Fracture Morphology of Gellan Gels

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The fracture morphology of cylindrical gellan gels (0.81%) containing various amounts of sodium chloride was studied as a function of the compression velocity. The velocity of compression was changed more than five orders of magnitude. Three characteristic velocities, which depend on the concentration of NaCl in the gel, were determined from the load-compression curves of gels. The space that consists of the characteristic velocity and the NaCl concentration is divided into four regimes. In each regime, unique fracture morphology was observed. The gel fractures with only single crack, which inclines at an angle of 45 degrees from the parallel surfaces of the gel, at higher compression velocities. In medium compression velocities, the fracture of gel occurs with multiple cracks that appear on the cylindrical surface of the gel along the axial direction. In this fracture, considerable amount of solvent is lost from the gel. The crossover regime appears between these two regimes. The gel can be compressed into a thin sheet without any macroscopic fractures at very low compression velocities. In addition, it was found that the radius of the thin sheet was almost the same with that of initial gel. The gels once broken and/or compressed regain the original volume when they are soaked in solvent. These results indicate that the fracture morphology was determined both by the elastic properties and the frictional properties of the gel.
Key words: Gellan; Gel; Salt effect; Fracture; Strength in compression

1. INTRODUCTION

Gel is a cross-linked polymer network swollen by absorbing a liquid. Many gels occur in the biological realm. One of the important classes of biological gels is polysaccharide gel that is used widely, for instance, in food industry. Recently, gellan is frequently used instead of other polysaccharides because of its clarity and good viscoelastic properties of the gel. Gellan is a polysaccharide that produced by the bacterium, *Pseudomonas elodea*. The chemical structure, the physical, and the chemical properties of gellan have been studied so far [1-3]. Among others, the viscoelastic properties of gellan gels are of importance from not only the industrial points of view but also scientific points of view [4]. Although many viscoelastic studies have been made, the fracture property of gellan gel has yet to be studied so far. Such studies will promote the better understanding of the gel under the large deformation that may be related to the viscoelasticity of the gel. In practical purpose of food industry, the fracture behavior of the gel plays essential roles in the mastication and the flavor release. It is, therefore, worth studying the fracture properties of gellan gels.

It is well established that the viscoelastic properties of gels are determined by three quantities; that is, the bulk modulus K, the shear modulus G, and the friction coefficient between the polymer network and the liquid f as follows [5],

$$D_{collective} = E/f \qquad 1)$$

where E = K + (4/3) G is the longitudinal modulus

of the gel and $D_{collective}$ the collective diffusion coefficient of the polymer network. It has been reported that the friction coefficient of the chemically cross-linked polymer gel is high enough to prevent the release of liquid from the gel [6]. On the other hand, the average pore size of polysaccharide gel is assumed to be larger than that of the synthetic gels because polysaccharide gels are usually formed from the dilute solutions. The liquid in the polysaccharide gels, thus, may be easily squeezed out of the gel under deformation. Accordingly, it is of importance to study the effects of the deformation velocity on the fracture behaviors of the gel. Here, we present a systematic study on the fracture morphology of gellan gel.

2. EXPERIMENTAL

The powdered gellan was kindly supplied by SAN-EI-GEN F. F. I. Ltd. (Osaka, Japan) and used without further purification. The amount of the cations that contained in the gellan was as follows: Na^+ 1900, K^+ 20800, Ca^{2+} 5120, and Mg^{2+} 1460 μg/g. The gellan solutions were prepared by dissolving the powdered gellan in solvent at a temperature of 90°C for 20min. The solution was poured into a glass test tube (13x100mm) and then kept in a water bath at a given setting temperature T_{set} for one day to obtain the gel. The gellan concentration is 0.81%. As a solvent, aqueous sodium chloride solutions were used. The concentration of NaCl in solutions varied from 10 to 60mM. An aqueous gellan solution formed a gel on cooling. The gelation temperature (T_{gel}) depended on NaCl concentration. T_{gel} for a 0.81% gellan gel in

water was 28.0 °C. T_{gel} of 0.81% gel containing 10, 20, 40, and 60mM NaCl were 31.7, 35.5, 38.4, and 41.3°C. T_{gel} corresponds to the maximum temperature to form a gel at a fixed concentration. If T_{set} was taken below T_{gel}, the gellan solution formed the gel. In the preliminary compression experiments, we observed that fracture stress and initial modulus calculated from the initial slope of load-compression curve depended on T_{set}. Fracture stress and initial modulus appreciably decreased with increasing the temperature difference between T_{gel} and T_{set}. In this experiment, T_{set} (temperature of the water bath) was taken as the gelation temperature T_{gel}. The gel thus obtained was taken out of a glass tube. Then the gel was cut into pieces by the ultrasonic sample cutter (USC-3305, YAMADEN, Co., Tokyo, Japan). The size of the cylindrical gel used in the compression measurements was 11.5mm in diameter and 10mm in height.

