Mechanical Properties of Concentrated Hydrogels of Agar-agar.
II. Creep under Constant Load in Compression

By Hiroshi FUJITA, Kazuhiko NINOMIYA and Terutaka HOMMA

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Introduction

Although there exists some information on the elastic properties of hydrogels of agar-agar, papers dealing with their viscoelastic behavior are still very meager in the literature in colloid chemistry or in rheology. Considering that agar-agar is a prototype of gel-forming natural substances but also a kind of polyelectrolytes, however, the investigation of the viscoelastic behavior of its gels seems to be an interesting problem. As is well known, creep under constant load is one of the most commonly observed and measured of the phenomena pertaining to viscoelastic behavior of materials. For these reasons, an investigation of the creep under compressive load was carried out for concentrated agar-agar gels in various environmental conditions and is reported in this paper.

Experimental

All agar-agar samples used in this work were taken from the same stock of a grade of powdered agar-agar as that which was prepared in a previous investigation⁽¹⁾ of this series. The process of making the test piece which was shaped cylindrically and whose dimensions were about 3 cm. both in height and in diameter was identical with that employed in I. All tests were commenced after the 90 min. chilling of the sol; this value is also the same as that adopted in I. The apparatus which was constructed in I for the measurement of the compression stress-strain curves was usable as an autographic machine for measuring creep under constant compressive load by making a slight modification as follows. This modification was simply attained by fixing the movable end of the chains (see Figure 1 in I) at a desired height. Then a constant compressive load could be applied on a given test piece over any desired operating interval of time, and thus our apparatus proved to be usable as an autographic creepmeter.⁽²⁾ The apparatus was equipped in an air thermostat which was regulated to about ±0.25°C. Humidity in the thermostat was maintained at an almost saturated state, and in addition, liquid paraffin was amply applied on the whole surface of the specimen. In this way, evaporation of the solvent from the gel was almost completely checked during the course of a creep test. The interval of time of measurement in each creep run was exclusively limited to 100 min.

There are probably a considerable number of factors which may have influence upon creep behavior in a gel-system. But, in this work, only the effects of temperature, concentration and load were considered. In order to study the effects of these factors, experimental measurements were carried out according to the following plan.

First, the effect of applied load was studied at a temperature 23°C. and a concentration 4 g./100 cc. by varying stress from 0 to 5×10^4 dyn./cm^2., where the stress was defined as applied load per unit original unstrained cross section of each test piece. Because the stress thus defined was not kept constant but continuously decreased with increasing deformation resulting from creep, our creep tests were not true creep tests. However, considering that the resultant maximum strains within the interval of time of measurement herein adopted were as small as less than, at most, 10 percent, it might be assumed that, to a first approximation, our creep tests were enough to elucidate the true creep behavior of the material in question.

The effect of temperature was studied at a concentration 4 g./100 cc. in the temperature range from 5° to 40°C., at each temperature the stress being varied from 0 to 4×10^4 dyn./cm^2.

The effect of concentration was studied at a temperature 23°C. in the concentration range from 2 g. to 4 g./100 cc., at each concentration the stress being varied in the same range as in the above.

Results and Discussion

General Remarks.—The general trend of the creep curves obtained is illustrated in Figure 1, where the experimental conditions are indicated in the legend. This shape of creep curve is one of the most commonly observed in many materials.⁽³⁾ It was found

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(1) H. Fujita, K. Ninomiya and T. Homma, This Bulletin, **25**, 374 (1952).

(2) Details of the present apparatus will be described in a separate paper by K. Ninomiya.

(3) W. J. Lyons, *J. Appl. Phys.*, **17**, 472 (1946); in particular, pp. 472-474.

