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Measurement of stress and strain during tensile testing of gellan gum gels: effect of deformation speed

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Abstract

Tensile tests were carried out on gellan gum gels of concentration 2% in order to observe the relation between deformation speed and deformation properties such as tensile modulus and rupture strain. The primary objective of this experiment is to show the validity of the measurement for the actual strain and strain rate during tensile tests. The tensile modulus decreased with decreasing deformation speed, showing the viscoelastic character of the gel, while the stress–strain curve was linear. The results were interpreted in terms of linear viscoelasticity theory. The instantaneous modulus was calculated and compared with the storage modulus found in the literature. A guide value of the relaxation time was also calculated and shown to be much larger than the observation time. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Gellan gum; Hydrogel; Tensile test; Large deformation; Deformation speed

1. Introduction

Rheological studies of model systems are usually performed at small deformations. The results are readily interpretable in terms of linear viscoelasticity theory; however, the small deformation regime is not always the most relevant condition. For example, many model studies on food structuring agents are performed in the small deformation regime, whereas the rupture properties of these materials are important (Clark & Ross-Murphy, 1987). Recent publications reported the large deformation rheology of gels with respect to deformation speed and analyses of stress–strain curves (Bot, van Amerongen, Groot, Hoekstra & Agterof, 1996a,b). The modes of deformation examined in these studies were determined in shear and compression.

From the viewpoint of materials engineering, the conventional mode of deformation is tensile, and often the test sample is in the form of a dumb-bell. Tensile testing to rupture is difficult to perform on a gel, particularly if the gel is weak. Attempts to clamp the specimen introduce irrecoverable damage. In order to circumvent this problem several methods were proposed, including the pioneering work of Ward (Cobbett & Ward, 1968), where the gel was floated on a mercury bed. Three-point bend configurations and tensile testing of ring shaped gels have also been used. (McEvoy, Ross-Murphy & Clark, 1985a,b; Wheeler & Fleming, 1988). In the present study, measurement of the stress–strain curve, including the rupture point, was attempted from the tensile test using a dumb-bell test geometry, because calculation of stress and strain was easier for this geometry.

The extracellular polysaccharide gellan gum is 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. Several studies have been performed on its solution properties and gelation phenomena (Nakamura, Tanaka & Sakurai, 1996; Ogawa, 1999). On the other hand, less has been reported on the physicochemical properties from the viewpoint of deformation and rupture of the gel. It is of interest to elucidate the relation between deformation speed and deformation properties. It is worthwhile to observe whether or not the difference in deformation mode affects the properties. This report describes the measured values of stress and strain from tensile tests on dumb-bell shaped gels. The results were interpreted using linear viscoelasticity theory.

2. Experimental

Powdered gellan in the deacetylated form was kindly supplied by San-Ei-Gen F. F. I and used without further

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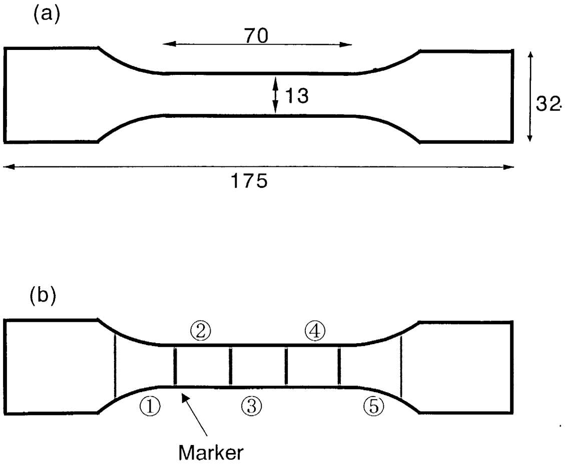

Fig. 1. (a) The geometry of the test sample. Units are mm. (b) The marker and the numbers showing the positions of the test piece.

