論 文

Dynamic Viscoelasticity of Iota Carrageenan Gelling
System near Sol-Gel TransitionKhandker S. HOSSAIN^{*1}, Norio NEMOTO^{*2†}, and Katsuyoshi NISHINARI^{*3}^{*1}*Department of Materials Science and Technology, Interdisciplinary Graduate
School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816, Japan*^{*2}*Department of Applied Physics, Faculty of Engineering, Kyushu University,
Hakozaki, Fukuoka 812-81, Japan*^{*3}*Department of Food and Nutrition, Faculty of Human Life Science, Osaka City
University, Sumiyoshi, Osaka 558, Japan*

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A dynamic viscoelastic (DVE) and creep study has been made on five iota carrageenan gelling samples with polymer concentration C ranging from 1 to 3wt% over a wide range of temperature including the sol-gel transition point. All gel samples below and at room temperature show nearly ideal elastic behavior. The gel point is determined as temperature T_c at which the storage and the loss shear moduli, G' and G'' , follow the power law with the same exponent n , which is smaller than the universal value of 0.66 for chemical gels and decreases monotonously with increasing concentration. Superposition of dynamic and creep data reveals that the power law holds at least four decades at the gel point. DSC measurement on the same samples reveals a broad sol-gel transition. The transition temperature T_m determined as the peak temperature is found to be close to the gel point T_c , but always higher than T_c . At T_m , the samples are viscous solution at lower C and viscoelastic at higher C , clearly indicating that T_m can not be considered as the gel melting temperature.

Key Words: Carrageenan/Dynamic viscoelasticity/Fractal structure/Sol-gel transition/DSC

1. INTRODUCTION

The carrageenans are sulfated polysaccharides extracted from a number of seaweed that have an ester sulfate content of 15-40% and contain an alternating disaccharide repeating unit of 1,3-linked - β -D-galactose, and 1,4-linked 3,6-anhydro- α -D-galactose¹⁾. Carrageenans are widely used in food industry because of its ability to form gel as well as viscous solution which are useful in texturing of food. There are three major types of carrageenans named ι (iota), κ (kappa) and λ (lambda) where the basic alternating unit backbone structure is same for all carrageenan material but sulfation can vary in extent and position. Iota carrageenan is the most highly sulfated one and its hot aqueous solution exhibits, on lowering the temperature, the sol-gel transition. The gelling mechanism is widely believed as being due to association of polymer chains through double helices which is followed by

a cation mediated side by side helix-helix aggregation, leading to a three dimensional cohesive network that means gel^{2), 3)}. Carrageenan gel is thermoreversible i.e. it requires heat to bring them into sol and cooling of the solutions sets to gel.

In chemical gelation, polymer molecules evolve in to larger cluster by covalent bonding with increasing extent of chemical reaction p and undergoes the sol-gel transition at $p = p_c$ called the gel point at which an infinite cluster starts to appear and the whole system is characterized at the same time by a self similar structure. Therefore the gel point for chemical gels should be considered as the gel point at which viscosity diverges for crosslinks with infinite life time and the equilibrium modulus is still zero. On the other hand, the situation appears to be completely different for thermoreversible gels in which the sol-gel transition point is usually regarded as the first order phase transition point (thermodynamically) because a jump in thermodynamic quantities such as enthalpy is observed at the sol-gel transition temperature T_m due to formation of physical junction zones. However,

[†]To whom correspondence should be addressed

there is essentially no reason to assume that the life time τ_c of these physical crosslinks is infinite and their number density is constant up to T_m , and they may depend on temperature, polymer concentration, concentrations and types of metallic ions etc⁴⁾. If it were really the case, the transient nature of these physical networks would make it difficult to define the gel point clearly.

In this connection, it is to be noted that DSC curves of biological polymer gels are not sharp but pretty broad in most cases⁴⁾. Accordingly, T_m conveniently taken as the endothermic or the exothermic peak temperature in the DSC curves may not be identical to the first order transition point. Stated in another way, such the first order transition does not exist in a strict sense for biological gels, but instead the self-similar structure might be realized at another T .

