Stress Relaxation of Thermo-Reversible Gels. Polyvinyl Alcohol—Congo Red—Water System

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In the previous paper the author reported the result of the stress relaxation experiment made on the gel of the polyvinyl alcohol-glycerin-water system[1]. As another example of thermo-reversible gels of polymeric nature, the gel of the polyvinyl alcohol-congo red-water system is known, and several studies on the properties of the gel have been reported[2].

As a part of the series of rheological studies of thermo-reversible gels[1,3] a stress relaxation experiment has been attempted on the gel, and the result is reported in the present paper.

Experimental

Apparatus. — The apparatus to measure the relaxing stress produced in the specimen under a given strain is the same one as that used previously[1,3]. The chainomatic balance part of the apparatus is shown in Fig. 1. A specimen is compressed between a plate attached to a bar and a bottom plate connected to a screw gauge by the rotation of the gauge, which is graduated to 0.01 mm. The stress in the specimen is calculated from the vertical length of the suspended chain which is balancing automatically with the stress. The specimen is dipped in liquid paraffin, as was done in the preceding studies[1,3].

Sample. — A commercial sample of polyvinyl alcohol was purified by precipitation from aqueous solution. The amount of residual acetate groups in the sample was 1.5% by mole. The intrinsic viscosity $[\eta]_{30}$ was 0.96 100 cc./g., which was determined by a capillary viscometer. The viscosity-average molecular weight M_V was calculated to be 8.5×10^4 according to the formula by

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[1] K. Arakawa, This Bulletin, **31**, 842 (1958).

[2] C. Dittmar and W. J. Priest, *J. Polymer Sci.*, **18**, 275 (1955); N. Hirai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 693 (1954); T. Danno, The 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1957.

[3] K. Arakawa, *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zasshi*), **80**, 133 (1959).

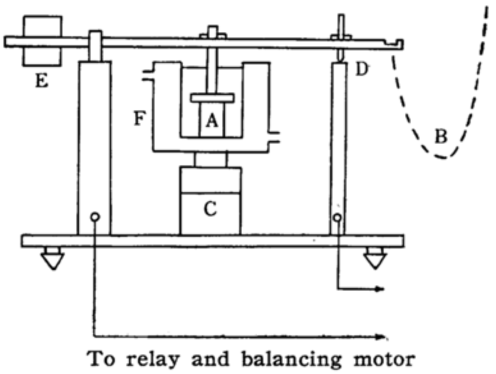

Fig. 1. Chainomatic balance relaxometer
A: specimen
B: chain
C: screw gauge
D: point contact
E: balancing weight
F: double jacket

A. Nakajima et al.[4] Congo red used was Merck's analytical grade chemical.

The preparation of specimens was as follows. A definite quantity of dried polyvinyl alcohol was mixed with dried congo red powder, the amount of which was adjusted to be accurately 1/10 of polyvinyl alcohol by weight (this weight ratio of congo red and polyvinyl alcohol was taken to be the same for all specimens used in the present study), and a calculated quantity of water was added to the mixture in a conical beaker. After being covered with liquid paraffin, the mixture was dissolved slowly by heating in a water bath. After complete dissolution the solution was poured into cylindrical moulds kept at about 85°C in a thermostat and was cooled down slowly to 50°C (the rate of temperature decrease: 5°C per hour), and then was aged at room temperature. After several days the specimens (diameter, 2 cm.; height, about 3 cm.) were taken out from the moulds, and were aged moreover at room temperature in liquid paraffin for about a month. The composition of the prepared specimens is described in Table I.

TABLE I. THE COMPOSITION OF GELS

Sample	Polyvinyl alcohol wt. %	Congo red wt. %
A	17.5	1.75
B	15.0	1.50

Samples A and B have typical rubber-like elasticity at ordinary temperature and make the sol-gel transition reversibly at about 80°C.

Results and Discussion

Stress Relaxation Data.—The data of stress relaxation of samples A and B are plotted in the form $(298/T)E_r$ vs. $\log t$, where $E_r=f/\gamma$ is relaxation Young's modulus; t time, and f stress, in Figs. 2a and 2b. The strain γ applied in the present experiment was 15% for all specimens. This value was in the range where the linear relation between stress and strain was almost maintained. These data are reduced to 25°C by multiplying E_r by a factor $298/T$.

