

## Effects of Deformation Rates on the Stress – Strain Curves and the Failure Properties in the Tensile Test of Gellan Gum Gels

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Tensile tests were carried out on gellan gum gels in order to observe the relation between deformation rates and deformation properties such as the stress-strain relation, the rupture strain and the rupture stress. A gripping tool was constructed to circumvent the problem of clamping the gel specimens. The tests were replicated to avoid the influence by the statistical nature due to the inhomogeneity in the network structure. The strain rate, which was determined from the strain – time plot observed, was in the range from  $5 \times 10^{-5}$  to  $1 \times 10^{-2}$ /sec. Two kinds of the stress-strain relations were observed, linear relations, curves of upward convex, according to the concentration of gels. The relations were interpreted in terms of linear viscoelasticity theory. The dependence of the tensile modulus on the crosshead speed, which can be substituted by the strain rate, varied with the concentration. The modulus altered by the change of crosshead speed in low concentration, whereas it didn't in high concentration. The plot of the rupture stress against the rupture strain was constructed to overview the failure properties. It was considered that the elastic energy stored by stretching was determined by the concentration of gels and less influenced by the strain rate.

Key words: gellan gum / gel / tensile test / deformation rate / failure properties

### 1. INTRODUCTION

To understand the behavior of polymer gels under large deformation is important problem from the standpoint of their mechanical properties. They will be questions of great interest; that, the detailed process during which the polymer network exhibits the stress against the deformation applied: the relation between the breaking of microscopic structure and the rupture of gels: the effect of solvents on the properties. In particular, the question of whether the deformation rate influences them or not is left unanswered.

A few reports can be found on gelatin gels and agarose gels concerning the large deformation rheology of polymer gels[1-4]. In these reports some consideration was given on the relations among condition of preparation, deformation rate, tensile modulus, rupture strain and nonlinearity defined by BST equation[5]. The authors are eager to clarify the relations on gellan gum gels so as to start the experiments.

Gellan gum, a kind of extracellular microbial polysaccharides, has attracted special interest recently[6]. Its chemical structure has been confirmed as a linear polymer consisting of tetrasaccharide repeating units with a carboxylate group. This polymer is soluble in water above 90°C, and on cooling, the solution forms a transparent gel at around 30-35°C. The solubility in water depends on the processes for producing gellan. Several studies have been reported on its solution properties and gelation phenomena. On the other hand, less has been reported on the physicochemical

properties from the viewpoint of deformation and rupture of the gel.

The cross-links ( often called "junction zones") of gellan gum molecules which are now accepted are that gellan gum molecules undergo a thermally reversible coil-to-helix (double helix) conformational transition, and aggregation of double helical molecules forms the junction zone[7-10]. While the image of junction zones are revealing, the three-dimensional distribution of the junction zones is very complicated and it is impossible at present to understand the distribution by applying any law (that is, to understand why the distribution arises). Further, the lengths of disordered chains between junction zones are generally shorter than the large sections of random coil described by rubber elasticity theory. Thus the assumption of a Gaussian distribution of chain lengths is likely to be of limited validity. These chains are certainly less flexible than in a synthetic random coil polymer because of the restricted rotation about glycosidic linkage. Therefore, a discussion based on the consideration of purely entropic contributions to elasticity is almost certain to be inappropriate. Additional complication may arise due to the fact that gellan gum gels as normally prepared contain a very large amount of water. Also the indispensable is a "sol fraction", that is, gellan molecules not physically connected to the infinite network.

Although the constitution of gellan gum gels is complicated as described above, their stress-strain

relations and rupture properties are expected to reflect it accurately. The theoretical treatment of these more complex networks has not been developed sufficiently, and, at least initially, the characterization of mechanical behaviors should be largely phenomenological.

The result of the tensile test will be influenced by the statistical nature due to the distribution of inhomogeneities in the network structure. Thus the tests were replicated. According to the description in the literature, the failure envelope, the plot of rupture stress against rupture strain was constructed to verify whether or not it defines a part of the full stress-strain curve[1]. It may be a convenient way to compare the rupture properties from the statistical point of view as a function of polymer concentration.