Concerning determination of the gel point for chemical gels, Winter and his coworkers proposed an elegant method for determination of the gel point which utilizes angular frequency (ω) dependencies of the storage and the loss shear moduli, G' and G'' , where both were proportional to a power of the angular frequency over the whole range experimentally accessible^{5), 6)}. This behavior is consistent with the concept that the critical gel at P_c takes the fractal structure characterized by n . The exponent n called the relaxation exponent, takes various values between 1 and 0 depending on polymer species and crosslinking condition⁷⁾. The possibility of extending the Winter and Chambon criterion to chemically end-linking gelation^{8) ~ 10)} and also to physically crosslinked gelation of poly(vinyl chloride) (PVC)^{11), 12)} has been explored, whereas these studies on physically crosslinked polysaccharide gel are still at the initial stage.

The work in this study was carried out by using the knowledge of chemical gelation with a view to examine whether the physically crosslinked polysaccharide gel passes through the intermediate state at a temperature T_c at which it exhibits the power law type of relaxation so that T_c can be assumed as the critical gel point. We shall report in this paper the dynamic viscoelastic properties of iota carrageenan gel, which reflects the onset of gelation, and discuss relations of various parameters of the viscoelastic data to the gel properties. The results of the DSC, and the creep and creep recovery measurements will also be reported in order to make comparison of the results obtained from dynamic viscoelasticity. From the creep results we determined the temperature T_{gel} which indicates the onset temperature of forming an elastic network with decreasing T and T_{sol} indicating the onset temperature of viscous fluid behavior with increasing T .

2. EXPERIMENTAL

2 • 1 Material and sample preparation

Commercial powdered sample of iota carrageenan, obtained from Saneigen F.F.I Inc., was used in this study without

further purification. The polymer sample contained various metal ions as listed in Table I. Uniform solutions were prepared by dispersing the carrageenan powder in distilled water and by stirring at 80°C for five concentrations C of 1.0, 1.5, 2.0, 2.5 and 3.0% (w/w) with the stirring time of 30, 45, 60, 75 and 90 minutes, respectively. A transparent gel was formed from the uniform solution by standing at the ambient temperature. The lowest gel forming concentration was 0.4 wt%. The gel sample was transferred in to the rheometer at 25°C within 2 hours after preparation of the samples for dynamic viscoelastic measurements.

2 • 2 Apparatus and Method

Table I Metal content in the iota carrageenan sample

Metal	Weight/%
Sodium	1.20
Potassium	5.08
Calcium	3.58
Magnesium	0.20

The oscillatory shear and shear creep measurement were performed using a stress-controlled rheometer (Carri-MED CSL-100 England) with a parallel plate type geometry of plate diameter 4 cm. A solvent trap equipped with the rheometer was used to protect the sample from evaporation. The storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ were measured at a strain of 0.1 as functions of angular frequency ω from 100 to 0.1 rad/s and of temperature T from 5 ~ 65°C. The creep compliance $J(t)$ and the recoverable compliance were measured as a function of time at various temperatures. In the creep measurement, a constant stress σ is instantaneously applied at $t=0$ and is kept constant. Then the compliance $J(t)$ ($=\gamma(t)/\sigma$) increases with time. After the removal of the stress at time t , the deformation gradually recovers more or less towards its initial shape, which is called creep recovery.

DSC measurement was carried out with a Setaram micro DSC-III calorimeter (Caluire, France). About 800~900 mg of gel samples were sealed hermetically into a DSC pan. Distilled water was used as a reference material. The temperature was raised to 95°C and kept for 10 minutes to annihilate the thermal history, and then lowered to 5°C at 0.5°C/min, and raised at 0.1°C/min from 0 to 90°C.