The compression measurements were made using a commercial apparatus (Mini 55, Instron, USA). The cylindrical gel was set on the lower disk of sample holder (60mm in diameter). Thin papers were placed in between the top of gel and the upper disk, and the bottom of gel and the lower disk, respectively, to prevent the slippage of a gel to lateral direction. The upper disk (40mm in diameter) was moved against the lower disk to compress a gel at various velocities v_a. The compression velocity was changed from 1000mm/min to 0.005mm/min. In the case of slow compression velocities, a commercial wrapping film for foods (Kureha-Kagaku Ind. Ltd.) was set around the compression disks (not around the gel itself) to minimize the vaporization of water from the sample gel. The photograph of the compressed gel was taken by a digital camera (Pix 2700, FUJIFILM, Japan). All the measurements were made at room temperature (22.5±1°C).

3. RESULTS AND DISCUSSION
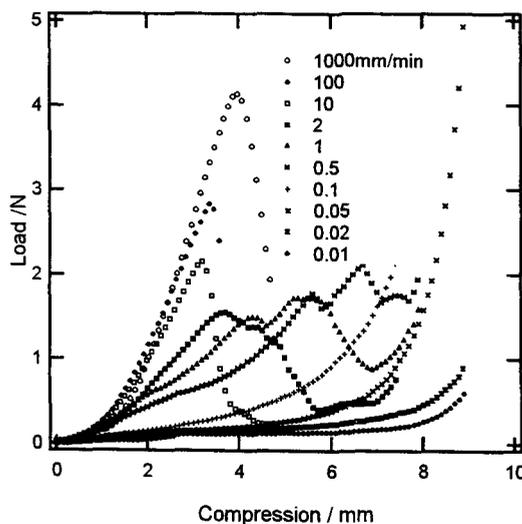
Fig. 1 shows the relationship between the load and the compression of gellan gel at a concentration of 0.81% containing 40mM sodium chloride (NaCl). These results indicate that the shape of the compression curve strongly depends on the velocity of compression. These compression curves can be divided into two types
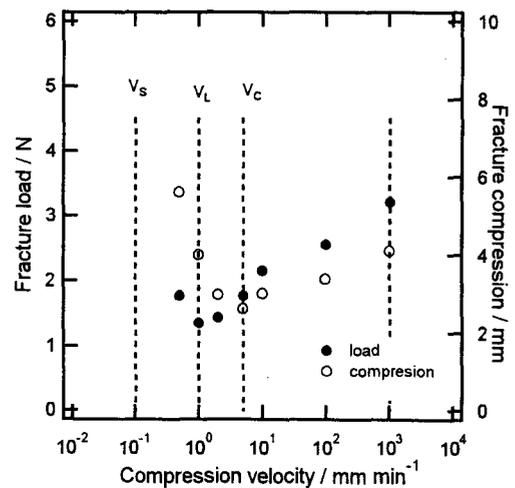
Fig.2 Load and compression at fracture plotted against compression velocity for 0.81% gellan gel (40mM NaCl).

by the characteristic behaviors. The one type is characterized by the appearance of clear maximum in the compression curve. It is found, and also confirmed by naked eyes, that the macroscopic fracture of the gel occurs at the maximum load in

Fig. 1 Load-compression curve for a gellan gel containing 40mM NaCl. Gellan concentration is 0.81%.
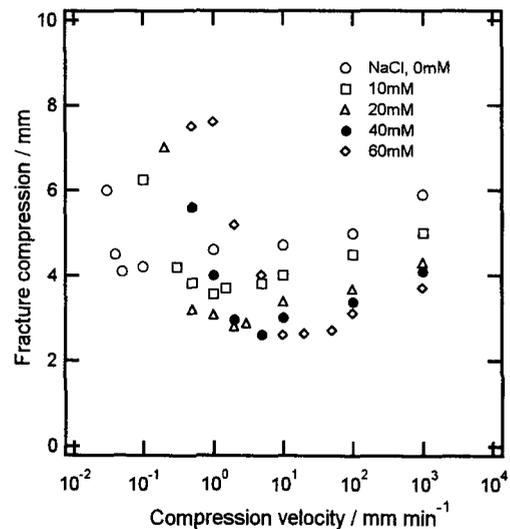
Fig. 3 Fracture compression plotted against compression velocity for 0.81% gellan gels containing NaCl in various concentration.

the compression curve. The other type does not show such maximum and the load continuously increases with the compression. This transition of the compression curve occurs at the compression velocity of 0.1mm/min. We define this characteristic velocity as V_S.