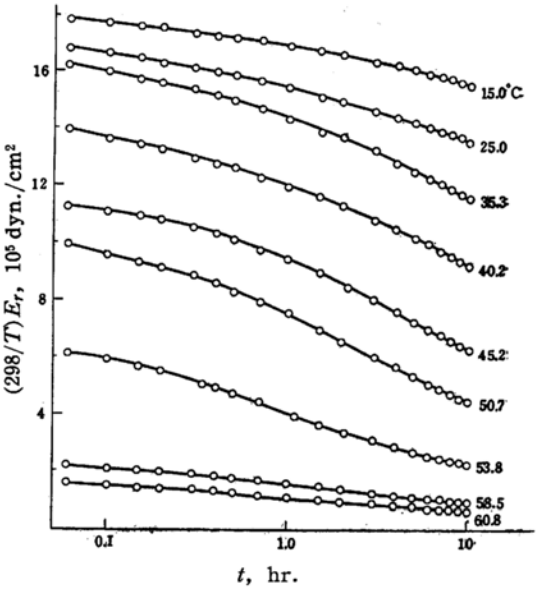

Fig. 2a. Reduced relaxation Young's modulus of 17.5% gel.

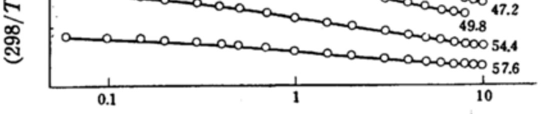

Fig. 2b. Reduced relaxation Young's modulus of 15% gel.

The master relaxation curve[5] at 25°C for each sample is obtained by means of arbitrary shift factors a_T. The curves,

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[4] A. Nakajima and K. Furutate, *Chem. High Polymers* (*Kobunshi Kagaku*), **6**, 460 (1949).

[5] J. D. Ferry, *J. Am. Chem. Soc.*, **72**, 3746 (1950); F. Schwarzl and A. J. Stavermann, *J. Appl. Phys.*, **23**, 838 (1952); C. A. Dahlquist and M. R. Hatfield, *J. Colloid Sci.*, **7**, 253 (1952).

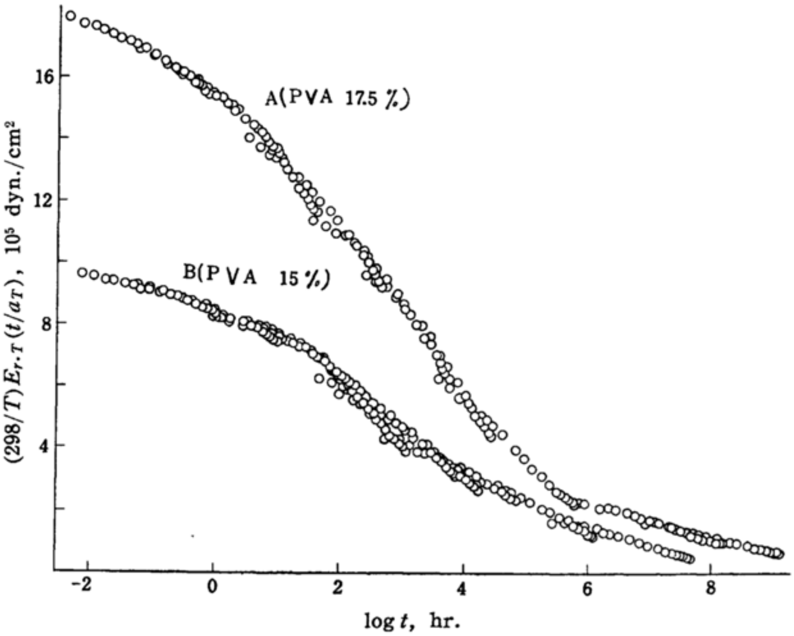

Fig. 3. Master relaxation curves at 25°C.

thus obtained, are plotted in Fig. 3. The superposition of each relaxation curve is seen to be fairly good.

Shift factors $\log a_T$ are plotted against $1/T$ in Fig. 4. It seems the $\log a_T$ vs. $1/T$ curve is approximately linear in the low temperature region, and that the deviation from linearity occurs at about 43°C. The apparent activation energy H_a which is calculated from the $\log a_T$ vs. $1/T$ curve is a constant value, 42 kcal., below 43°C. This value of H_a is smaller than that of the gel of polyvinyl alcohol, glycerin, and water system. The value of H_a increases with temperature above 43°C. This tendency differs from that observed in the polyvinyl alcohol-glycerin-water gel, but is similar to that observed in the hydrogel of agar-agar in which the deviation from linearity appears at about the same temperature, but the value of H_a below the temperature is much smaller*,3).

