Stress Relaxation of Non-electrolytic Thermo-reversible Gels.—Concentration Dependence of Distribution Function of Relaxation Times. Polyvinyl Alcohol-Glycerin-Water Gels*

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According to the reversibility of sol-gel transition with temperature, gels are classified into two groups, thermo-reversible and thermo-irreversible. As typical thermo-reversible gels we have agar, gelatine, etc. But most of these are polyelectrolytes, rheological properties of which are complicated by charge effects. In the present work the rheological property of non-electrolytic thermo-reversible gels was examined. A system consisting of polyvinyl alcohol, glycerin, and water was used as an example of such a gel. The elastic behavior of the gel has been studied previously by N. Hirai[1], but the distribution function of relaxation times was not obtained for this gel. Such a function has been determined from stress relaxation of the gel and discussed here briefly.

Experimental

Apparatus.—A chainomatic balance relaxometer shown in Fig. 1 was used to measure Young's modulus of a sample under constant strain. The relaxometer is of similar type with those used by S. L. Dart and E. Guth[2] for the study of stress relaxation in cork, and recently by several workers in studies of polymers[2].

In this relaxometer a sample is strained by compression betweeen two plates, the upper of which is attached to the horizontal bar of chainomatic balance. The lower plate is connected with a screw gauge. The stress produced by the constant strain is balanced with a chain, whose unfixed end is moved by a balancing motor. The

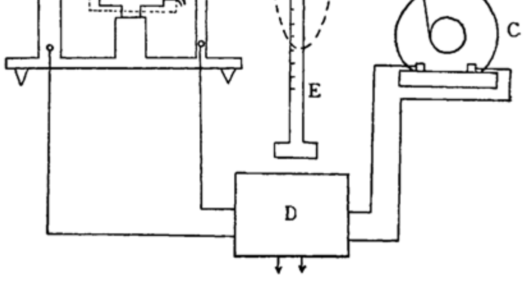

Fig. 1. Schematic diagram of chainomatic balance relaxometer.
A: specimen
B: chain
C: balancing motor
D: relay circuit
E: scale

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[1] N. Hirai, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **74**, 235 (1953); ibid., **74**, 259 (1953).

[2] S. L. Dart and E. Guth, *J. Appl. Phys.*, **17**, 314 (1946); H. Fujita and K. Ninomiya, *J. Polymer Sci.*, **24**, 233 (1957); This Bulletin, **26**, 24 (1953); K. Ogino, the 9th Annual Meeting of Chem. Soc. Japan (1956).

motor is driven through a relay circuit which is connected with a point contact attached to the bar. From the suspended length of the chain the stress is calculated and Young's modulus of the sample under constant strain can be obtained. The temperature of the sample is controlled by water circulated from a thermostat into a double jacket which contains the sample.

Materials.—In the present study a commercial polyvinyl alcohol was used throughout. The amount of residual ester groups in the sample was 2 % by mole. The intrinsic viscosity $[\eta]_{20}$ of this unfractionated sample was 0.27, which was determined by means of a capillary viscometer of Ostwald type. The viscosity average molecular weight M_V was 1.1×10^4 according to the formula by H. Staudinger and H. Warth[3].* As solvent a mixture of glycerin and water was used with a mixing ratio of 4:1 by volume.

The preparation of testing specimens was as follows. A definite quantity of polyvinyl alcohol powder was mixed with glycerin and water in a conical beaker. Being covered with liquid paraffin, the powder was dissolved slowly by heating in an oil bath kept at 125±5°C. In adjusting of the mixing ratio 4:1 of glycerin and water the presence of adsorbed water in polyvinyl alcohol powder, the amount of which was determined before each preparation, was taken into account. After the polyvinyl alcohol powder was dissolved completely, the solution was poured into a mould and kept at about 90°C for about thirty minutes. It was then cooled down slowly to about 50°C in four hours, and was aged at room temperature. Gels of three different concentrations, 8.3%, 9.9% and 12.1 % by weight were prepared.

Results and Discussion

Stress Relaxation Data.—The data of stress relaxation of gels of three different concentrations are plotted in the form $\log(298E_r/T)$ vs. $\log t$, where E_r is Young's relaxation modulus and t time, in Fig. 2 a, b and c*.