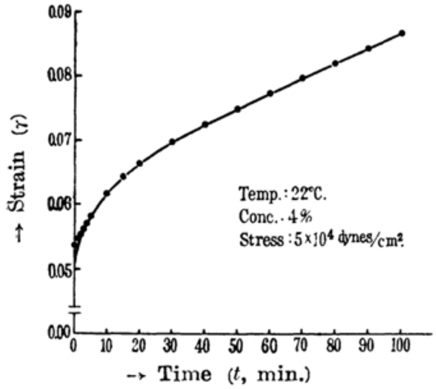

Fig. 1.—A fitting of Eq. (1) to an experimental creep curve; ● represents a calculated value, and — the observed curve.

that this shape of curve was well fitted by a well-known creep equation of the form:

$$\gamma(t)=\gamma(0)+A(1-e^{-t/\tau})+\lambda t, \qquad (1)$$

where $\gamma(t)$ is the strain at time t, $\gamma(0)$ is the initial strain, λ is the constant creep rate in the viscous flow region, A is the final, maximum strain due to retarded elasticity of the material (retarded elastic strain was defined as transient creep minus viscous flow), and τ is the retardation time. Dependencies of $\gamma(0)$ on various environmental factors such as temperature, concentration, stress, and gelation time were studied in a previous paper I. Consequently, our present investigation concerning creep behavior of concentrated agar-agar gels was reduced to determining parameters λ, A and τ as functions of such environmental factors as mentioned above.

An example showing the conformity of Eq. (1) with an observed curve is given also in Figure 1, where the circles indicate the calculated values from Eq. (1). Such a degree of agreement between Eq. (1) and the observed curve as seen here was found to hold for all data obtained in the present work.

As is seen in Figure 1, or will be seen in Figure 2, relative length of the transient creep region is generally so much shorter than that of the viscous flow region that it may be considered that the general trend of the creep behavior in concentrated agar-agar gels herein concerned is primarily determined by the behavior of the constant rate term λt in Eq. (1). For this reason, in what follows, we shall be interested mainly in examining the effects of environmental factors on the value of λ.

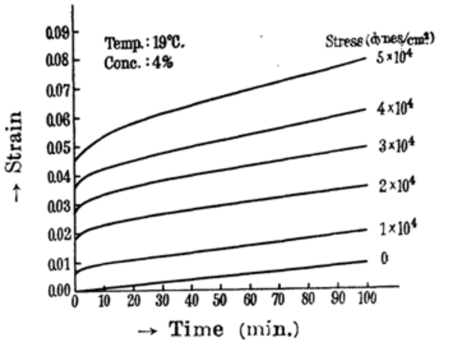

Fig. 2.—Effect of stress upon the shape of creep curve.

Effect of Stress.—Figure 2 shows how creep curves for a concentrated agar-agar gel differ for different stress magnitudes. We can see from this figure a number of interesting things. Of special interest is a clear evidence showing that even at zero stress state there occurred definitely a creep process which was closely linear over the range of observation time indicated. Such an apparent creep at zero stress state was always observed in this work irrespective of temperature and concentration. This fact seems to indicate that all test specimens employed were not at true thermodynamic equilibria within the interval of the present observations, though thermal equilibrium had previously been established before the beginning of the observations. In connection with this phenomenon, we must describe a characteristic fact observed simultaneously during the course of this apparent creep. This was a continuous, though small in amount, expulsion of the solvent from the test piece. It took place at a very slow rate as the specimen was deformed. It was observed clearly even in the absence of any external force. The solvent expulsion in the case of non-external force necessarily resulted in spontaneous and isotropic contraction of the specimen gel; this is nothing but the phenomenon usually called syneresis. The spontaneous contraction of a gel block should look to an observer as if creep (compressive) is occurring in it. Thus, the apparent creep observed in the present work at zero stress state is interpreted as arising from the volume contraction due to syneresis. Ferry(4) has stated that the progressive closer binding, or coming-together, of the network strands in a gel results in syneresis of the gel. It is, however, beyond the present authors' scope to discuss in what way this Ferry's idea can be formulated as a quantitative theory for describing the contractility of gel-systems.