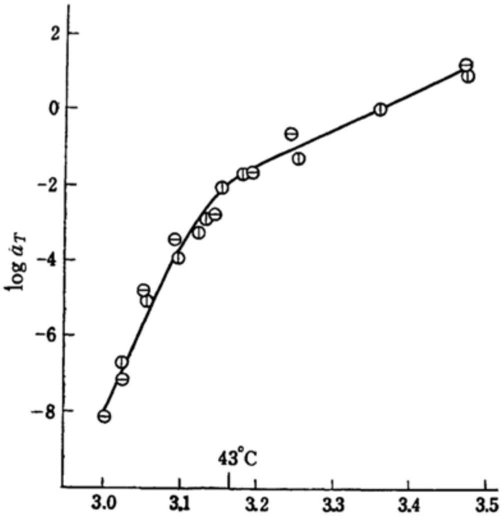

Fig. 4. Log a_T vs. $1/T$ relation.
⊖ Sample A
⦶ Sample B

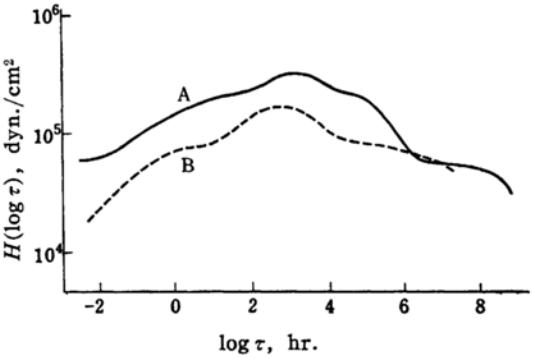

Fig. 5. Relaxation spectra

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* In the hydrogels of agar-agar the superposition of each relaxation curve is not so good, except in the case of 2.6% gel, above ca. 40°C. The mechanical behavior of 2.6% gel was as described in the text. In the gels of the other concentration a similar tendency was seen, though exact master curves were not obtained.

As seen in the fact described above, the $\log a_T$ vs. T relation does not obey the equation of WLF form[6].

Distribution Functions of Relaxation Times.— The relaxation spectra $H(\log\tau)$ are shown in Fig. 5, which were calculated from the master relaxation curves shown in Fig. 3 by the second order approximation[7].

$$H\left(\log\frac{\tau}{2}\right)=2.303\left[E_r\left\{-\frac{\mathrm{d}\log E_r}{\mathrm{d}\log t}+\frac{1}{2.303}\frac{\mathrm{d}^2(\log E_r)}{\mathrm{d}(\log t)^2}+\left(\frac{\mathrm{d}\log E_r}{\mathrm{d}\log t}\right)^2\right\}\right]_{t=\tau}$$

Each curve in Fig. 5 is seen to exhibit the character of the box type region of the whole spectrum, which corresponds to the rubbery and fluid state of materials.

Each spectrum is similar in shape except at the long time end, and the spectrum for 15% gel is seen to conform to that for 17.5% gel when slid upwards and to the right.

From the above facts it seems to be possible that two curves shown in Fig. 3 are composed to a single curve approximately, but this reduction on concentration has turned out to need the multiplication factor $(C_0/C)^n$, where the value of n is 3.5~4 and C_0 is a reference concentration. This value of n is too large, being compared with the value, 2, reported previously by DeWitt et al.[8] on the solution of polyisobutylene. More data are required.

Summary

Stress relaxation curves were obtained for the gels of the polyvinyl alcohol-congo red-water system in the temperature range, 15~60°C, by means of a chainomatic relaxometer. The molecular weight of polyvinyl alcohol was 8.5×10^4, and gels of 15.0 and 17.5% were used, where the concentration of congo red was adjusted to be 1/10 of that of polyvinyl alcohol. Master relaxation curves were obtained for each concentration over the range, $10^{-2}\sim10^9$ hr, and relaxation spectra were calculated by the second order approximation. The following results were obtained.

1) The $\log a_T$ vs. T relation gives a single curve for two concentrations, and does not obey the equation of WLF form. Also it has characteristics similar to that of agar-agar gels.

2) The apparent activation energy is kept constant to be 42 kcal. below about 43°C, and above this temperature it sharply increases with temperature.

3) The reduction on concentration to a single composite relaxation curve seems to be possible in rough approximation.

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[6] M. L. Williams, R. F. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

[7] R. D. Andrews, *Ind. Eng. Chem.*, **44**, 707 (1952); F. Schwarzl and A. J. Staverman, *Physica*, **18**, 791 (1952).

[8] T. W. DeWitt, H. Markovitz, F. J. Padden and L. J. Zapas, *J. Colloid Sci.*, **10**, 174 (1955).