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

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Abstract:

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

Keywords: *κ*-carrageenan; gel film; birefringence; stress-optical coefficient; moisture

Introduction

The first-order molecular structures of polymer chains are intrinsically anisotropic, that is, the local refractive index with respect to the direction of main chain is different from that normal to it, although such local anisotropies are cancelled out in macroscopically isotropic systems, where the chain segments are randomly oriented. However, once such a system undergoes deformation, the total difference in the refractive index with respect to the direction of deformation can be detected as birefringence reflecting the global chain orientation in the system. Therefore, it is often helpful for understanding the way in which polymer chains behave against deformation to use optical techniques measuring the birefringence together with the conventional mechanical tests. To give a good example, the modified stress-optical rule (MSOR) holds well for polymer melts and solutions: Both the stress and the birefringence are considered consisting of two components, which are usually referred to as the rubber and the glass components, and the proportionality between the birefringence and the stress holds for each component. A great number of studies on the viscoelasticity and the birefringence for amorphous polymers, especially for styrene polymers, have established the proportionality, and the orientation relaxation of polymer chains has been analyzed by using MSOR so that the contribution of each component can be estimated (Inoue et al. 1991; Janeschitz-Kriegl 1983; Okamoto et al. 1992; Read 1983). In our previous study, mechanical measurement for amorphous pullulan films by the uniaxial stretching has been combined with birefringence measurement, and a set of stress-optical coefficients for the rubber and the glass components of pullulan have been determined as the material constants on the basis of MSOR (Horinaka et al. 2018b).

Carrageenan is a group of polysaccharides consisting of repeating units of D-galactose alternating β-1,4- and α-1,3-linkages. Among them κ-carrageenan is characterized in terms of the chemical structure by a 3,6-anhydro-galactose ring as well as a single sulfate group in the companion ring. κ-Carrageenan has been widely used as an additive in the food and cosmetic industries due to its favorable function of forming hydrogels. Regarding the network structure of κ-carrageenan hydrogels, it should be noted that the crosslinks are very likely composed of aggregates of κ-carrageenan chains in the helical conformation, that is, κ-carrageenan hydrogels have fairly large sizes of crosslinks in comparison with ordinary chemical and physical gels (Ikeda et al. 2001; Morris et al. 1980; Viebke et al. 1994). When κ-carrageenan films are prepared by drying κ-carrageenan hydrogels, it is almost certain that there remain the large crosslinks of aggregates inside the films and that the obtained κ-carrageenan films do not become amorphous as a whole due to the crystal-like aggregates. This implies that MSOR cannot be applied to the correlation between the stress and the birefringence for the κ-carrageenan films in the same manner as the pullulan films mentioned above. Although the mechanical tests of κ-carrageenan hydrogels have been extensively carried out from the point of the industrial applications (Sason et al. 2018; Rochas et al. 1990; Watase et al. 1986), the mechanism of the mechanical behavior has not been fully understood on the molecular level, nor is the role of the large crosslinks.

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

Experimental

Sample preparation

In order to use *κ*-carrageenan films for birefringence measurement, we needed to prepare transparent and isotropic samples, so that the intrinsic birefringence of the samples at the as-prepared states (Δn_0) could be neglected. However, the preliminary test showed that *κ*-carrageenan films prepared just by drying *κ*-carrageenan hydrogels on a flat plate exhibited substantial birefringence. This matter was finally settled by using a monosaccharide as an additive to the film. Practically, isotropic *κ*-carrageenan films used in this study, which had $\Delta n_0 < 10^{-6}$, were prepared in the following manner. Powdery κ-carrageenan (TCI, Japan) and a monosaccharide fructose (Wako, Japan) were dissolved in distilled water. The concentrations of the κ-carrageenan and the monosaccharide were fixed at 10 g/L and 30 g/L, respectively. The mixture was stirred at 80 °C for 3 h and the obtained aqueous solution was spread on a Teflon plate at 80 °C. Then evaporation of the solvent water was allowed for several hours until a transparent film formed on the plate. The film that was in the roughly dried state was cut into rectangular pieces and each one was dried further under vacuum at 80 °C for more than 6 h to be a constant weight. The dimensions of the thoroughly dried film were 10 mm × 30 mm × 0.1 mm. The addition of moisture was performed by leaving the thoroughly dried films in a moist atmosphere for more than 24 h. It was impossible to prepare moist films at arbitrary water contents. The water content of the moisturized films was estimated from the weight reduction in the re-drying process executed after the measurement described below.