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(4) J. D. Ferry, "Advances in Protein Chemistry," IV, Academic Press Inc., Publishers, New York, 1948, pp. 1-78; in particular, Chapt. III.

Now, we shall proceed to examine the effect of stress quantitatively. From Figure 2 and other similar data obtained, λ is plotted against stress S as shown in Figure 3, from which the plotted curves are seen to be well fitted by an equation of the form:

$$\lambda=\lambda_0+\frac{S}{\eta}, \qquad (2)$$

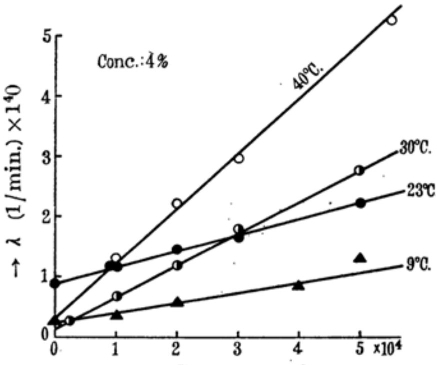

Fig. 3.—Effect of temperature upon the viscous flow behavior.

where λ_0 is the creep rate observed at zero stress condition, that is, the rate of the apparent creep discussed above, and η is a parameter having the dimension of viscosity. The linearity between λ and S as seen here implies that the viscous flow of the material exhibits a so-called Newtonian behavior⁽⁵⁾ so far as the environmental conditions indicated are concerned.

Effect of Temperature.—Figure 3 also shows how the λ_0 value and the viscosity η are affected by temperature θ. We see that (1) the value of λ_0 is changed with temperature just as it reaches a maximum near about 20°C.; and (2) the value of η is decreased with increasing temperature, as should be expected. To make it clear, the logarithm of η is plotted against the reciprocal of the absolute temperature $T(=273+\theta)$ as shown in Figure 4. It is seen that the temperature dependency of the viscosity does not follow the well-known Andrade equation with a constant activation energy. However, by replacing the experimental curve by a straight line as indicated in the figure, the corresponding apparent activation energy U is estimated approximately at

$$U \doteqdot 12 \text{ kcal./mol.}$$

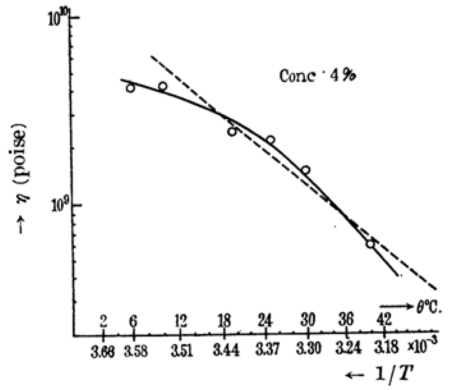

Fig. 4.—Temperature dependency of viscosity η.

This value of the energy of activation for viscous flow may suggest that the strength of flow units involved in concentrated agar-agar gels is of a secondary nature as should be expected from the current view of the molecular structure of polymer gels. The deviation of the experimental curve from the Andrade relation may partly be ascribed to the change in the effective number of cross-linkages in the gel network with change in temperature.

Effect of Concentration.—The effect of concentration on λ vs. S plot is shown in Figure 5, where all data presented were obtained at a constant temperature 23°C. We see that (1) the concentration effect on λ_0 is not appreciable, though detailed information on it is not ensured due to the paucity and inaccuracy of the data; and (2) the concentration dependency of η is, on the contrary, rather remarkable, and, so far as the plotted data are concerned, it is represented approximately by

$$\eta=kC^3,$$

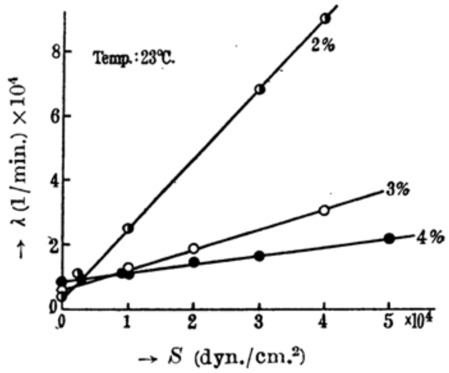

Fig. 5.—Effect of concentration upon the viscous flow behavior.

