Stress Relaxation of Gels of Polyvinyl Alcohol-Glycerin-Water System

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In the previous paper[1] the results of the stress relaxation study on the gels of the polyvinyl alcohol-glycerin-water system were reported. This was taken as an example of non-electrolytic thermo-reversible gel systems of polymeric nature, and some discussions were held concerning the concentration dependence of relaxation spectrum.

The average molecular weight of the sample of polyvinyl alcohol used in the previous study was 1.1×10^4, which was comparatively low as a polymer. Another study on the mechanical behavior of polyvinyl alcohol-glycerin-water gels has been attempted for a polyvinyl alcohol sample of higher molecular weight in order to investigate the effect of the molecular weight difference on its mechanical behavior and to obtain further knowledge concerning the concentration dependence of relaxation spectrum.

Experimental

Sample. — A commercial sample of polyvinyl alcohol was used. The amount of residual acetyl group of this powder sample was 1.0% by mole, which was determined by the titration method. The intrinsic viscosity $[\eta]_{25}$ obtained by means of a capillary viscometer of Ostwald type was 1.27 (100 cc./g.), and the viscosity average molecular weight which was calculated from the value of viscosity by Diew's formula[2] was 8.5×10^4.

The preparation of specimen gels was made according to the same procedure as that described in the previous paper[1] and also the mixing ratio of glycerin and water was made to be precisely the same as before. Gels of three different concentrations of polyvinyl alcohol were prepared, namely: 6.05, 7.95 and 9.07% by weight.

Apparatus and Procedure for Measurements. — The same relaxometer as has been used in the preceding studies[3] on the rheological properties of thermo-reversible gels was used in this experiment. The measurement of relaxation Young's modulus under a given constant strain was carried out for two hours after sudden imposition of the strain. The imposed strain was 5% for 7.95% and 9.07% gels, and 20% for 6.05% gels, respectively. The temperature was varied with about 10°C interval.

Results and Discussion

Relaxation Data. — The relaxation Young's modulus under constant compressional strain at various temperatures is plotted in the form of $(298/T)E_r$ versus log t, where $(298/T)$ is a reduction factor to 25°C concerning rubber-like elasticity. The results are shown in Figs. 1(a), 1(b) and 1(c) for each concentration.

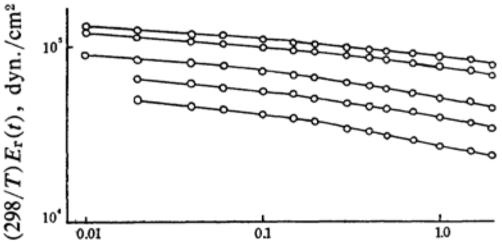

Fig. 1 (a). Reduced relaxation Young's modulus $(298/T)E_r(t)$ of 6.05% gel.

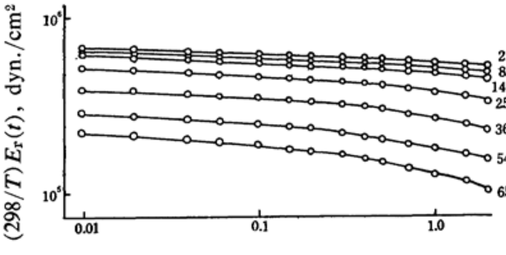

Fig. 1 (b). Reduced relaxation Young's modulus $(298/T)E_r(t)$ of 7.95% gel.

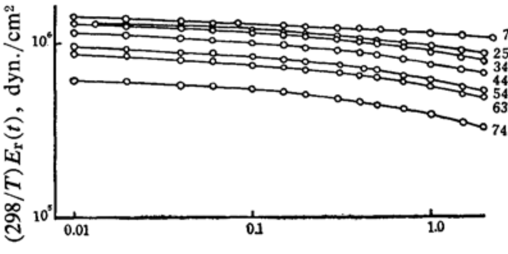

Fig. 1 (c). Reduced relaxation Young's modulus of 9.07% gel.

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

[2] H. Diew, *J. Polymer Sci.*, 12, 147 (1954).

[3] K. Arakawa, This Bulletin, 32, 1248 (1959); ibid., 33, 1568 (1960); K. Arakawa and K. Atsumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*) 80, 133 (1959).

According to the time-temperature superposition principle[4], a master relaxation curve at 25°C for each concentration is obtained by shifting the relaxation curves at different temperatures horizontally along the $\log t$ axis. The master relaxation curves, thus obtained, are shown in Fig. 2. The coincidence of each relaxation curve by superposition is good as seen in Fig. 2.