Measurement

Simultaneous measurement of the stress and the birefringence for the κ-carrageenan films was carried out using a homemade apparatus for the birefringence coupled with a commercial tensile machine (TENSILON RTM-500, Orientec Corp., Japan). Details of the homemade apparatus and the principles of the birefringence measurement using the polarization modulation method were described in our previous manuscript (Horinaka et al., 2018b). First the film sample was uniaxially stretched between cramps at a constant speed of 5 mm/min up to a nominal tensile strain (ε) so that the measurement could be performed in the linear viscoelasticity region. The initial length between the cramps was around 15 mm. Then the birefringence (Δn) as well as the stress (σ) was monitored during the following relaxation process with time (t) until t = 3000 s at the longest with ε fixed. Actually, σ was calculated from the force with the cross section of the film measured before stretching; hence, σ obtained in this study was the nominal tensile stress. The measurement temperature was 25 °C.

Results and discussion

Figure 1 shows the stress-strain curves for the dry and moist κ-carrageenan films with fructose. To check the effect of species of the monosaccharide additive, the stress-strain curves for κ-carrageenan films with glucose of the same content are also given in the figure. The weight fraction of moisture has been estimated to be 19 % for the film with fructose and 16 % for the film with glucose. It is seen that the stress-strain behavior is independent of the species of the monosaccharide additive within the experimental error and is significantly affected by the moisture; each stress-strain curve appears almost linear within the ε-range examined but the slope of the curve, which is defined as the Young's modulus (E), greatly decreases as the moisture is added. In fact, the values of E for the dry and moist films with fructose estimated from Fig. 1 are 7.4×10^8 and 6.6×10^7 Pa, respectively. We have previously examined plasticizing effects of saccharides and alditols on the uniaxial tensile behavior of κ-carrageenan films (Horinaka et al. 2017). Although the measurement temperature in this study is slightly lower and the procedure of sample preparation is different compared to the previous study, E for the dry film with fructose coincides well with our previous value for the film of the same content; E of the order of 10^8 Pa indicates that this film is under the “physical” plasticizing effect which can be explained by the blending law for immiscible blends (Dekkers et al. 2016; Katopo et al. 2012; Takayanagi et al. 1963). It has been proposed that the κ-carrageenan film has three domains; namely, crosslinks of helical κ-carrageenan aggregates, continuous phase of amorphous κ-carrageenan, and voids without κ-carrageenan (Horinaka et al. 2017, 2018a, 2019). Then the additive is situated in the voids as an assembly of micro-granules having very low modulus compared with the κ-carrageenan matrix, which decreases E as a whole. On the other hand, E of the order of 10^7 Pa estimated for the moist film is close to those obtained in our previous study for the κ-carrageenan films under the conventional plasticization, as it were, the “chemical” effect; the additive has a good miscibility with κ-carrageenan and swells continuous phase of amorphous κ-carrageenan to soften the network (Horinaka et al. 2017). Regarding the moist film examined in this study, water from the moisture very probably works as the additive miscible with κ-carrageenan.

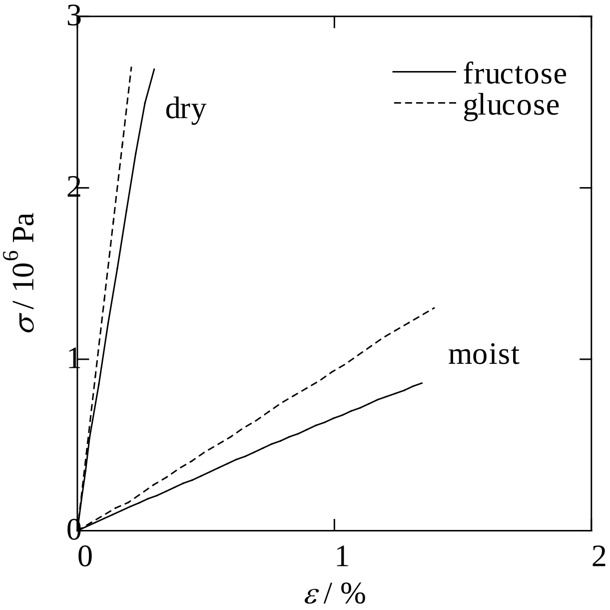

Fig. 1 Stress-strain curves for dry and moist κ-carrageenan films with fructose or glucose.