purification. Distilled water was purchased from Nacalai. Inc. After the aqueous solution was prepared by heating at a concentration of 2%, the solution was poured into the dumb-bell mould and cooled to form the test sample. Fig. 1(a) shows the geometry of the strip, which is similar to that used by Cobbett and Ward (1968). Before the test, markers were put on the surface of the sample perpendicular to the direction of stretching as shown in Fig. 1(b) in order to observe the elongational behavior. The sample was mounted on the tensile tester (ORIENTEC, UTM-II) using a gripping tool constructed in our laboratory. Then the test started. In mounting, the sample was not clamped but put into the gripping tool to prevent any irrecoverable damage. In the course of the test, the elongation was monitored with a video camera and the load–time data were collected using a chart recorder. The test ended when the gel ruptured. The instrument was kept in a temperature-controlled room with an ambient temperature around 25°C. The value of elongation was calculated from the variation of the distance between markers measured on the video image. The stress was determined by dividing the load by the original cross sectional area because changes in the horizontal length of the sample were not detected during the test. The minimum detectable length change was 0.3 mm. The crosshead speed (*S*) varied from 0.05 to 100 mm/min.

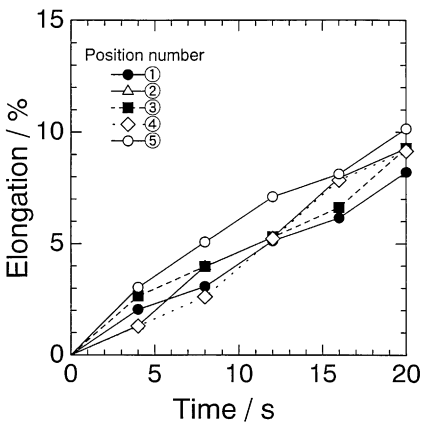

Fig. 2. Time dependence of elongation for the 2% gel. The crosshead speed is 50 mm/min.

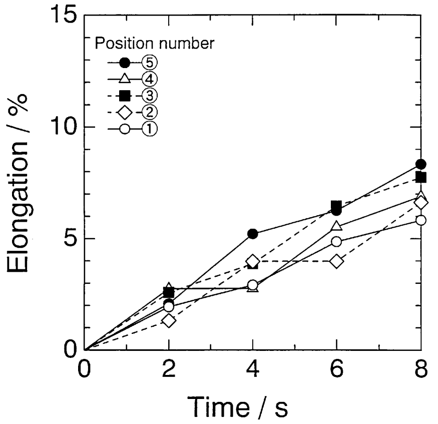

Fig. 3. Time dependence of elongation for the 2% gel. The crosshead speed is 100 mm/min.

3. Results

It is necessary to confirm the uniform deformation for every portion of the sample during the tensile test to obtain the strain data. The numbers from ① to ⑤ were used to describe the position of the sample as shown in Fig. 1(b). Figs. 2 and 3 show the time dependence of elongation for each position of the sample during the test at $S = 50$ and 100 mm/min, respectively. The values on the abscissa indicate the time (t) in seconds from the start of the test. The elongation was determined as $(L - L_0)100/L_0$, where L_0 is the distance between the markers at $t = 0$ and L the distance at a given time. The rupture occurred at $t = 20$ and 8 s in Figs. 2 and 3, respectively. The tests were repeated from four to six times and the rupture always occurred at the neck position, ① or ⑤, with rapid cracking perpendicular to the stretching direction. The time at which the rupture occurred decreased with increasing *S*. The crack appeared between two markers not in their neighborhood, and hence the markers are considered to have no influence on the elongation and the rupture. From elastic fracture mechanics the fact that the rupture occurred in the necking position is interpreted in terms of a concentration of local stress (Anderson, 1995). The elongation of the sample, however, is independent of the position from ① to ⑤ from the results shown in Figs. 2 and 3. The elongation in each position was verified to be uniform and, consequently, the elongation in ① or ⑤ at the moment of rupture is equal to that in the position from ② to ④. Since the cross sectional area can be determined easily in the position from ② to ④, the stress and strain data are measured from the variation of the load

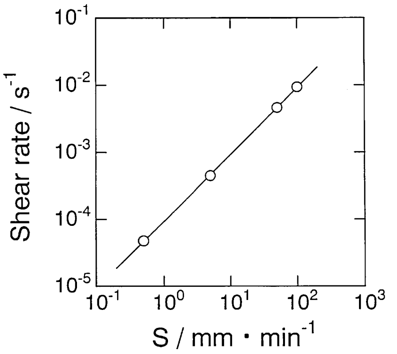

Fig. 4. The relation between strain rate and the crosshead speed (*S*).

and the distance between the markers on the outer edge of ② and ④.

