 known that  $E(t)$  is constant against  $t$  in the case of a polymer system having the ideal network  
 155 structure and that the ultimate initial value of  $E(t)$  becomes roughly  $10^7$  Pa almost regardless of  
 156 polymer species (Okamoto et al. 1992; Inoue et al. 1995, 2003). These facts indicate that the  
 157 practical  $E(t)$  much greater than  $10^7$  Pa for the dry and moist films and their relaxation observed  
 158 in Fig. 2 must be attributed to some components other than the rubber component.

159 The stress relaxation as well as the simultaneous change in  $\Delta n$  is compared between the dry  
 160 and moist films with fructose in Figure 3. It should be noted that  $\Delta n$  for a polymer system is not  
 161 necessarily positive but  $\Delta n$  for the  $\kappa$ -carrageenan films are actually positive, so that the  
 162 logarithmic value of  $\Delta n$  is plotted using the right axis of the figure for ease of identification. The  
 163 decreasing trend of  $\sigma$  is similar between the dry and moist films, as expected from Fig. 2, but  
 164 change in  $\Delta n$  with  $t$  is completely different:  $\Delta n$  for the dry film increases, while that for the moist

165 film decreases. That is, addition of 19 % moisture greatly affects the relaxation of  $\Delta n$  to be  
 166 seemingly vertical mirror images to each other. Further consideration gives the following  
 167 information:  $\sigma$  for the dry film is still greater than that for the moist film, although relative  
 168 difference in  $\sigma$  is smaller than that in  $E(t)$  (Fig. 2) due to the difference in  $\varepsilon$  applied. On the other  
 169 hand, it is obvious that  $\Delta n$  for the dry film is significantly smaller than that for the moist film.  
 170 Assuming that components of the  $\kappa$ -carrageenan films responsible for  $\sigma$  necessarily contribute to  
 171  $\Delta n$  on the analogy of MSOR, these facts imply that the main components responsible for  $\sigma$  and  
 172  $\Delta n$  on the uniaxial deformation are different between the dry and moist films, and accordingly  
 173 different stress-optical coefficients are expected for the two systems.



174

175 Fig. 3 Comparison of  $\sigma$  and  $\Delta n$  between dry and moist  $\kappa$ -carrageenan films with fructose.

176 In the framework of MSOR, there is a correlation between  $\sigma$  and  $\Delta n$  observed with deformation,  
177 which is given by the following equation:

$$178 \quad \Delta n = C_R \sigma_R + C_G \sigma_G \quad (1)$$

179 where  $C$  is the stress-optical coefficient, and the subscripts R and G stand for the rubber and the  
180 glass components respectively (Okamoto et al. 1992; Inoue et al. 1995, 2003). Concerning  
181 amorphous polymers in the glassy zone, it is recognized that R-component arises from orientation  
182 of polymer segments, while G-component is attributed to planar orientation of monomer units.  
183 Although MSOR cannot be applied to our  $\kappa$ -carrageenan films in the same manner due to the  
184 crystal-like aggregates, as mentioned above, we have tried to analyze the correlation between  $\sigma$   
185 and  $\Delta n$  for the  $\kappa$ -carrageenan films using the basic idea of MSOR, that is,  $\sigma$  and  $\Delta n$  have the same  
186 origins and the ratio of  $\Delta n$  to  $\sigma$  for each origin is defined as the stress-optical coefficient. The  
187 solid lines in Figure 4 represent the measured simultaneous relaxation processes of  $\sigma$  and  $\Delta n$  for  
188 the dry film. To express the decreasing trend of  $\sigma$  as precise as possible, an empirical five-  
189 component equation given below has been used:

$$190 \quad \sigma = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) + A_4 \exp\left(-\frac{t}{\tau_4}\right) + A_5 \quad (2)$$

191 where  $A_i$  ( $i = 1-5$ ) is the fraction of the mode with the relaxation time of  $\tau_i$ , though  $\tau_5$  is assumed  
192 infinity. At present, it is impossible to quantitatively explain each relaxation mode in terms of the  
193 chain motion, but the decreasing trend of  $\sigma$  can be expressed by eq 2 using the parameters in Table

