Mechanical Properties of Concentrated Hydrogels of Agar-agar.
I. Modulus of Elasticity in Compression

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Introduction

The variation in mechanical properties of gels of high-polymeric substances is perhaps one of the most interesting problems of research in the field of rheology. Recent advances in rheology have resulted in the development of theories which permit interpretation of various mechanical properties of high polymers in terms of molecular quantities. However, papers dealing with the mechanical properties of polymer gels from the rheological point of view are still few in the literature. Remarkable progress has recently been made by Ferry(1) and his coworkers for the mechanical behavior in a variety of protein gels such as gelatin and fibrinogen gels. The experimental data accumulated in their studies have since been almost all concerned with the elasticity of the materials investigated, and few data have yet been obtained for the viscoelastic behavior of the materials.

Various aspects of physico-chemical properties of agar-agar gels have been reported, but there is little information available on their mechanical properties. For this reason, Nakagawa et al.(2~5) have set up a series of experimental studies on the rheological properties of hydrogels of agar-agar, and have published several interesting papers which are chiefly concerned with the elastic behavior at very low concentrations. In order to complete our understanding of the mechanical behavior of hydrogels of agar-agar, it is also of considerable interest to extend their research to a region of higher concentrations than they treated.

In this paper, the results of a study of the elastic behavior in compression of agar-agar hydrogels at concentrations between 2g./100 cc. and 4 g./100 cc. are reported.

Material and Apparatus

The material used was a grade of powdered agar-agar, from which the test pieces of agar-agar hydrogels were made according to the procedure which will be described below. No fractionation of the sample was made. It is well realized that the physico-chemical properties of any gel-system are appreciably influenced by the

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(1) See, for example, J. D. Ferry, "Advances in Protein Chemistry," IV, Academic Press Inc., Publishers, New York, 1948, p. 1-78.

(2) T. Nakagawa, *Kagaku*, **20**, 130 (1950).

(3) T. Nakagawa, *J. Chem. Soc. Japan*, **72**, 390 (1951).

(4) T. Nakagawa and T. Danno, *J. Chem. Soc. Japan*, **72**, 518 (1951).

(5) T. Danno, *J. Chem. Soc. Japan*, **72**, 1061 (1951).

conditions under which the gel to be studied was formed. Accordingly, in order to produce experimental data which will ultimately be suited for quantitative discussions, it is necessary to take a consistent process in the course of preparing the sample gels. In this investigation the following procedure was employed consistently.

A mixture of the agar-agar powder and distilled water which was prepared to a desired concentration was boiled for 30 min. to make it sol. The sol was transferred into a glass cylinder, whose height and inner diameter were both about 3 cm., and chilled for 1 hr. in rest air kept at 25°C. to make it hard. Picking out the gel thus formed from the cylinder, a rod-shaped test specimen was obtained; over the concentration range as was treated in this work (2 g./100 cc.∼4 g./100 cc.), all the specimens were rigid enough to support their own weight, or to be amenable to measurements by means of an apparatus which will be described below. The specimen was then quickly inserted in the apparatus and stood there for 30 min. The apparatus was installed in an air thermostat which had been previously controlled to a desired temperature. Some preliminary observations indicated that the test piece, as a whole, reached a temperature almost equal to that in the thermostat when it was placed there for about 30 min. In the case of as low temperature as 5° to 10°C., a somewhat longer time was required before arriving at the thermal equilibrium. For these reasons, except in the case of investigating the effect of gelation time, all the measurements were taken after 30 min. from the introduction of the specimen into the apparatus.

The apparatus used in this experiment was a modified form of the chainomatic balance used by Dart and Guth⁽⁶⁾ for the study of the mechanical properties of natural cork. A schematic diagram of the apparatus is shown in Figure 1. Differing from Dart and Guth's original apparatus where desired compression stress-strain curves had to be determined manually, the present apparatus was designed so that a continuous smooth locus corresponding to a compression stress-strain curve could be recorded automatically on a chart paper mounted on the rotating cylinder. Because of the limit of space, accounts of the mechanical principle of the apparatus as well as the method of measurement must be omitted here; detailed descriptions of them will be made in a separate paper.⁽⁷⁾

Temperatures inside the thermostat (from about 5° to 60°C.) were controlled to about ± 0.25°C. over the entire operating range in a particular run. Humidity was maintained at an almost saturated state to prevent drying of the specimen gel as much as possible.