Below the compression velocities smaller than V_S, gellan gels are compressed into a thin sheet. The radius of the resultant sheet at the compression velocity of 0.02mm/min is unchanged from that of initial gel.
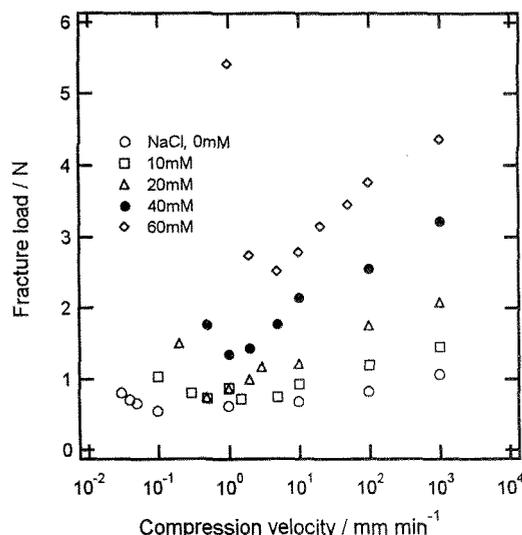

Fig.4 Fracture load plotted against compression velocity for 0.81% gellan gels containing NaCl in various concentraion.

The load F_b and the compression L_b at the fracture point of gellan gel at a concentration of 0.81% (40mM NaCl) are plotted as a function of the velocity of compression in Fig 2. These results indicate that both the load and the compression at the fracture point first decrease, attain a minimum, and then increase with decreasing the velocity of compression. It is clear that the compression velocities, at which the load and the compression at the fracture point show the minimum value, are different each other. We, thus, define two characteristic compression velocities V_L and V_C from Fig 2. The compression velocity that corresponds to the minimum of the fracture load is V_L. In the same manner, V_C corresponds to the minimum the fracture compression.

The same experiments are made using the 0.81% gellan gel at various NaCl concentrations, 0mM, 10mM, 20mM, and 60mM. Similar compression curves are obtained in the gel prepared at different NaCl concentrations. The values of L_b and F_b thus obtained are shown in Fig. 3 and Fig. 4, respectively. In these gels F_b and L_b also show a minimum in the compression velocity range studied here. At higher compression

velocities, F_b increases linearly with the logarithm of v_a. The slope of the semi-logarithmic plot of F_b and v_a increases with increasing NaCl concentration.
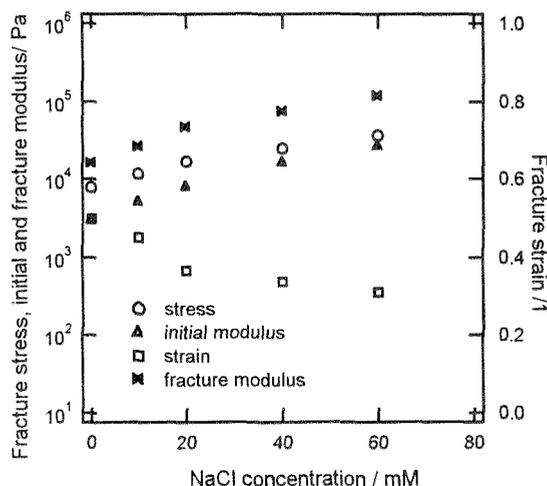

Fig.5 The NaCl concentration dependence of stress and strain at fracture for 0.81% gellan gels. The compression velocity used is 100mm/min.