194 1 as drawn by a broken line in Fig. 4. According to the idea of MSOR, the measured  $\Delta n$  should  
 195 be fitted by five components of the product of the stress-optical coefficient and the stress by  
 196 analogy with eq 1. Actually, however, two stress-optical coefficients instead of five are enough  
 197 to express the increasing trend of  $\Delta n$  as demonstrated by a broken line in Fig. 4. That is,  $\Delta n$  for  
 198 the dry  $\kappa$ -carrageenan film can be represented by the following equation:

$$199 \quad \Delta n = C_{d1} \left( A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) + A_4 \exp\left(-\frac{t}{\tau_4}\right) \right) + C_{d2} A_5 \quad (3)$$

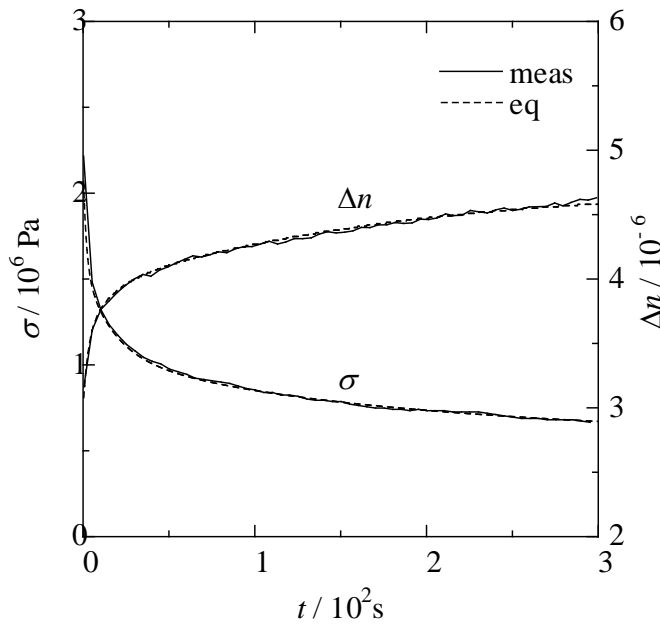
200 As given in Table 1, one negative coefficient  $C_{d1} = -1.4 \times 10^{-12} \text{ Pa}^{-1}$  covers the four components  
 201 having finite relaxation times, which explains the increasing trend of  $\Delta n$ . The other coefficient  
 202  $C_{d2} = 1.1 \times 10^{-11} \text{ Pa}^{-1}$ , assigned to the fifth component, is positive and the absolute value is greater  
 203 than that of  $C_{d1}$ , so that the measured  $\Delta n$  is the positive as a whole. This result means that  $\sigma$  and  
 204  $\Delta n$  for the dry  $\kappa$ -carrageenan film arise from two components: Since  $C_{d1}$  corresponds to a single  
 205 component that relaxes even in the stiff dry film and the glass component proposed in MSOR  
 206 appears at shortest times due to the much-localized mode, it seems appropriate that  $C_{d1}$  is  
 207 identified as the glass component. It is natural that such a localized mode exists in any polymer  
 208 system whether the system is amorphous or not. Now, let us turn to the fifth component. It is seen  
 209 in Table 1 that the stress of this component is constant during the relaxation process at  $A_5 = 4.4 \times$   
 210  $10^5 \text{ Pa}$ , which corresponds to a modulus of  $1.0 \times 10^8 \text{ Pa}$ . As mentioned above,  $E(t)$  becomes  $10^7$   
 211  $\text{Pa}$  at the highest, and therefore the fifth component cannot be attributed to the rubber component.

212 Table 1 Fitting parameters of eqs 2 and 3 for dry  $\kappa$ -carrageenan film.

$i$	$A_i$ (Pa)	$\tau_i$ (s)	(Pa <sup>-1</sup> )
1	$5.9 \times 10^5$	$1.8 \times 10^0$	$C_{d1} = -1.4 \times 10^{-12}$
2	$4.9 \times 10^5$	$1.6 \times 10^1$	
3	$2.9 \times 10^5$	$1.0 \times 10^2$	
4	$3.6 \times 10^5$	$5.9 \times 10^2$	
5	$4.4 \times 10^5$	$\infty$	$C_{d2} = 1.1 \times 10^{-11}$

213

214



215

216 Fig. 4 Fitting of  $\sigma$  and  $\Delta n$  for dry  $\kappa$ -carrageenan film with eqs 2 and 3. The measured value is  
217 represented by solid lines and the values calculated using parameters in Table 1 are shown  
218 by broken lines.