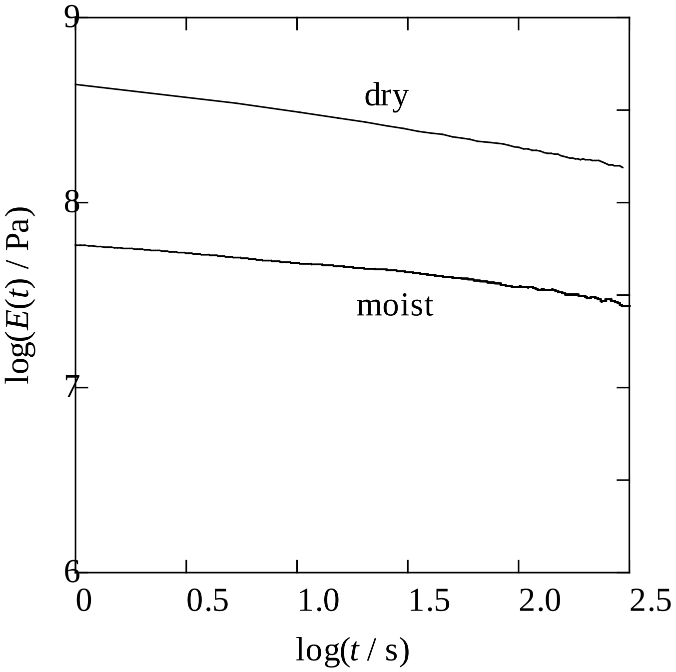

Fig. 2 Young’s relaxation modulus for the dry and moist κ-carrageenan films with fructose after uniaxial stretching.

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

The stress relaxation as well as the simultaneous change in Δn is compared between the dry and moist films with fructose in Figure 3. It should be noted that Δn for a polymer system is not necessarily positive but Δn for the κ-carrageenan films are actually positive, so that the logarithmic value of Δn is plotted using the right axis of the figure for ease of identification. The decreasing trend of σ is similar between the dry and moist films, as expected from Fig. 2, but change in Δn with t is completely different: Δn for the dry film increases, while that for the moist film decreases. That is, addition of 19 % moisture greatly affects the relaxation of Δ*n* to be seemingly vertical mirror images to each other. Further consideration gives the following information: *σ* for the dry film is still greater than that for the moist film, although relative difference in *σ* is smaller than that in *E*(*t*) (Fig. 2) due to the difference in *ε* applied. On the other hand, it is obvious that Δ*n* for the dry film is significantly smaller than that for the moist film. Assuming that components of the *κ*-carrageenan films responsible for *σ* necessarily contribute to Δ*n* on the analogy of MSOR, these facts imply that the main components responsible for *σ* and Δ*n* on the uniaxial deformation are different between the dry and moist films, and accordingly different stress-optical coefficients are expected for the two systems.