Fig. 5 shows the NaCl concentration dependence of the fracture stress σ_f, the fracture strain ε_f, and the initial modulus E_a at v_a =100mm/min. Both σ_f and ε_f are defined as $\sigma_f = F_b /\pi r_0^2$ and $\varepsilon_f = L_b /L_0$, where r_0 is the initial radius, and L_0 the initial height of the gel. The initial modulus E_a was calculated from the initial slope of compression curve. In the case of fast compression, σ_f, ε_f at fracture and E_a increase with increasing NaCl concentration. The NaCl concentration dependence of fracture modulus K_f
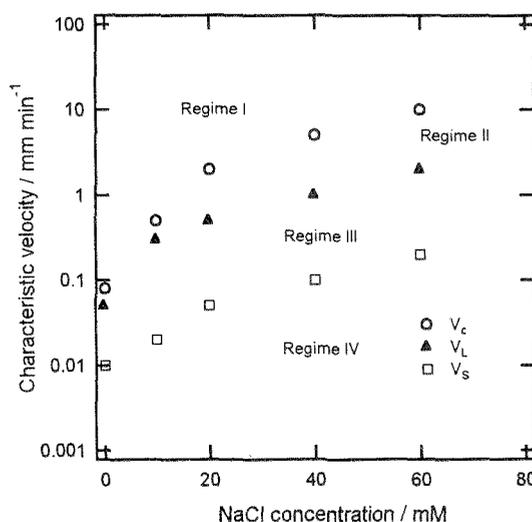

Fig.6 Characteristic velocities plotted against NaCl concentration. Gellan concentration is 0.81%.

defined as $\sigma_f = K_f \varepsilon_f$ was in good agreement with that of initial modulus E_a, as shown in Fig. 5. In the case of fast compression, the fracture point of gel is determined by the elasticity.

In Fig. 6, the characteristic rates, V_S, V_L, and V_C, are plotted as a function of the NaCl concentration. We found that these characteristic rates increase with increasing NaCl concentration. The space, which constructed by the characteristic rate and the NaCl concentration, was divided into four regimes as given in Fig 6.

The shapes of gels that compressed at four compression velocities, each corresponds to the typical compression velocity of regime I, II, III, and IV are given in Fig 7. The snapshots were taken at typical stages of compression process. These results indicate that the gel fractures macroscopically at higher compression velocities. The aspects of fracture are, however, totally different from each other. The gel fractures by only single crack, which inclines at an angle of 45 degrees from the parallel surfaces, in the regime I. The volume of the gel immediate after fracture was unchanged from initial volume. Thus, water in the gel is kept during compression in regime I. It indicates that the elastic properties of gel mainly govern the fracture of the gel at higher compression velocities. Several vertical cracks appear on the surface of the gel in the regime III. In this case, the volume of the gel is decreased immediate after fracture. It suggests that water in the gel is lost during compression. In this regime, therefore, the gel fracture and the flow of water inside gel simultaneously occur during compression of the gel. Milas & Rinaudo have presented schematically the observation of the change from regime I to regime III in the presence of salt excess at a constant deformation rate (25mm/min) [7]. In regime II, both the single crack and the multiple cracks those observed in the regime I and III are observed. The regime II is, therefore, the crossover regime from regime I to regime III. The gel is compressed into a thin sheet without any macroscopic fracture in the regime IV. The size of a gel (4-c, v_a =0.02 mm/min) was 11.9mm and 1mm in height. We named this type of gel as "Gel Senbei". The radius of the sheet thus obtained is almost the same with that of the initial radius. This result indicates that most water within the gel flows out of the gel without macroscopic fracture.

In regime IV, a gel can be compressed to 90% without breakup under extremely slow deformation. When the gel is compressed vertically at a very slow rate, the gel dilates along the radial direction according to the incompressible fluid. The compression of the gel may also cause the non-equilibrium spatial distribution of polymer network within the gel. Since the rate of compression is small enough the dilated region regains its original position within a short time interval by the collective diffusion as given eq. 1, that is, the gel recovers the initial radius. The

water within the dilated region simultaneously flows out of gel. We expect that the gel collapses into a sheet without dilation along the radial direction by repeating such cycle.

The gels thus fracture and compressed were soaked in solvent to gain the information on the structure of the polymer network in the fracture and the compressed states. The gellan gel can re-swell to its original volume even the gel is compressed until one tenth of its original height, although the shapes of gels are not shown in figure. In the case of very slow compression velocity, the fluid inside the gel squeezed out of gel to make a sheet of the gel. The sheet of gel thus obtained regains its original volume in 11 days if soaked in solvent.