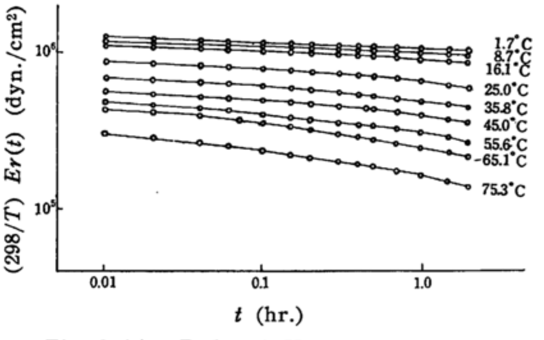

Fig. 2 (a). Reduced Young's relaxation modulus $\frac{298}{T}E_r(t)$ of 8.3% gel.

These data are reduced to 25°C by multipling E_r by a factor $298/T$. The multiplication by this factor is often subjected to objection, but in the present work the stress relaxation experiment was made in rubbery region mainly, and therefore this reduction is thought to be reasonable.

According to the time temperature superposition principle[4] a master relaxation curve at 25°C for each concentration may be composed by shifting these relaxation curves along the $\log t$ axis. The master relaxation curves for each concentration, thus obtained, are plotted in Fig. 3.

The amounts of the shift along the $\log t$ axis at various temperatures, $\log a_T$, are plotted against $1/T$ in Fig. 4. They give a nearly straight line. The apparent

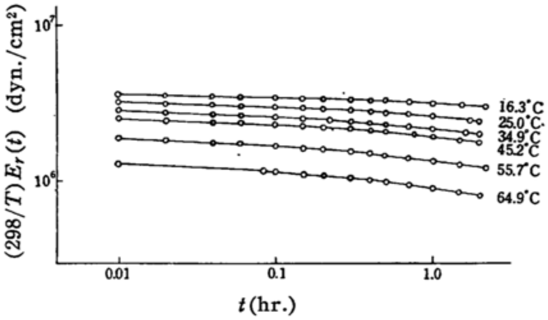

Fig. 2 (b) Reduced Young's relaxation modulus $\frac{298}{T}Er(t)$ of 9.9% gel.

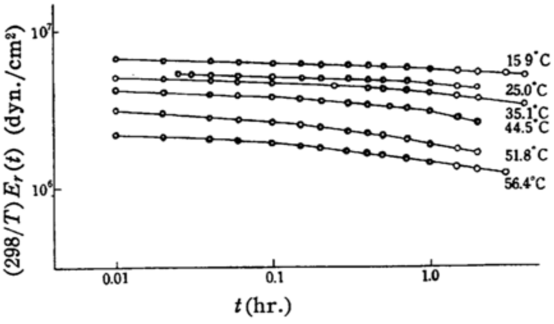

Fig. 2 (c). Reduced Young's relaxation modulus $\frac{298}{T}E_r(t)$ of 12.1% gel.

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[3] H. Staudinger and H. Warth, *J. Prakt. Chem.*, **155**, 261 (1944).

* In application of this formula, the effect of the residual ester groups was ignored.

[4] A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.*, **11**, 125 (1943); R. D. Andrews, N. Hofman-Bang and A. V. Tobolsky, *J. Polymer Sci.*, **3**, 669 (1948); J. D. Ferry, *J. Am. Chem. Soc.*, **72**, 3746 (1950); F. Schwarzl and A. J. Staverman, *J. Appl. Phys.*, **23**, 838 (1952); C. A. Dahlquist and M. R. Hatfield, *J. Colloid Sci.*, **7**, 253 (1952).

** Compressions applied in the present experiment were 3% in 12.1% and 9.9% gels, and 5% in 8.3% gel. In this range of compressions the linear relation between stress and strain was almost maintained.