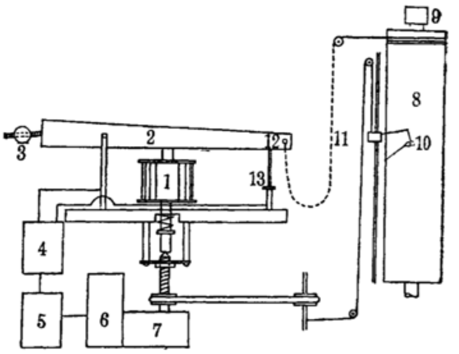

Fig. 1.—Experimental apparatus; 1: sample. 2: balance arm. 3: balast. 4: relay. 5: battery. 6: motor. 7: gear box. 8: chart cylinder. 9: driving clock. 10: pen. 11: chains. 12: hanger. 13: contact point.

The bundle of chains in the apparatus was lowered at a constant rate of falling with rotation of the chart cylinder at a constant speed. Accordingly, all the stress-strain curves obtained in this experiment should be accepted as the stress-strain curve for a constant rate of loading, or approximately, for a constant rate of increase in stress. The rate used herein was about 1000 dynes/cm.²/sec. In converting the locus recorded on the chart cylinder to the corresponding stress-strain curve it was necessary to know the value of Poisson's ratio for the sample. In this study, it was simply presumed to be 0.5 without making any experimental determination for it.

Results and Discussion

Typical compression stress-strain curves obtained at various conditions are shown in Figures 2 and 3, where γ denotes the strain and S the stress. All the stress-strain curves obtained invariably have a general tendency similar to that found in the curves in the

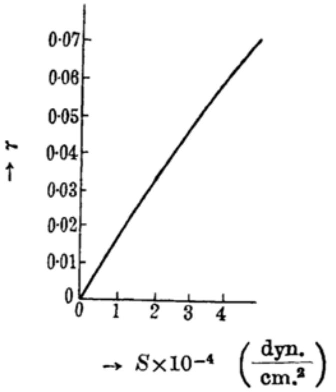

Fig. 2.—Stress-strain curve for a sample of 3 g./100 cc. conc. at 25°C. after 90 min. chilling.

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(6) S. L. Dart and E. Guth, *J. Appl. Phys.*, **17**, 314 (1946); ibid., **18**, 476 (1947). See, also, R. S. Witte and R. L. Anthony, *J. Appl. Phys.*, **22**, 689 (1951).

(7) K. Ninomiya, *J. Chem. Soc. Japan*, in preparation.

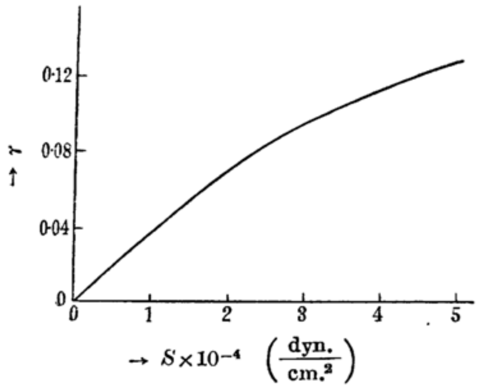

Fig. 3.—Stress-strain curve for a sample of 2 g./100 cc. at 23°C. after 90 min. chilling.