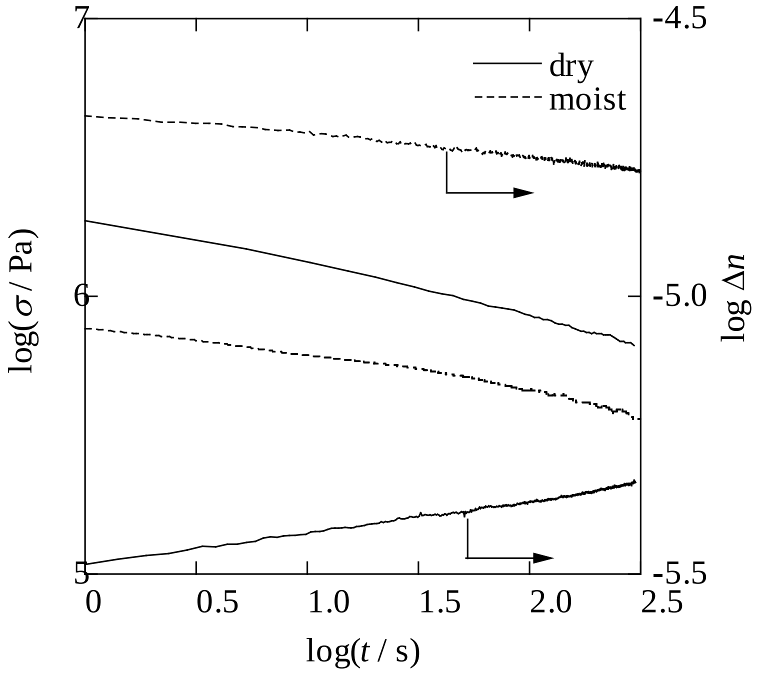

Fig. 3 Comparison of *σ* and Δ*n* between dry and moist *κ*-carrageenan films with fructose.

In the framework of MSOR, there is a correlation between σ and Δn observed with deformation, which is given by the following equation:

$$\Delta n = C_{\mathrm{R}}\sigma_{\mathrm{R}} + C_{\mathrm{G}}\sigma_{\mathrm{G}} \tag{1}$$

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

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

where A_i (i = 1–5) is the fraction of the mode with the relaxation time of τ_i, though τ_5 is assumed infinity. At present, it is impossible to quantitatively explain each relaxation mode in terms of the chain motion, but the decreasing trend of σ can be expressed by eq 2 using the parameters in Table

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

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

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

Table 1 Fitting parameters of eqs 2 and 3 for dry κ-carrageenan film.

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

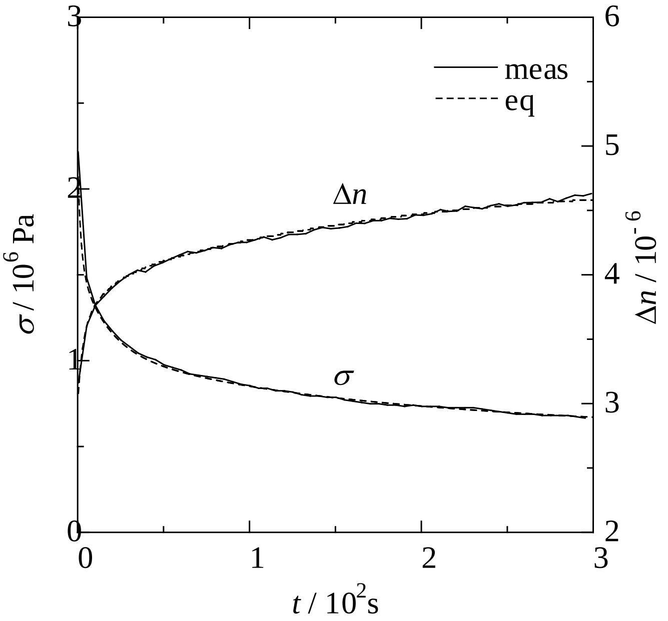

Fig. 4 Fitting of σ and Δn for dry κ-carrageenan film with eqs 2 and 3. The measured value is represented by solid lines and the values calculated using parameters in Table 1 are shown by broken lines.

Based on the structure of the κ-carrageenan film consisting of three domains as well as on the “physical” plasticization for the dry film, the fifth component should be primarily attributed to the continuous phase of amorphous κ-carrageenan. It is likely that the κ-carrageenan chains are forced to align the backbones along the deformation direction to some extent and then remain unchanged during the following relaxation process because of the very low mobility in the dry film. The modulus higher than that of the rubber component might be due to the constraints on the chain motion of κ-carrageenan chains densely assembled within that domain.