219

220 Based on the structure of the  $\kappa$ -carrageenan film consisting of three domains as well as on the

221 “physical” plasticization for the dry film, the fifth component should be primarily attributed to

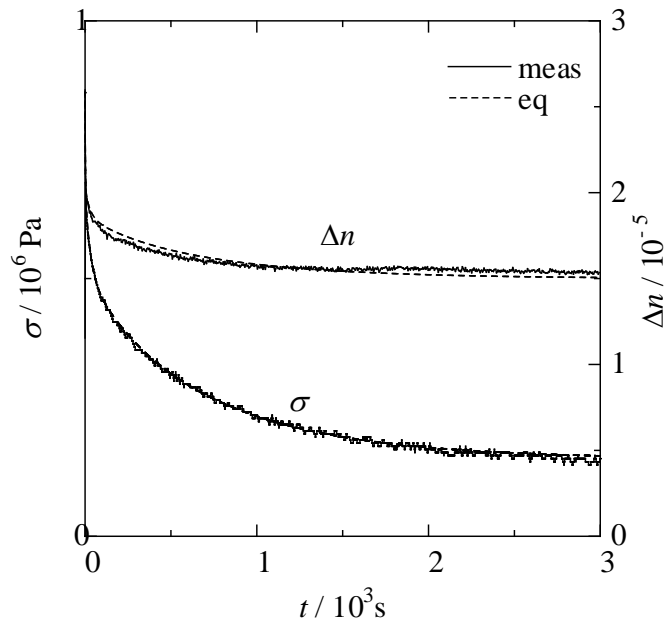
222 the continuous phase of amorphous  $\kappa$ -carrageenan. It is likely that the  $\kappa$ -carrageenan chains are

223 forced to align the backbones along the deformation direction to some extent and then remain

224 unchanged during the following relaxation process because of the very low mobility in the dry  
225 film. The modulus higher than that of the rubber component might be due to the constraints on  
226 the chain motion of  $\kappa$ -carrageenan chains densely assembled within that domain.

227 The results for the moist film are shown in Figure 5. The decreasing trend of measured  $\sigma$  is  
228 well expressed by the empirical equation likewise with the parameters listed in Table 2, as drawn  
229 by a broken line in the figure. Then the parameters are used for fitting the measured  $\Delta n$  so that  
230 the stress-optical coefficients can be obtained. It is found that the decreasing trend of  $\Delta n$  can be  
231 also represented by a similar equation to eq 3 where the two stress-optical coefficients  $C_{d1}$  and  
232  $C_{d2}$  are replaced with  $C_{m1}$  and  $C_{m2}$  as demonstrated by a broken line in Fig. 5. As shown in Table  
233 2, one positive coefficient  $C_{m1} = 1.0 \times 10^{-11} \text{ Pa}^{-1}$  is common to the four components having finite  
234 relaxation times and the other coefficient  $C_{m2} = 1.1 \times 10^{-10} \text{ Pa}^{-1}$  for the constant term is greater  
235 than  $C_{m1}$ . In the previous paragraph, the negative  $C_{d1}$  has been correlated with the glass component.  
236 Hence, it is hardly likely that the positive stress-optical coefficients for the moist film are  
237 attributable to that component. Although the glass component indeed exists even in the moist film,  
238 the relaxation time of such a localized mode becomes too short under the “chemical” plasticizing  
239 effect of the moisture to be detected using our apparatus. Water from the moisture works as the  
240 plasticizer in the moist film and swells the continuous phase of amorphous  $\kappa$ -carrageenan to  
241 soften the network. Therefore the addition of moisture would make it possible for  $\kappa$ -carrageenan





242

243 Fig. 5 Fitting of  $\sigma$  and  $\Delta n$  for moist  $\kappa$ -carrageenan film with eqs 2 and 3. The measured value  
244 is represented by solid lines and the values calculated using parameters in Table 2 are  
245 shown by broken lines.