figures; for moderately small values of stress the strain increases linearly with the stress, while at higher stresses the plot is gradually curved toward the stress-axis, thus revealing a certain non-linearity. Relative length of the portion where Hooke's law holds very closely was found to be largely affected by experimental conditions. Some hysteresis loop was observed in the stress-strain curve when a cyclic process of loading was applied to the specimen. Since, however, it was almost negligible within the limits of deformations tested, it was presumed that all test pieces used in this work would be purely elastic for at least sufficiently small strains. The modulus of elasticity (Young's), E, was evaluated using the slope of the linear part in the stress-strain curve, and it was found that, in the range of test conditions herein adopted, the value of E fell in a range of about 10^5 dynes/cm.$^2\sim10^6$ dynes/cm.^{2}; for example, E for an agar-agar hydrogel of concentration 4 g./100cc. was about 10^6 dynes/cm.^{2} at temperature 25°C. This value is, in effect, almost comparable to the value of E for a gelatin hydrogel of concentration 18.6 g./100 cc.$^{(8)}$ Generally speaking, it may be concluded that an agar-agar hydrogel is considerably more rigid than a gelatin gel.

There have been various opinions regarding the origin of the elasticity of a hydrogel of agar-agar, but no definite conclusion has yet been attained. Recently, Hirai$^{(9)}$ has attempted to interpret the elastic behavior of an agar-agar gel in terms of the kinetic theory of rubber-like elasticity, by taking partly into account the energy contribution due to interactions between the chain molecules of agar-agar. Although he has reached a result which is apparently in accordance with the experimental results on the relation between the modulus of elasticity and the temperature, there seem to be some ambiguous points in his development concerning the consideration of the energy contribution.

Dependence of the Modulus of Elasticity upon Concentration.—This is a primarily interesting problem in the study of mechanical properties of a gel-system. Experiments were performed at 25°C. by varying the concentration from 2 g./100 cc. to 4 g./100 cc. The results obtained are plotted in Figure 4, where C is the concentration in percentages. From this figure the data prove to fit the following simple relation:

$$E=k\cdot C^{1.7}, \qquad (1)$$

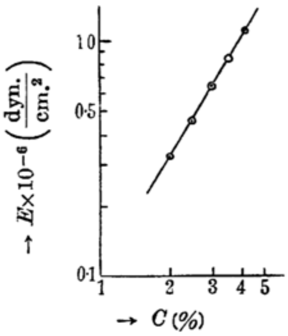

Fig. 4.—Concentration dependence of the modulus of elasticity, E, at 25°C. after 90 mim. chilling.

where k is a proportionality constant. With hydrogels of gelatin, it was frequently reported by many workers$^{(10\sim12)}$ that the relation:

$$E=k\cdot C^2 \qquad (2)$$

well described the data, though in some cases the exponent in Eq. (2) had to be taken as slightly less than 2. With fibrin clots (gel of fibrinogen containing small amount of thrombin), Ferry and Morrison$^{(13)}$ provided the relation:

$$E=k\cdot C^{1.57}. \qquad (3)$$

Ferry$^{(11)}$ also showed for hydrogels of gelatin that the exponent 2 in Eq. (2) was hardly affected by change in temperature.

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(8) R. Houwink, "Elasticity, Plasticity and Structure of Matter" Cambridge University Press, London, 1937, p. 275.

(9) N. Hirai, *J. Chem. Soc. Japan*, **73**, 65 (1952).

(10) S. E. Sheppard and S. S. Sweet, *J. Am. Chem. Soc.*, **43**, 539 (1921).

(11) J. D. Ferry, *J. Am. Chem. Soc.*, **70**, 2244 (1948); See, also, reference (1).

(12) N. Hirai, *J. Chem. Soc. Japan*, **72**, 837 (1951).

(13) J. D. Ferry and P. R. Morrison, *J. Am. Chem. Soc.*, **69**, 388 (1947); See, also, reference (1).

Dependence of the Modulus of Elasticity upon Temperature.—Keeping the agar-agar concentration at 4 g./100 cc., measurements were made at several temperatures between 5° and 63°C., and the plot indicated in Figure 5 was obtained, where θ is the temperature in centigrades. This plot is seen to have a similar appearance to that obtained by Ferry et al.$^{(14)(11)}$ for gelatin hydrogels and, also, to that by Nakagawa et al.$^{(4)(5)}$ for agar-agar hydrogels of very low concentrations. At higher temperatures than about 60°C. the test pieces used became less rigid even at a concentration as high as 4 g./100 cc. The apparatus used in this work, however, was safely applicable only to the specimen rigid enough. Accordingly, the data given above would necessarily be somewhat incorrect in such an elevated temperature region. Hysteresis of the modulus in a cyclic temperature change was not studied in this work.