These results are similar to the volume phase transition phenomena of gels. The parameter that governs such phenomenon is the collective
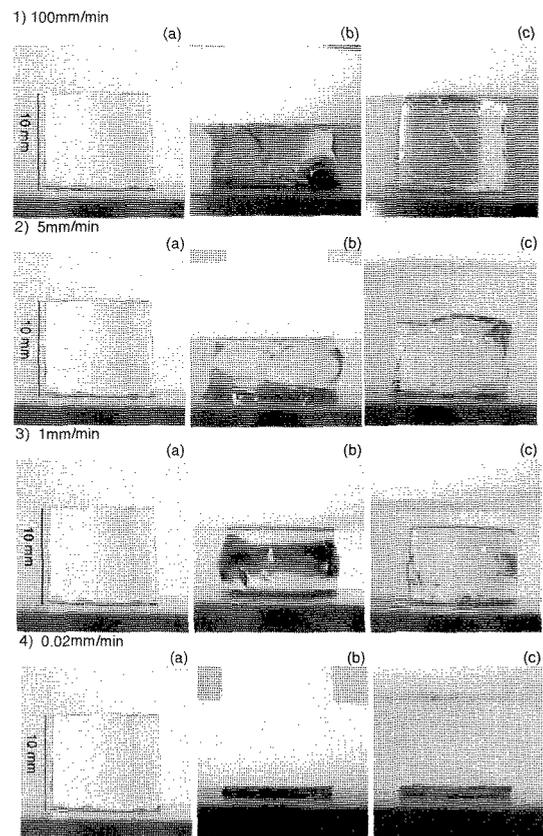

Fig. 7 Photographs of the profile for a 0.81%gellan containing 40mM NaCl solutions at different compression velocities. 1); Regime I (100mm/min), 2); Regime II (5mm/min), 3); Regime III (1mm/min), 4); Regime IV (0.02mm/min). (a); an undeformed gel (11.5mm in diameter and 10mm in height), (b); a compressed gel by the cross head, (c); a compressed gel after removing the cross head.

diffusion coefficient of polymer network, the elastic modulus of gel, and the friction coefficient between the solvent and the polymer network as given in eq. 1. Among these, the friction between the solvent and the polymer network is important. Because the explicit measurement of friction in polysaccharide gel is difficult, such study has yet to be made so far. Here we calculate the friction coefficient of gellan gel from above experimental results. The sheet of 0.81% gellan gel (40mM) regains its original volume in 11 days. It indicates that the top surface of the sheet moves over a distance of about 5mm in 11 days. The collective diffusion coefficient of gellan gel at a concentration of 0.81% (40mM NaCl), thus, can be calculated by using the following equation,

$$D_{collective} \sim \Delta x^2/t \qquad (2)$$

where Δx is the distance over which the surface moves and t the time. Using above values the collective diffusion coefficient of gellan gel is calculated to be the order of 3×10^{-7} cm^2/s. On the other hand, the elastic modulus of 0.81% gellan gel (40mM), which determined from the compression curve, is of the order of 3×10^4 dyn/cm^2. The friction coefficient of 0.81% gellan gel (40mM), thus, becomes 5×10^{-10} dyn s/cm^4. This value is almost one order of magnitude smaller than that of typical synthetic polymer gels such as poly (acrylamide) gel [8]. The friction of the polymer network of gellan is, thus, much smaller than that of synthetic polymer gels. The friction of porous materials is determined by the viscosity of liquid and the void area that is reasonably assumed to be proportional to the square of the correlation length of the gel, ξ^2 as follows.

$$f \sim \eta/\xi^2 \qquad (3)$$

It is well established that the correlation length of the polymer network increases with decreasing concentration. The void area becomes larger as the concentration of gel decreases. In the present case, gellan gels are prepared from dilute solutions. The void area of the gel is large and hence the friction is small. Besides, in the case of gellan gel, the polysaccharide chains form ordered junction zones which are thought as the aggregates of double helices. Because of such structural features, the friction may be much smaller than that of synthetic polymer gels such as poly-(acrylamide) gel [8]. The gellan gel, thus, may have low friction coefficient, and hence, high collective diffusion coefficient, suggesting that the water within the gellan gel was easily exuded from the surface of the gel by the compression.

4. CONCLUDING REMARKS

The cylindrical gellan gels are compressed until fracture. The fracture morphology of the gel varies with the compression velocity and the concentration of NaCl. Four regimes are observed in the space that consists of the compression velocity and the concentration of the gel. The characteristic velocities that appear in the compression curves express the boundaries between morphological regimes of gellan gels. A new morphology is found in gellan gel at extremely slow compression velocities where the gel is compressed into a sheet without any macroscopic fractures. Besides, the radius of the sheet is unchanged from the initial radius. These results indicate that the pore size of gellan gel is much larger than that of synthetic polymer gels. The liquid inside the gel, therefore, easily squeezed out of the gel by the mechanical compression.

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