In spite of the sensitivity to errors in experimental conditions, we adopted the strain rate ($\dot{\epsilon}$) as the deformation speed rather than the *S* value in the discussion, since the former is more meaningful from the theoretical point of view. It can be calculated from the plot of strain and time. The relation between strain rate and *S* was shown in Fig. 4. The strain rate range in this study is similar to that reported for previous studies on the deformation rheology of gelatin gels (Bot et al., 1996a,b; McEvoy et al., 1985a,b).

Fig. 5 shows the relation between stress and strain at a crosshead speed of 50 mm/min. The relation followed a straight line from the start to rupture in every experiment. The scattering of the measured stress value ranged within 8 kPa. Similar behavior was observed for other *S* values. The non-linear elasticity previously reported as the discernible curvature of the stress–strain curve for gelatin gel, was not observed in these experiments (Bot et al., 1996a,b). Several properties of gellan gum gel can be determined from the stress–strain curve, such as tensile modulus (*E*), rupture strain (ϵ_r), rupture stress, and rupture energy per unit volume. Results from repeated tests were averaged and *E* and ϵ_r are plotted against *S* in Fig. 6. The *E* value decreased with decreasing *S*, showing a relaxation phenomenon. The values of rupture stress ranged about 3–17 kPa, and those of rupture energy ranged from 80 to 780 J/m^3.

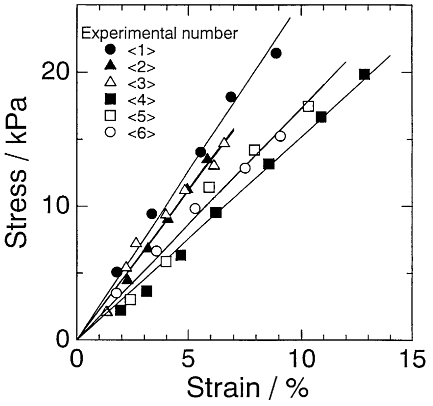

Fig. 5. The relation of stress and strain of the gum gel. The crosshead speed is 50 mm/min. The tests were repeated six times.

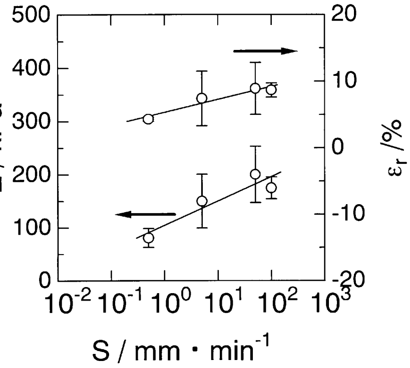

Fig. 6. Tensile modulus (*E*) and rupture strain (ϵ_r) plotted against crosshead speed (*S*).

4. Discussion

The results of the variation of *E* with deformation speed indicate visocoelastic relaxation during the tensile tests. We have previously demonstrated relaxation behavior of a Maxwell type for the dynamic viscoelasticity of gellan gum gels (Nakamura, Harada & Tanaka, 1993). The application of a Maxwell model was attempted here in order to account for the decrease in *E* with deformation speed. The instantaneous modulus, *G*, was derived, which may be related to the three-dimensional network of the gel. Throughout the following discussion, the strain on the spring element and the dashpot element in the Maxwell model, strain rate, stress, viscosity, relaxation time and the time elapsing from the start of the test will be denoted by, ϵ_1, ϵ_2, $\dot{\epsilon}$, σ, η, τ and t, respectively. Thus $\tau = \eta/G$ and $\epsilon = \epsilon_1 + \epsilon_2$. The assumption of incompressibility implies that Poisson's ratio is 0.5. Linear viscoelastic theory gives the following equation (Barnes, Hutton & Walters, 1996).