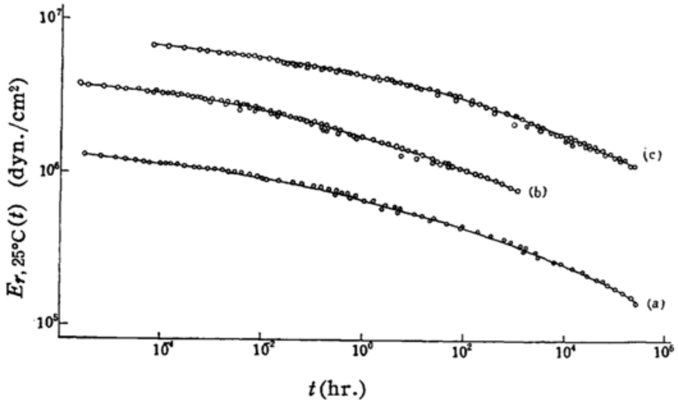

Fig. 3. Master relaxation curves at 25°C. (a) 8.3%, (b) 9.9%, (c) 12.1%

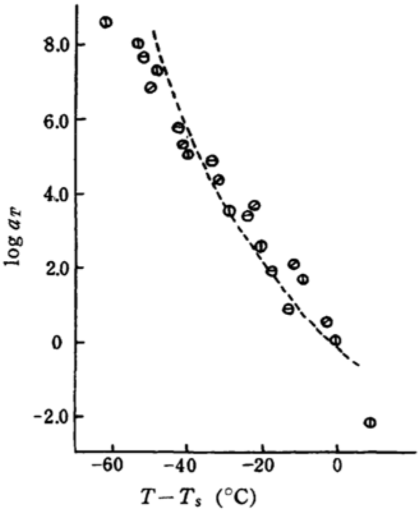

Fig. 5. Log a_T versus $T-T_s$ relation.
⦶ 8.3%, ⊘ 9.9%, ⊖ 12.1%
T_s: 338°K for 8.3%
340°K for 9.9%
342°K for 12.1%
------ equation of WLF form[5]
$C_1=8.86$, $C_2=101.6$

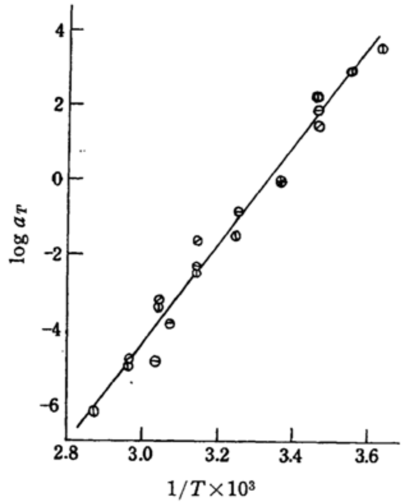

Fig. 4. Log a_T versus $1/T$ relation.

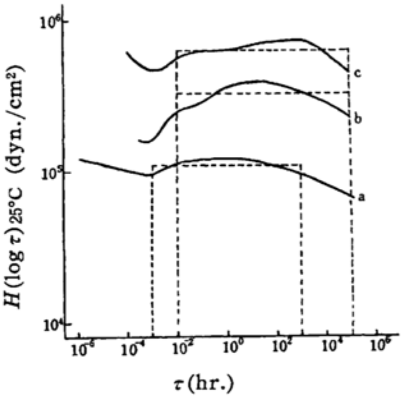

Fig. 6. Distribution functions of relaxation times.
(a) 8.3%, (b) 9.9%, (c) 12.1%

activation energy H_a, defined as $R\partial\ln a_T/\partial(1/T)$ is 60 kcal./mole, which is nearly kept constant over the temperature- and concentration-range in the present work. As for the temperature dependence of the factor a_T a function on the $\log a_T$ vs. $T-T_s$ relation has been proposed recently by M. L. Williams, R. F. Landel and J. D. Ferry[5], where T_s is a reference temperature. The coincidence between the values of a_T obtained in this work and the function is fairly good in the range of $T-T_s$, $-40\sim0$°C, but outside this range they deviate from the curve, as seen in Fig. 5.

Distribution Functions of Relaxation Times.—A distribution function of relaxation times $H(\log\tau)$ may be determined from a master curve, using the following first order approximation[6]

$$H(\log\tau)=-2.303[E_r\mathrm{d}\log E_r/\mathrm{d}\log t]_{t=\tau} \tag{1}$$

It was found that the difference between the first and the second order approximation was small enough in the calculated values to be ignored. Therefore the former was used throughout.