3. RESULTS AND DISCUSSION

3 • 1 Viscoelastic behavior at 5~25°C

Fig. 1 shows angular frequency ω dependence of G' and G'' for five gels with concentration C from 1.0 to 3.0 wt% at 25°C. As shown in the figure, G' is substantially higher than G'' and takes a plateau value over the whole ω range. Such ω dependence corresponds to the behavior of an elastic gel so that the gel can be characterized by the equilibrium

modulus G_{eq}^{13} . The mechanical loss tangent ($\tan \delta = G''/G'$) decreased with increasing C , though not shown in the figure, which indicates that gels with higher concentration are more solid-like, reflecting that networks formed by the polymers become more dense with increasing C . The $\tan \delta$ value at 5 °C is slightly lower than that of 25 °C for all concentrations, indicating that a gel becomes stronger with decreasing T . At 5 and 25 °C, the dependence of G' on concentration can be expressed as a power law with an exponent 2. This result is coincident with the well known relation $G' \sim C^2$ observed for an entanglement network of flexible polymer chains. The second power of the concentration dependence of the elastic modulus was also observed in the case of kappa carrageenan gel in the presence of added alkali metal ions^{14), 15)}.

Fig. 1 Frequency dependence of G' and G'' for gels with five different concentrations at 25 °C.

3 • 2 Viscoelasticity near the sol-gel transition temperature T_c

Fig. 2 shows frequency dependence of G' and G'' with increasing temperature for the 2.0 wt% gel sample. The data are shifted along both the horizontal and the vertical axes by using shift factors a and b respectively in order to avoid the data overlapping. G' and G'' at 45 °C slightly increase with frequency ω but a plateau is observed in the lower frequency region. With further increase in temperature T , the value of G' decreases while G'' increases and the ω dependence of G' and G'' becomes stronger gradually so that the plateau observed in the lower frequency region started to disappear gradually and constant value of G_{eq} is no longer observed within our measuring angular frequency range. Similar kind of behavior was observed for rest of the samples.

3 • 3 Viscoelasticity at T_c

In Fig. 2, both G' and G'' become proportional to ω^n over

Fig. 2 Change in frequency dependence of G' and G'' with temperature near the gel point for the 2.0 wt% gel sample. The data are shifted along horizontal and vertical axes by using the shift factor a and b respectively.

the whole ω range at $T_c = 57$ °C for the 2.0 wt% gel sample. With further increase in temperature, a crossover of G' and G'' occurs and G' becomes smaller than G'' .

As mentioned in Introduction, G' and G'' of chemical gels show a power law behavior with a same relaxation exponent n at the gel point and the system has a self similar structure i.e. the fractal structure, which can be expressed by the following equations to be simultaneously satisfied at the gel point.

$$G' \sim G'' \sim \omega^n \quad (1)$$

$$G''/G' = \tan \delta = \tan(n\pi/2) \quad (2)$$

The proportionality of G' and G'' to ω^n means that $\tan \delta$ ($= G''/G'$) is independent of ω . The Kramers-Kronig relationship¹⁶⁾ gives the second equality of equation 2 between $\tan \delta$ and n , which can be used for an estimate of n using the $\tan \delta$ value. Following the argument of Winter et al., we may consider that the sol-gel transition occurs at 57 °C for the 2.0 wt% carrageenan gel and the structure at the gel point can be characterized by the critical gel structure or the fractal structure. The gel point was determined in exactly the same way for samples of different concentrations which are summarized in Fig. 3. Values of the relaxation exponent n were calculated from the $\tan \delta$ value, which were in good agreement with the value of n obtained directly from the slope as in Table II. Fig. 4 shows concentration dependence of n and T_c . The gel point shifts to higher temperatures with increasing concentration. The n for the 1.0 wt% gel takes the value 0.42 smaller than the universal value of 0.66 for the end linking chemical gel⁸⁾. With increasing concentration n tends to decrease monotonously and takes the value of 0.32 for the 3.0 wt% gel sample. Percolation theory^{17), 18)} relates

Table II Experimental results obtained from rheological and DSC measurements.