## 2. EXPERIMENTAL

Powdered gellan in the deacetylated form was kindly supplied by San-Ei-Gen F. F. I., Inc., and used without further purification. Distilled water was purchased from Nacalai. Inc. The concentrations of the prepared gellan solutions were 1.5, 2 and 2.5%. After the aqueous solution was prepared by heating, it was poured into the dumb-bell mould and cooled to form the test sample. The tensile tests were performed with four kinds of crosshead speeds (S), 0.5, 5, 50 and 100 mm/min. In the course of the tensile test, the lengths of both the stretching direction and the direction perpendicular to it were observed using a video camera. However, the change in the length of the direction perpendicular to stretching could not be detected. The minimum detectable change in length was 0.3mm. The tests were repeated seven times for samples of concentrations of 1.5 and 2%. That is, after the samples ruptured and the test finished, the gel was heated to melt, then poured into the dumb-bell mould once again to be used for next test. Other details of the experiments were described elsewhere[11].

## 3. RESULTS AND DISCUSSION

### *Stress-strain relations*

In this study we investigated the effects of deformation rates on stress-strain relations of gellan gum gels. In each test the strain ( $\epsilon$ ) was confirmed to increase linearly with the time (t) while the crosshead was moving. The strain rate ( $\dot{\epsilon}$ ) can be obtained from the slope of strain- time plot and was shown as a function of S in Fig. 1. The strain rate range in this study is similar to that reported for previous studies on the deformation rheology of gelatin gels[1,3].

Fig. 2 shows the relation of stress and strain for 2% gellan gum gel in the tests of S=100. The relation followed a straight line from the start to the rupture in every experiment. The linear relations are also observed for 1.5% gels in the tests of S=0.5~100. The physical extent of slow growth of crack during the tensile test must be small under our experimental condition, since no appreciable drop in stress due to a reduction in load-bearing area occurs prior to rapid rupture.

Fig. 3 shows the relation of stress and strain for 2.5% gellan gum gel where the range of S was from 5 to 100. The relation wasn't linear but curved upwards convexly. Previously we attempted to explain the

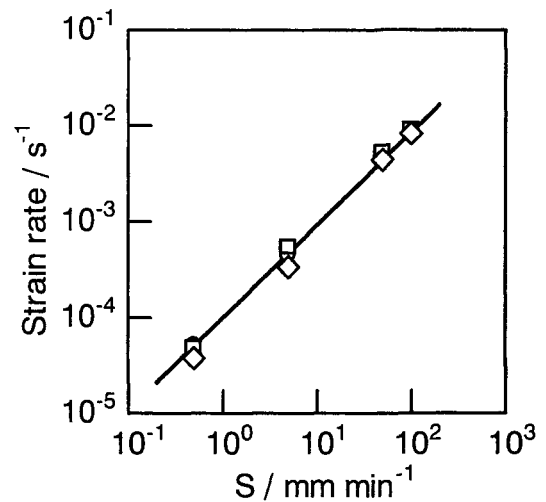


Fig. 1. Dependence of strain rate on the crosshead speed (S). □:1.5% gel; ○:2% gel; ◇:2.5% gel.

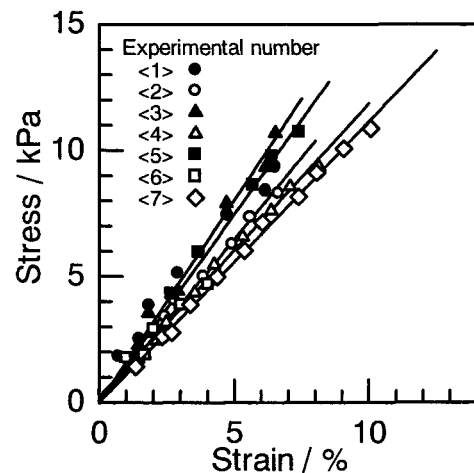


Fig. 2. The stress - strain relation for 2% gellan gum gel. The crosshead speed is 100mm/min. The tests were repeated seven times.

stress-strain relation of gellan gum gel using the constitutive equation of Maxwell model[10].

$$\frac{d\epsilon}{dt} = \frac{1}{G} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad (1)$$

$\sigma$ , G and  $\eta$  are the stress, the elastic constant of spring element and viscosity of dashpot element in Maxwell model, respectively. One can derive from equation (1) the expression of  $\sigma$  as a function of t as;

$$\sigma(t) = G \int \dot{\epsilon} \times \exp\left(-\frac{t}{\tau}\right) dt \times \exp\left(-\frac{t}{\tau}\right) \quad (2)$$

where  $\tau = \eta/G$ .  $\dot{\epsilon}$  was confirmed to be constant from the slope of strain- time plot. In the case that  $\tau$  is in an appropriate value,  $\sigma(t)$  expressed by equation (2) shows an upward convex curve, while the curve apparently becomes linear as the  $\tau$  value becomes smaller. Therefore the difference in the stress-strain relation between 2.5% gel and gels of lower concentration must come from the difference of the