Logarithms of $H(\log\tau)$, thus obtained, are plotted against $\log\tau$ in Fig. 6.

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

[6] R. D. Andrews, *Ind. Eng. Chem.*, **44**, 707 (1952); F. Schwarzl, *Physica*, **17**, 830, 865 (1951).

TABLE I

VALUES OF PARAMETERS OF BOX-TYPE DISTRIBUTION

Concn. (wt. %)	τ_1 (hr.)	τ_2 (hr.)	$\overline{H}\times10^{-5}$ (dyn./cm²)	τ_m (hr.)	$H_m\times10^{-5}$ (dyn./cm²)
8.3	10^{-3}	10^{3}	1.1	10^{0}	1.2
9.9	10^{-2}	10^{5}	3.3	$10^{1.5}$	4.0
12.1	10^{-2}	10^{5}	6.3	10^{3}	7.1

Concentration Dependence of Master Relaxation Curve and Relaxation Spectrum.—It is seen in Fig. 3 that the master curve shifts upwards and to the longer time side with increase of concentration. But, when seen in details, the concentration dependence of the master curve is fairly complicated. Therefore, it is impossible to reduce the curves for different concentrations to a composite curve, as carried out by T.W. DeWitt et al.⁷⁾ on the decalin solution of polyisobutylene and previously by J. D. Ferry et al.⁷⁾

Also, in Fig. 6 we can see that the relaxation spectrum exhibits a fairly complicated nature on the concentration dependence. Simple approximations of box type for each spectrum are shown by dotted lines. Three parameters characterizing a box type distribution, two abscissae τ_1 and τ_2 ($\tau_1<\tau_2$), corresponding to two vertical sides, and the height $\overline{H}$ of the box are tabulated in Table I, together with the maximum value of $H(\log\tau)$, H_m and the abscissa τ_m at the maximum point. The value of $\overline{H}$ is taken to be an average value of $H(\log\tau)$ between τ_1 and τ_2. As seen in Fig. 6 and Table I, the maximum point in the region shifts upwards and to the longer time side with increase of concentration. The relation between $\overline{H}$ and concentration seems to be complicated. To draw any conclusion on this relation, further studies are required. Also it is evident that the shift of the spectrum due to the change of concentration is not uniform over the region covered in the present study. Concerning the shift along the $\log\tau$ axis, the minimum point which appears in the short time region nearly retains its position, while the maximum point shifts to the longer-time side, as the concentration increases. From this non-uniformity of the shift it is tentatively supposed that the relaxation mechanism in this region consists of two or more groups of mechanisms, which exhibit the different dependence on the concentration of polyvinyl alcohol.

Summary

From a stress relaxation experiment by means of a chainomatic balance relaxometer the stress relaxation curves were obtained for the gel of polyvinyl alcohol-glycerin-water system, which was taken as an example of non-electrolytic thermo-reversible gel. Gels of 8.3%, 9.9% and 12.1% were used. The temperature of the samples was changed between about 2°C and 75°C. Master relaxation curves were obtained for each concentration over the range of time, $10^{-4}\sim10^{5}$ hours, using the time temperature superposition principle. According to Alfrey's approximation, relaxation spectra were calculated.

The following results were obtained.

1) The master relaxation curves exhibit a fairly complicated nature on concentration dependence.

2) The $\log a_T$ vs. $T-T_s$ relation obeys approximately the formula by Williams, Landel and Ferry in the range of $T-T_s$, $-40\sim0$°C, but outside the range deviates fairly from it.

3) The apparent activation energy is 60 kcal./mole, which is nearly kept constant over the temperature- and concentration-range in the present work.

4) The shift of the relaxation spectrum due to the change of concentration is not uniform over the region of box type. The maximum point in that region shifts upwards and to the longer-time side with increase of concentration.

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7) T. W. DeWitt, H. Markovitz, F. J. Padden and L. J. Zapas, *J. Colloid Sci.*, **10**, 174 (1955); J. D. Ferry, *J. Am. Chem. Soc.*, **72**, 3746 (1950); W. M. Sawyer and J. D. Ferry. ibid., **72**, 5030 (1950).