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

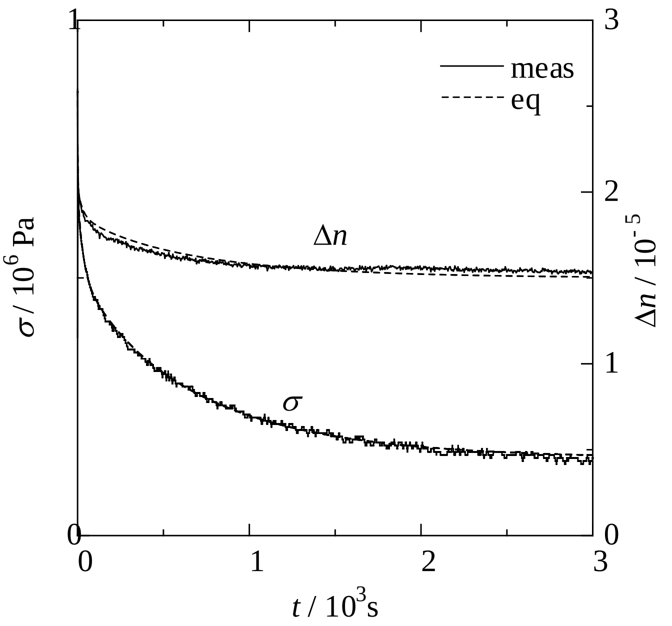

Fig. 5 Fitting of σ and Δn for moist κ-carrageenan film with eqs 2 and 3. The measured value is represented by solid lines and the values calculated using parameters in Table 2 are shown by broken lines.

Table 2 Fitting parameters for moist κ-carrageenan film.

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

chains in the continuous phase to contribute not only to σ and accordingly of Δn appearing with the uniaxial deformation but also to the following relaxation. In fact C_{m1} agrees well with C_{d2}, suggesting that the relaxation mode of the moist film represented by C_{m1} is mainly attributed to the continuous phase of amorphous κ-carrageenan. It should be emphasized that σ as well as Δn for a polymer system having the ideal network structure does not change during the measurement with ε fixed. Therefore κ-carrageenan chains whose one end or both ends are not included in the crosslinks of κ-carrageenan aggregates would be charged with the relaxation of σ and Δn mentioned above. Now we focus on C_{m2}; $C_{\mathrm{m2}}A_5$ corresponds to the value of birefringence at long times. As is obvious from Tables 1 and 2, $C_{\mathrm{m2}}A_5$ is greater than $C_{\mathrm{d2}}A_5$ for the dry film. If moisture just acts as a plasticizer for the continuous phase of amorphous κ-carrageenan, $C_{\mathrm{m2}}A_5$ should naturally be smaller than $C_{\mathrm{d2}}A_5$. The increase in birefringence at long times is not simply due to moisture acting as a plasticizer and must be attributed to some structural change. The present results clearly show that some structure change is generated. In the framework of the three-domain model, the greater value of birefringence for the moist film could be mainly explained by the contribution of the third domain, the large crosslinks consisting of helical κ-carrageenan aggregates. Because the continuous phase of network is linked with the crosslinks by sharing a great number of κ-carrageenan chains, the plasticization of the former by the moisture will indirectly activate the global motion of the latter even though the crosslinks themselves are not plasticized by the moisture. Then the large crosslinks would rotate accompanying deformation of the surrounding κ-carrageenan chains in the plasticized continuous phase. The crosslinks would not rotate back in the following relaxation process, because the overall network existing in the κ-

carrageenan film remains unchanged under the fixed ε. At present, it is impossible to identify the origins of the force and the optical anisotropy in the third domain based on the structure of the crosslinks, but it is probable that an aggregate of helical κ-carrageenan chains is very anisotropic. Despite the fact that the network of κ-carrageenan chains in the continuous phase also contribute to the constant σ and Δn under the fixed ε, C_{m2} should be essentially attributed to the crosslinks taking the relation $C_{\mathrm{m1}} << C_{\mathrm{m2}}$ into consideration.

Conclusions

The uniaxial tensile and the relaxation behavior for κ-carrageenan films was examined by means of the conventional mechanical tests and the birefringence measurement using the polarization modulation method. A picture on the molecular level regarding the deformation and the following relaxation of κ-carrageenan chains was obtained based on the three-domain model for κ-carrageenan films and on the idea of MSOR. It was suggested that the continuous phase of amorphous κ-carrageenan chains in the dry film is deformed by the uniaxial stretching together with the local glass component and only the glass component contributes to the decrease in σ and the increase in Δn in the relaxation process. This situation totally changes regarding the moist film: the crosslinks of κ-carrageenan aggregates in addition to the continuous phase become responsible for the observed σ and Δn with deformation and the relaxation is attributed only to the unbridged *κ*-carrageenan chains in the continuous phase.

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