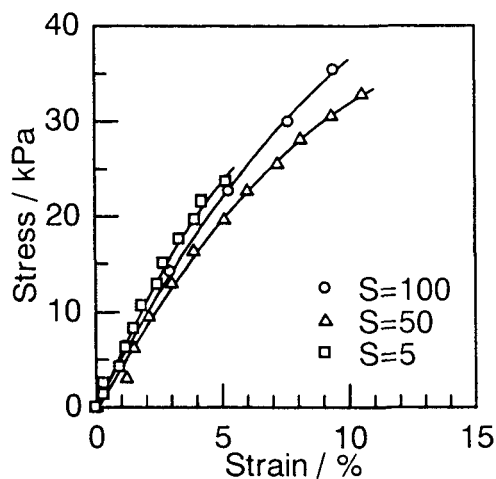


Fig. 3. The stress - strain relation for 2.5% gellan gum gel. The crosshead speed ( $S/ \text{mm min}^{-1}$ ) is shown in the figure. The tests were performed one time.

relaxation time.

Several properties of gellan gum gel can be determined from the relation of stress and strain, such as tensile modulus ( $E$ ), rupture strain ( $\epsilon_r$ ), rupture stress ( $\sigma_r$ ) and rupture energy per unit volume.

$E$  values of 1.5% gel in the tests of  $S=0.5$  are shown in Fig. 4. As can be seen, the modulus didn't increase, also it didn't decrease against the experimental number. It can be said that, gellan gum gel doesn't change the modulus in spite of the repeat of melting and gelation. The average value of  $E$  is plotted against  $S$  in Fig. 5. In the test of 2.5% gel  $E$  value was determined from the initial slope of the stress-strain curve. Although the strain rate is more meaningful from the theoretical point of view, the  $S$  value was adopted to construct the plot since it was the experimental condition and the strain rate is the value determined from the results observed. The relations of  $E$  and  $S$  varied according to the concentration of gels as shown in Fig. 5. The moduli of 2.5% gels were independent of  $S$ , which meant the gel to be quite elastic. Those of 2% gels decreased with the decrease in  $S$ , which must be a manifestation of the viscous behavior. We have not elucidated the mechanism of the viscous behavior of gellan gum gels. Similar behavior, however, was reported on gelatin gels and an explanation was added as; [2] the network could partially relax the applied strain by breaking and reforming cross-links for the slow deformation. The fact that the 'sol fraction' is more in 2% gels than in 2.5% gels may lead to the result of the decrease in  $E$  of 2% gels with  $S$  in spite of no variation of  $E$  of 2.5% gels. The relation of  $E$  and  $S$  showed a shallow minimum for 1.5% gels. In the range of  $S=5 \sim 100$  the moduli decreased with the decrease in  $S$ . The slope of the  $E$ - $S$  relation was more steep in 1.5% gels than that in 2% gels, showing the enhancement of viscous behavior. We can't explain at present the result of the shallow minimum of the  $E$ - $S$  relation.

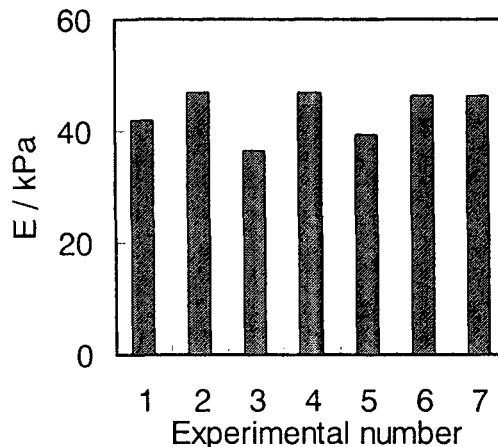


Fig. 4. The modulus of each tensile test for 1.5% gellan gum gel. The crosshead speed was 0.5mm/min.

Rupture properties

Rupture properties can be described in terms of stress concentration at some microscopic crack or heterogeneity of polymer networks. According to the literature, [1] we constructed the failure envelope, the plot of the rupture stress against the rupture strain as shown in Fig. 6, to overview their behavior of gels of different concentrations. The plots showed some large scatter, which must indicate the statistical nature of rupture, namely, a distribution of micro-flaws of different 'strength'. Although they showed scatter,