Concentration /wt%	Rheological Measurement							DSC Measurement	
	Oscillation Mode				Creep Mode			T_m /°C	T_s /°C
	T_c /°C	$\tan \delta$	n *Calculated value	n Obtained from slope	m	T_{gel} /°C	T_{sol} /°C		
1.0	52.0	0.79	0.43	0.42 ± 0.01	0.45 ± 0.01	30	55	56.4	55.8
1.5	55.0	0.66	0.37	0.39 ± 0.01	0.41 ± 0.01	34	57	58.6	58.0
2.0	57.0	0.65	0.37	0.37 ± 0.01	0.40 ± 0.01	36	62	61.1	59.3
2.5	60.0	0.64	0.36	0.35 ± 0.01	0.35 ± 0.01	40	63	61.9	61.6
3.0	61.5	0.60	0.34	0.32 ± 0.01	0.33 ± 0.01	44	65	64.6	63.5

*from eq(2)

Fig. 3 Frequency dependence of G' and G'' at the gel point T_c for five carrageenan gels which show power law behavior. Data are shifted by using the shift factor a in order to avoid overlapping. Fig. 4 Concentration dependence of n and T_c , T_m and T_s

the exponent n to the fractal dimension^{19), 20)}. Gels with higher fractal dimensions have smaller values of the relaxation exponent n . With increasing C , molecular cluster may become more dense and because of high functionality of physical gels each crosslink involves many chains and thus fractal dimension increases. So decreasing tendency of n with increasing C is observed. In contrast, the branching point of the chemical gels is well-defined by the functionality of the molecules and thus n of chemical gels is observed to retain the same value. But the n values of chemically crosslinked gel may be affected by the presence of entanglement effect⁸⁾.

3 • 4 Thermal Behavior

Differential Scanning Calorimetry (DSC) measurements were carried out to obtain heating and cooling DSC curves. Fig. 5 shows the heating DSC curves for carrageenan gels of various concentrations. A broad endothermic peak accompanying gel melting was observed, which may suggest that a junction zone consists of various aggregates of helices with different thermal stabilities. This is caused by the coexistence of various metal ions and the distribution of molecular weight and so on. The temperature of the gel melting T_m , determined as the endothermic peak temperature of a DSC heating curve shifted to higher temperature with increasing concentration. Gel melting point was not significantly affected by the heating rate from 0.1°C/min to 0.5°C/min. The transition temperature T_s for the gel formation of carrageenan obtained from the exothermic DSC curve is slightly lower than T_m by about 1~2°C. T_s also shifted to higher temperature with increasing C . The endothermic and exothermic enthalpy evaluated from the areas surrounded by the peaks and base line shown in Fig. 5, increases with increasing concentration. Both the endothermic and exothermic enthalpies ΔH divided by C shows an increasing trend with increasing C . The temperatures T_m , T_s and T_c are plotted against C in Fig. 4 in which all these temperatures increase with increasing concentration. T_c is always lower than T_m and T_s . At $T = T_m$ the dynamic viscoelastic measurements have been made as shown in Fig. 6 for all concentrations of carrageenan where data are shifted along both the horizontal

Fig. 5 Heating DSC curve of iota carrageenan for five different concentrations. Left and right vertical lines denote the positions of the temperatures T_{gel} and T_{sol} respectively determined from creep and recovery experiment.

Fig. 6 Frequency dependence of G' and G'' for gels of five different concentrations at $T = T_m$. Solid and broken straight lines represent slopes 1 and 2 respectively. The data are shifted along horizontal and vertical axes by using the shift factors a and b respectively.

and vertical axes using shift factors a and b respectively. For 1.0 and 1.5 wt% sample G' and G'' are proportional to ω^2 and ω^1 over the measured ω range respectively, which reflects that these two samples show typical behavior of viscous fluid. However, slopes of G' and G'' of other samples start to decrease with increasing concentration i.e. the samples are viscoelastic. So it is clear from this result that T_m can not be

considered as the gel point from rheological point of view.