$$\frac{\mathrm{d}\epsilon}{\mathrm{d}t} = \frac{1}{G}\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \frac{\sigma}{\eta} \tag{1}$$

The time from the start of the test was divided into t_0, t_1, $t_2,\ldots,t_n$ at a common interval of Δt; that is, $\epsilon = \dot{\epsilon}\cdot n\cdot\Delta t$, n is the number that indicates the observation time. If we regard the strain at constant-rate applied to the gellan gum as the continuous application of a stepwise strain, ϵ_1 and σ at t_n can be derived from the familiar solution of Eq. (1) using the superposition principle. The expressions for ϵ_1 and σ are summarized in Table 1. ϵ_0 is the initial strain applied in the tensile test. We have the tensile modulus by taking $\Delta\sigma/\Delta\epsilon$. The reciprocal of Δt becomes the strain rate provided that $\epsilon_0 = 1$, and we obtain the following relations.

Table 1
The expression for the strain of the spring element ϵ_1 and the stress σ at each observation time, t_n

	ϵ_1	σ
t_0	ϵ_0[a]	$G\epsilon_0$
t_1	$\epsilon_0 \exp(-\Delta t/\tau)$	$G\epsilon_0(1 + \exp(-\Delta t/\tau)$
t_2	$\epsilon_0(\exp(-\Delta t/\tau) + \exp(-2\Delta t/\tau))$	$G\epsilon_0(1 + \exp(-\Delta t/\tau) + \exp(-2\Delta t/\tau))$
t_n	$\epsilon_0(\exp(-\Delta t/\tau) + \exp(-2\Delta t/\tau)\ldots + \exp(-n\Delta t/\tau))$ $= \epsilon_0\{\frac{e - \exp(-n\cdot\Delta t/\tau)}{e - 1} - 1\}$	$G\epsilon_0(1 + \exp(-\Delta t/\tau) + \exp(-2\Delta t/\tau)\ldots + \exp(-n\Delta t/\tau)) = G\cdot\epsilon_0 \frac{e - \exp(-n\cdot\Delta t/\tau)}{e - 1}$

[a] ϵ_0 is the initial strain.

$$E = G \times \exp\left(\frac{-n}{\tau \times \dot{\epsilon}}\right) \tag{2}$$

$$\epsilon_1 = \frac{1 - \exp(-n/\tau\cdot\dot{\epsilon})}{e - 1} \tag{3}$$

Eq. (2) shows that E decreases with decreasing strain rate, $\dot{\epsilon}$, which agrees with the experimental results. By taking natural logarithms in Eq. (2), we obtain the following relation,

$$\log E = \log G - \frac{n}{\tau} \times \frac{1}{\dot{\epsilon}}$$

showing that the plot of $\log E$ vs $1/\dot{\epsilon}$ will be linear and G and n/τ can be obtained from the intercept and the slope, respectively. Fig. 7 shows this plot, from which G was estimated as 180 kPa and $n/\tau = 3.9 \times 10^{-5}$. Note that n corresponds to t. The linear plot indicates that Eq. (2) is valid for tensile tests of 2% gellan gum gel under these experimental conditions. If deviation from linearity is found between $\log E$ and $1/\dot{\epsilon}$ for other experiments such as those at lower strain rates and lower concentrations, the gel's behavior will be outside the linear viscoelastic region. Work along these lines is in progress.

The fact that the stress–strain relation followed a straight line up to rupture in every tensile test indicates that the relaxation time is much longer than the observation time; namely $n \ll \tau$, which is consistent with the above estimated value of n/τ. The observation time was around $t =$ 10–1000 s in this study when S varied from 0.5 to 100 mm/min. Therefore the τ value cannot be lower than $\sim 10^6$ s. If the tensile test is carried out on gels of lower concentration, the τ value will decrease and relaxation will be observed.

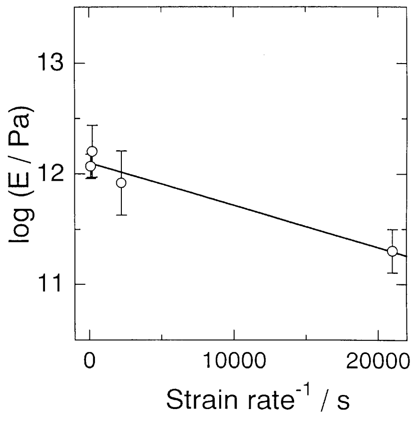

Fig. 7. The relation between the natural logarithmic moduli and the inverse of the strain rate.