246

247 Table 2 Fitting parameters for moist  $\kappa$ -carrageenan film.

$i$	$A_i$ (Pa)	$\tau_i$ (s)	( $\text{Pa}^{-1}$ )
1	$3.0 \times 10^5$	$2.0 \times 10^0$	$C_{m1} = 1.0 \times 10^{-11}$
2	$1.6 \times 10^5$	$2.8 \times 10^1$	
3	$6.6 \times 10^4$	$2.5 \times 10^2$	
4	$3.0 \times 10^5$	$7.7 \times 10^2$	
5	$1.5 \times 10^5$	$\infty$	$C_{m2} = 1.1 \times 10^{-10}$

248

249

250 chains in the continuous phase to contribute not only to  $\sigma$  and accordingly of  $\Delta n$  appearing with

251 the uniaxial deformation but also to the following relaxation. In fact  $C_{m1}$  agrees well with  $C_{d2}$ ,

252 suggesting that the relaxation mode of the moist film represented by  $C_{m1}$  is mainly attributed to

253 the continuous phase of amorphous  $\kappa$ -carrageenan. It should be emphasized that  $\sigma$  as well as  $\Delta n$   
254 for a polymer system having the ideal network structure does not change during the measurement  
255 with  $\varepsilon$  fixed. Therefore  $\kappa$ -carrageenan chains whose one end or both ends are not included in the  
256 crosslinks of  $\kappa$ -carrageenan aggregates would be charged with the relaxation of  $\sigma$  and  $\Delta n$   
257 mentioned above. Now we focus on  $C_{m2}$ ;  $C_{m2}A_5$  corresponds to the value of birefringence at long  
258 times. As is obvious from Tables 1 and 2,  $C_{m2}A_5$  is greater than  $C_{d2}A_5$  for the dry film. If moisture  
259 just acts as a plasticizer for the continuous phase of amorphous  $\kappa$ -carrageenan,  $C_{m2}A_5$  should  
260 naturally be smaller than  $C_{d2}A_5$ . The increase in birefringence at long times is not simply due to  
261 moisture acting as a plasticizer and must be attributed to some structural change. The present  
262 results clearly show that some structure change is generated. In the framework of the three-domain  
263 model, the greater value of birefringence for the moist film could be mainly explained by the  
264 contribution of the third domain, the large crosslinks consisting of helical  $\kappa$ -carrageenan  
265 aggregates. Because the continuous phase of network is linked with the crosslinks by sharing a  
266 great number of  $\kappa$ -carrageenan chains, the plasticization of the former by the moisture will  
267 indirectly activate the global motion of the latter even though the crosslinks themselves are not  
268 plasticized by the moisture. Then the large crosslinks would rotate accompanying deformation of  
269 the surrounding  $\kappa$ -carrageenan chains in the plasticized continuous phase. The crosslinks would  
270 not rotate back in the following relaxation process, because the overall network existing in the  $\kappa$ -

271 carrageenan film remains unchanged under the fixed  $\varepsilon$ . At present, it is impossible to identify the  
272 origins of the force and the optical anisotropy in the third domain based on the structure of the  
273 crosslinks, but it is probable that an aggregate of helical  $\kappa$ -carrageenan chains is very anisotropic.  
274 Despite the fact that the network of  $\kappa$ -carrageenan chains in the continuous phase also contribute  
275 to the constant  $\sigma$  and  $\Delta n$  under the fixed  $\varepsilon$ ,  $C_{m2}$  should be essentially attributed to the crosslinks  
276 taking the relation  $C_{m1} \ll C_{m2}$  into consideration.

277

## 278 **Conclusions**

279 The uniaxial tensile and the relaxation behavior for  $\kappa$ -carrageenan films was examined by  
280 means of the conventional mechanical tests and the birefringence measurement using the  
281 polarization modulation method. A picture on the molecular level regarding the deformation and  
282 the following relaxation of  $\kappa$ -carrageenan chains was obtained based on the three-domain model  
283 for  $\kappa$ -carrageenan films and on the idea of MSOR. It was suggested that the continuous phase of  
284 amorphous  $\kappa$ -carrageenan chains in the dry film is deformed by the uniaxial stretching together  
285 with the local glass component and only the glass component contributes to the decrease in  $\sigma$  and  
286 the increase in  $\Delta n$  in the relaxation process. This situation totally changes regarding the moist  
287 film: the crosslinks of  $\kappa$ -carrageenan aggregates in addition to the continuous phase become  
288 responsible for the observed  $\sigma$  and  $\Delta n$  with deformation and the relaxation is attributed only to

289 the unbridged  $\kappa$ -carrageenan chains in the continuous phase.

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