3 • 5 Shear creep and creep recovery behavior

Creep and creep recovery measurements have been performed for all the carrageenan samples. The creep compliance $J(t)$ can be represented by the equation

$$J(t) = J_g + \Phi(t) + t/\eta \quad (3)$$

where J_g is the instantaneous compliance term, $\Phi(t)$ the retardation term and t/η the viscous flow term. Fig. 7 shows three creep and creep recovery curves for 2.0 wt% sample at $T=36^\circ\text{C}$, $T=T_c=57^\circ\text{C}$ and $T=62^\circ\text{C}$. At $T=36^\circ\text{C} \ll T_c$, $J(t)$ increases instantaneously and stays constant and then after the removal of the stress most part of the $J(t)$ instantaneously recovers its initial shape with no viscous response i.e. the sample has infinite viscosity. We designate T_{gel} as the temperature below which $J(t)$ fully recovers, which corresponds to an elastic gel and viscosity is infinite. At $T=62^\circ\text{C} \gg T_c$, $J(t)$ linearly increases with time from the beginning of stress application, which is due to viscous flow and the elastic recovery does not appear on removal of the stress which may be called sol or liquid without any elasticity. This temperature we call here as T_{sol} . The values of T_{gel} and T_{sol} of all concentration samples are listed in Table II. Fig. 8 shows raw data of creep and creep recovery results of all samples at the gel point where the compliance $J(t)$ is plotted against time t . J_g , the instantaneous compliance term is found to be negligibly small but the t/η term is found to contribute to $J(t)$ for all samples which is fairly large, indicating that viscosity is finite. The same kind of behavior was observed for other samples.

Fig. 7 Compliance of creep and creep recovery for 2.0 wt% sample at $T=36^\circ\text{C} \ll T_c$, $T=57^\circ\text{C} = T_c$ and $T=62^\circ\text{C} \gg T_c$ which represents the typical creep curve of elastic and viscoelastic gel and sol respectively.

Fig. 8 Creep and creep recovery behaviors for five gels at $T = T_c$.

In Fig. 9 the viscosities η of all the samples were plotted as a function of ε . Here ε is the relative distance from the point where viscosity of the samples has infinite value and this can be defined as $\varepsilon = |T - T_{gel}| / T_{gel}$. Viscosity η shows nearly same kind of ε dependence for all samples. The vertical lines drawn in this figure from right to left denote the position of T_c from 1.0 wt% to 3.0 wt% respectively. From this figure we see that near T_c all the samples show finite viscosity. This viscosity increases gradually with decreasing temperature and turns to infinity at their respective T_{gel} .

The finite viscosity at the gel point looks in contradiction to the definition of the gel point at which an infinite network is formed so that η diverges. This can be interpreted in the following manner. At the gel point, the junction zones that are made up of the reversible weak bonds among the finite clusters may break and recombine again and again. Even if an infinitely large cluster is formed in the samples, capability of exchange in network strands does not produce equilibrium modulus and thus an appearance of finite viscosity is observed here. Light scattering experiment may reveal further information about the structure and concentration fluctuation of these samples between the temperature T_{gel} and T_{sol} which is now in progress. At present it is not clear whether only iota carrageenan show the above mentioned behavior or it can also be found in other biopolymeric systems. So investigation to other systems may enlighten us in this regard.

3 • 6 Comparison of the dynamic and creep data

The power-law behavior of G' and G'' is observed over whole ω range of about three decades for the iota carrageenan samples at the gel point, and it is desirable to extend the time domain where the fractal concept applies for or

Fig. 9 Semilogarithmic plot of viscosity η , estimated from creep measurement vs. ε for five different concentrations. Here ε is a relative distance from the point T_{gel} defined as $\varepsilon = |T - T_{gel}| / T_{gel}$.

to determine the long time limit for its applicability. Creep and creep recovery experiments are suitable for this purpose. We can estimate the retardation term $\Phi(t)$ for gels of all the concentrations at the gel point by subtracting viscous flow term t/η from $J(t)$ in equation 3. $\Phi(t)$ is logarithmically plotted against t for all samples which is shown in Fig. 10 by filled symbols. Data with different concentrations all follow the power law $\Phi(t) \sim t^m$ and take their respective value of the exponent. The value of m is nearly equal to the value n that was measured in the dynamic experiment as shown in Table II. In order to compare the results obtained from the static and dynamic viscoelastic measurements, here we attempt to superpose the two data utilizing the conversion formula in the phenomenological theory of linear viscoelasticity. The dynamic data can be converted to creep data using the approximation relation proposed by Ninomiya and Ferry¹³⁾ which reads as

$$J(t) = J'(\omega) + 0.40J''(4\omega) - 0.014J''(10\omega)|_{t=1/\omega} \quad (4)$$