Measurement of dynamic viscoelasticity at 2.5 Hz for the same gellan sample has been reported, showing storage Young's modulus of 70 kPa for 2% gels at 25°C (Watase & Nishinari, 1993). The instantaneous modulus corresponds to the dynamic modulus at the highest frequency, and hence the measured value of $G = 180$ kPa is considered to be higher than that seen in literature.

Eq. (3) shows that the strain of the spring element at a given time during the tensile test decreases with strain rate. The increase in ϵ_r with S can be explained provided that the rupture occurs when ϵ_1 reaches a certain value. Recently compressive deformation tests on gellan gum gels were reported with a wide range of deformation speeds (Nakamura, Tago & Sakurai, 1999). The rupture strain–deformation speed curve was reported to go through a shallow minimum, falling with decreasing speed and rising again at the slowest speed. If the same behavior can be observed in further experiments of our own, it can be expected to make a quantitative contribution for the non-linear dependence of rupture strain on deformation speed because the value of strain rate can be determined in our experiments.

References

Anderson, T. L. (1995). *Fracture mechanics, fundamentals and applications*, . (2nd edn.)Boca Raton: CRC Press (p. 40).

Barnes, H. A., Hutton, J. F., & Walters, K. (1996). *An introduction to rheology*, Amsterdam: Elsevier (p. 40).

Bot, A., van Amerongen, I. A., Groot, R. D., Hoekstra, N. L., & Agterof, W. G. M. (1996a). Large deformation rheology of gelatin gels. *Polymer Gels and Networks*, *4*, 189–227.

Bot, A., van Amerongen, I. A., Groot, R. D., Hoekstra, N. L., & Agterof, W.

G. M. (1996b). Effect of deformation rate on the stress–strain curves of gelatin gels. *J. Chim. Phys.*, *93*, 837–849.

Clark, A. H., & Ross-Murphy, S. B. (1987). Biopolymer. *Advances in Polymer Science*, *83*, 57.

Cobbett, N. W., & Ward, A. G. (1968). A simple extension apparatus for dilute gelatin gels. *Rheol. Acta.*, *7* (3), 217–222.

McEvoy, H., Ross-Murphy, S. B., & Clark, A. H. (1985a). Large deformation and ultimate properties of biopolymer gels: 1. Single biopolymer component systems. *Polymer*, *26*, 1483–1492.

McEvoy, H., Ross-Murphy, S. B., & Clark, A. H. (1985b). Large deformation and ultimate properties of biopolymer gels: 2.Mixed gel systems. *Polymer*, *26*, 1493–1500.

Nakamura, K., Harada, K., & Tanaka, Y. (1993). Viscoelastic properties of aqueous gellan solutions: the effects of concentration on gelation. *Food Hydrocolloids*, *7* (5), 435–447.

Nakamura, K., Tago, M., & Sakurai, M. (1999). The compression velocity dependence of the strength for gellan gum. *Polymer Preprints, Japan*, *48* (3), 594.

Nakamura, K., Tanaka, Y., & Sakurai, M. (1996). Dynamic mechanical properties of aqueous gellan solutions in the sol–gel transition region. *Carbohydrate Polymers*, *30*, 101–108.

Ogawa, E. (1999). Temperature dependence of the conformational properties of sodium-type gellan gum in aqueous solutions. *Progress in Colloids and Polymer Science*, *114*, 8–14.

Watase, M., & Nishinari, K. (1993). Effect of potassium ions on the rheological and thermal properties of gellan gum gels. *Food Hydrocolloids*, *7* (5), 449–456.

Wheeler, G. E., & Fleming, S. A. (1988). Modulus of rupture for room temperature gels derived from methyltrimethoxsilane. *Engineering Geology Ancient Works, Monuments and Historical Sites*, 2083–2085.