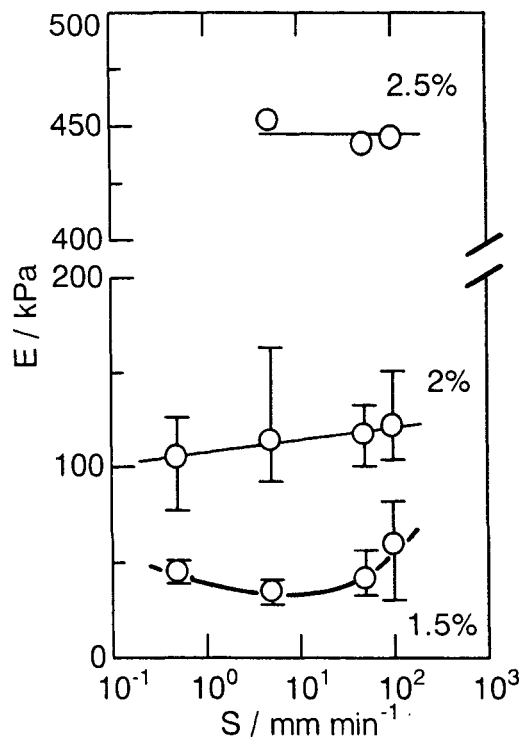


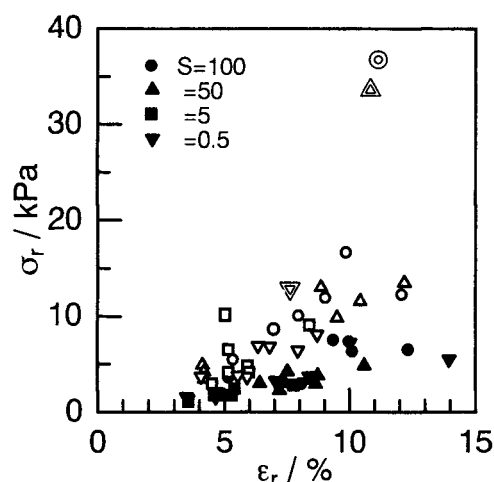
Fig. 5. Tensile modulus ( $E$ ) plotted against crosshead speed ( $S$ ) for gellan gum gels. The concentration is indicated in the figure.

the result of the plot agreed with the assumption that the failure envelope defines part of the full stress-strain curve. The rupture stress increased with the concentration. The relation between  $S$  and the rupture energy was ambiguous. Since rupture occurs with the dissipation of elastic energy stored by the stretching, the amount of energy is mainly determined by the concentration of the gel and seems to be less influenced by the crosshead speed.

We plotted rupture strain against crosshead speed. In consequence of the plot the  $\epsilon_r - S$  curve showed a minimum, falling with the decrease in  $S$  and rising again at the slowest crosshead speed. It was in  $S=5$  (corresponding to  $\dot{\epsilon} = 5 \times 10^{-4}/\text{sec}$ ) that the  $\epsilon_r$  took the minimum value for gels of all concentrations. Recently a compressive deformation tests on gellan gum gel was reported with a wide range of deformation speed, and a minimum was reported on the rupture strain - deformation speed curve[12]. The experimental result that the rupture strain shows a concave function of strain rate with a minimum at a certain value has already reported for gelatin gels[1,2]. To explain the result, McEvoy et al. assumed that the network structure of the gel consists of rigid junction zones and rather flexible chains. The gel ruptures if a critical number of cross-links are broken. The larger rupture strain at high deformation rate, was supposed to originate from the fact that the breaking of a cross-link is not a instantaneous process, but rather a process, that takes time (much like unzipping). This unzipping speed is the limiting factor determining the rupture of gel at the high deformation rates, resulting in an increase of the breaking strain with increasing deformation rate. At low deformation rates, when unzipping of the cross-links is not a limiting process, it was proposed that two processes contribute to the increase in the rupture strain with the decrease in strain rate. Firstly, unzipping of cross-links can merge two short strained network bonds into one long less extended network bond. Secondly, reformation of cross-links may make it necessary to break some connections more than once. Although the mechanism described above is speculative and by no means proven, it is probable that the crosshead speed at which  $\epsilon_r$  took a minimum ( $\dot{\epsilon} = 5 \times 10^{-4}/\text{sec}$  in our experimental condition) is characteristic to the network structure of gellan gum gels. If this speculation makes right sense, a new prediction concerning the deformation properties of gels can be derived; there will be distinct difference between chemical and physical gels. The former having very stable cross-linking domains doesn't show a minimum on the  $\epsilon_r - S$  relation, while the latter does.

#### 4. ACKNOWLEDGEMENT

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**Fig. 6.** The relation between rupture stress ( $\sigma_r$ ) and rupture strain ( $\epsilon_r$ ), failure envelope, for gellan gum gels in the tests of various crosshead speeds. Filled symbols are tests for 1.5% gels, open symbols are for 2% gels, twofold symbols are for 2.5% gels.

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