First, $J'(\omega)$ and $J''(\omega)$ were calculated from $G'(\omega)$ and $G''(\omega)$ using the relation $J'(\omega) = 1/G'(\omega)$ and $J(t)$ was approximated by equation 4. $\Phi(t)$ was then calculated using the relation 3 in which η is the viscosity directly obtained from the creep measurement. $\Phi(t)$ calculated from dynamic data is plotted logarithmically against time t . It is seen from the Fig. 10 that all the data are observed to be superposed with each other with an error of at most 10~20%, and the slopes are observed to be nearly equal. The deviation of results obtained from dynamic and static data may be partially attributed to the use of different gel samples in dynamic and creep measurements where a little difference in polymer

Fig. 10 Superposition of $\Phi(t)$ calculated from $G^*(\omega)$ data (open symbol) on to $\Phi(t)$ data (filled symbol) directly obtained from creep measurement.

concentration may occur in preparation, and partially to inaccurate estimate of the viscous term. Here it is seen that the power law holds at least four decades in contrast to the data obtained in the dynamic measurement in which the law followed up to three decades. This superposition assures the reliability of the value n determined from the dynamic viscoelastic measurement.

3 • 7 Application of Eldridge-Ferry equation

Eldridge and Ferry²¹⁾ proposed the following equation for the gel melting temperature T_m using van't Hof's law.

$$\log C = \frac{-\Delta H_m}{2.303RT_m} + \text{const} \quad (5)$$

Where C is the concentration, T_m is the melting temperature, ΔH_m is the heat of reaction in kJ/mol of crosslinks and R is the gas constant.

In fact, as the supplied sample contained metallic ions, it is almost impossible to use the Eldridge-Ferry plot for the present system because metallic ion contents also increase with increasing concentration of polymers. The plot should be performed at a constant ionic strength. Nevertheless, we have attempted to use the Eldridge-Ferry equation in order to obtain an apparent value of heat of reaction during sol-gel transition.

Applying this analysis, $\log C$ is plotted against reciprocal absolute temperature T_c obtained from rheological results of iota carrageenan gel in Fig. 11. Since the relationship between $\log C$ and T_c^{-1} is found to be linear, ΔH_c by using equation 5 can be calculated from the slope of the straight line as 103 kJ/mol. As the same way using T_m and T_s , determined by DSC measurement, ΔH_m and ΔH_s are calculated as 143 kJ/mol and 141 kJ/mol respectively. As the sol-gel transition of the present system is not the first order transition, these ΔH values may be considered as the activation energies of association and dissociation processes of the junction zones at

Fig. 11 Eldridge-Ferry plot for carrageenan gels.

respective temperatures.

In the case of agarose gels where the same procedure has also been applied to estimate the enthalpy of agarose gel formation as from =220~1100 kJ/mol for seven kinds of commercial agars²²⁾. Agarose has structural similarity to carrageenan but it is a neutral polysaccharide while both iota and kappa carrageenans carry sulfate group. These sulfate groups hinder the formation of helix-helix aggregation and thus less heat energy is likely to be needed for the sol-gel transition of iota and kappa carrageenans. Watase and Nishinari²³⁾ reported ΔH of iota carrageenan as 33 kJ/mol which is lower than that of kappa carrageenan as 60 kJ/mol. This is because iota carrageenan is known to have more sulfate content than kappa carrageenan. This ΔH value of iota carrageenan is lower than that of our present value. This may be due to the difference of added metallic ions in the present samples that shield electrostatic repulsion between helices thus increase gelling ability.

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