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(5) H. Leadermen, *J. Colloid Sci.*, **4**, 193 (1949).

where C is the concentration of agar-agar in the gel and k is a proportionality constant.

Remarks on the Behavior in the Transient Creep Region. — Finally, short discussions will be made for the behavior of the transient creep region. As is understood from Eq. (1), this behavior can be characterised by two parameters τ and A. Figure 6 shows the effect of stress on the retardation time τ at several temperatures and a constant concentration 4 g./100 cc. Because of the marked scattering of the experimental points it is difficult to draw the definite conclusions on both the stress and temperature effect on the retardation time. We must restrict ourselves to pointing out that the value of τ appears to be little influenced by either stress or temperature. In Figure 7, instead of A, the modulus of retarded elasticity E' defined by S/A is plotted against concentration C.

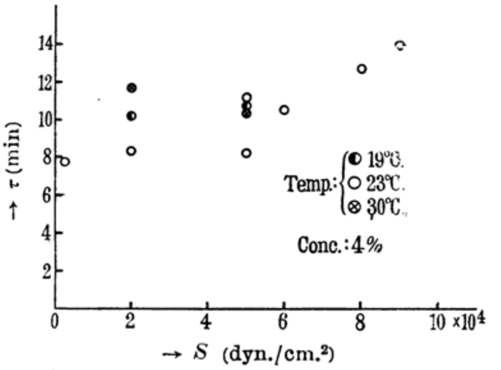

Fig. 6.—Effect of stress upon retardation time τ.

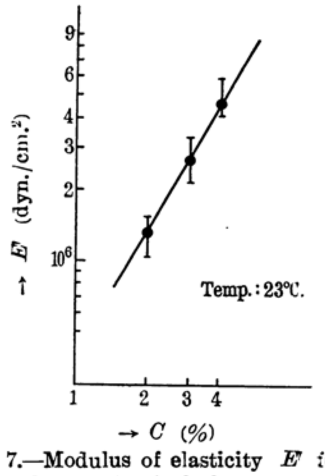

Fig. 7.—Modulus of elasticity E' for the retarded mechanical element.

Summary

In this report, we have presented the results of an experimental investigation carried out of the creep under constant compressive load for concentrated hydrogels of agar-agar.

The apparatus which was designed in a previous paper I of this series for the measurement of the compression stress-strain curve was modified to suit the measurement of the creep under constant compressive load. The shape of the creep curves obtained was found to be well fitted by Eq. (1). The influences of temperature, concentration and applied stress on the creep rate in the viscous flow region were investigated separately. One of the interesting facts found was a clear evidence showing that even at zero stress condition there occurred a definite creep process which was closely followed by a straight line within the interval of time of observation employed. It seemed likely that this phenomenon should be associated primarily with the molecular structural feature of the agar-agar gel network which leads the gel to syneresis.

It was found for all the data obtained that the relation between λ and S followed Eq. (2) within the limits of experimental error, where λ is the creep rate in the viscous flow region and S is the magnitude of stress applied. This equation involves two parameters λ_0 and η, where λ_0 stands for the value of λ in the absence of external stress, and η is the Newtonian viscosity corresponding to the region in which a linear viscous flow appears. The influences of various environmental parameters on these two quantities were investigated, obtaining the results as shown in Figures 3, 4 and 5.

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Applied Physics Laboratory, Department of
Fisheries, Faculty of Agriculture,
Kyoto University, Maizuru