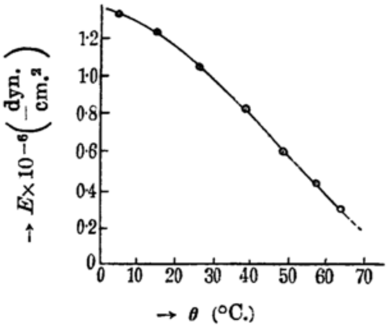

Fig. 5.—Temperature dependence of the modulus of elasticity, E, at 4 g./100 cc. after 90 min. chilling.

Effect of Gelation Time upon the Modulus of Elasticity.—For hydrogels of gelatin and fibrin clots, the effect of gelation time upon their rigidity was investigated in detail by Ferry et al.,$^{(11)(13)(1)}$ but for agar-agar gels there is no information on this problem. In view of this, the following experiment was conducted.

A number of glass cylinders filled with a hydrosol of agar-agar of known concentration were inserted simultaneously in the thermostat kept at 25°C. and allowed to stand there for an appropriate time (from 40 to 60 min.) to make the sol hard. The specimen gels were then successively subjected to measurements one by one at a suitable interval of time. The measurement was extended over an interval of about 170 min. for each concentration. Thus, the results plotted in Figure 6 were obtained, where t_g is the gelation time in minutes, being defined as the time which has elapsed after the cylinders were introduced in the cooling chamber. It is seen that within the first several ten minutes there was a fairly rapid increase of the modulus of elasticity but this increase was followed by a very gradual approach to a constant value. The higher the concentration, the more rapid the initial development of E resulted. It is worthy of notice here that the plotted curves indicate that the 90 min. chilling procedure as used in all other measurements than those described in this section was almost enough to assure the steady state values of E. Similar plots as shown in Figure 6 were already obtained by Ferry et al.$^{(11)(13)}$ for both gelatin hydrogels and fibrin clots; for gelatin hydrogels the plot did not approach a final state even after more than 10 hr. had elapsed for all the cases investigated, while for fibrin clots it required only about 1 hr. before attaining a steady state. The latter result may be compared with our result for hydrogels of agar-agar.

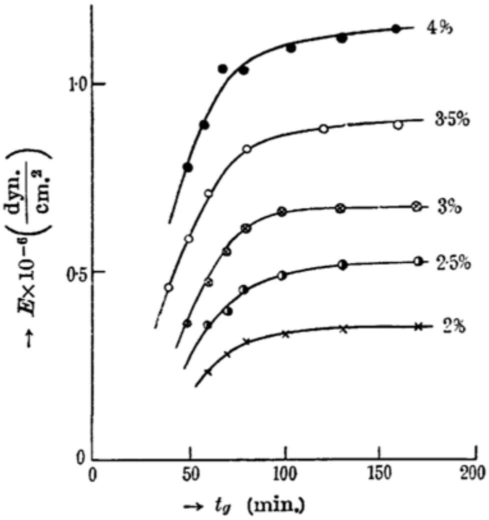

Fig. 6.—Effect of gelation time, t_g, on the modulus of elasticity, E, at various concentrations.

Summary

As the first step in a series of works on the mechanical behavior of a concentrated hydrogel of agar-agar, the experimental determination of its elastic behavior in compression was made. An apparatus which could record a compression stress-strain curve automatically

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(14) J. D. Ferry and J. E. Eldridge, *J. Phys. & Colloid Chem.*, **53**, 184 (1949).

was devised and used to obtain the results reported in this paper. Influences of temperature, concentration, and gelation time upon the modulus of elasticity (Young's) were considered and plotted in Figures 4, 5 and 6.

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