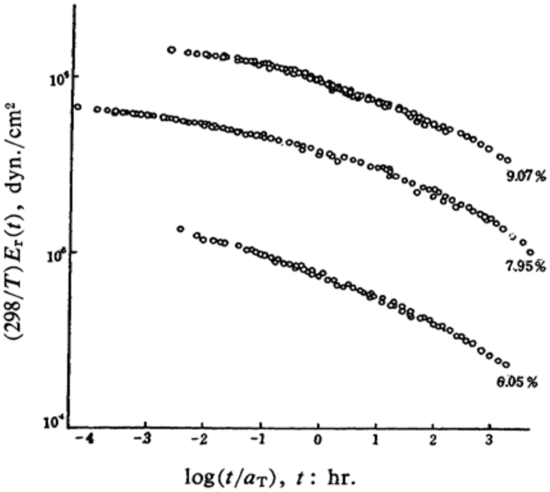

Fig. 2. Master relaxation curves at 25°C.

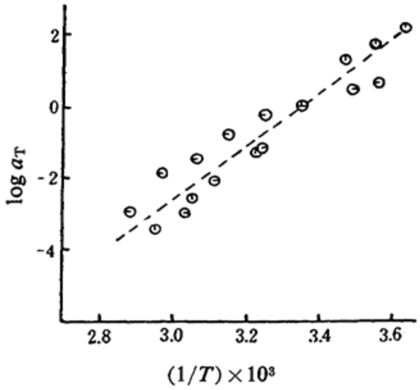

Fig. 3. $\log a_T$ versus $1/T$ relation.
⊖ 6.05%, ⦶ 7.95%, ⊝ 9.07%

The shift factors $\log a_T$ are plotted against $1/T$ in Fig. 3. This plotting shows a nearly linear relation, as in the case of the previous study[1], where the molecular weight of the polyvinyl alcohol was 1.1×10^4. Thus, the apparent activation energy H_a calculated from the gradient of the $\log a_T$ versus $1/T$ curve is kept constant within the temperature and concentration ranges in the present study. When the apparent activation energy is constant, shift factors a_T are expressed as follows,

$$a_T = A\exp(H_a/RT) \tag{1}$$

The values of $\log A$ and H_a are given in Table I, together with those of molecular weight 1.1×10^4 in the previous paper[1].

TABLE I. VALUES OF $\log A$ AND H_a

Mol. wt. of polyvinyl alcohol	8.5×10^4	1.1×10^4
$\log A$	−25.7	−43.8
H_a (kcal./mol.)	35	60

The constancy of H_a as well as the good coincidence of each relaxation curve by superposition is said to support the adequacy of the application of the superposition method, which exhibits the equality of the temperature dependence of all relaxation mechanisms within these ranges of temperature and concentration[5].

In order to compare the temperature dependence of shift factors in this case with the equation of the WLF form[6], the values of $\log a_T$ referred to T_S are plotted against $T-T_S$ in Fig. 4, where T_S is a reference temperature. The values of $\log a_T$ agree with the curve of WLF equation within the range of $(T-T_S)=-20\sim 20$°C, but outside of this range they deviate from the curve.

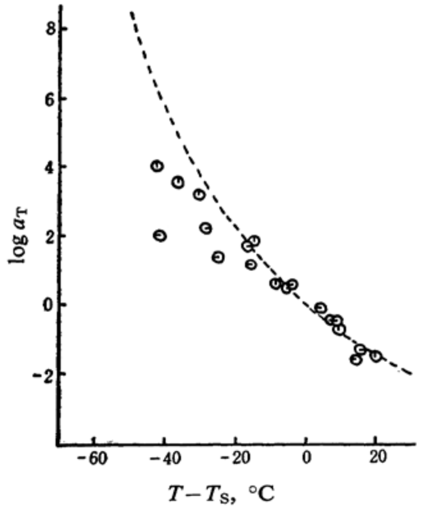

Fig. 4. $\log a_T$ versus $T-T_S$ relation.
⊖ 6.05%, ⦶ 7.95%, ⊝ 9.07%
---- Equation of WLF form, C_1: 8.86, C_2 : 101.6
Values of T_S 315°K for 6.05%
319°K for 7.95%
323°K for 9.07%

Concentration Dependence of Distribution Functions of Relaxation Times.—From the

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[4] A. V. Tobolsky, "Properties and Structure of Polymers", John Wiley and Sons, Inc., Publishers, New York (1960), Chapter 4, Sec. 2 and 3.

[5] C. A. Dahlquist and M. R. Hatfield, *J. Colloid Sci.*, 7, 253 (1952).

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

master curves shown in Fig. 2 distribution functions of relaxation times, $H(\log \tau)$, which are defined by Eq. 2 are obtained by Alfrey's first order approximation, Eq. 3.

$$E_r(t)=\int_0^{\infty} H(\log \tau) e^{-(t/\tau)} \mathrm{d} \log \tau \qquad (2)$$

$$H(\log \tau)=-2.303\left[E_r \frac{\mathrm{d} \log E_r}{\mathrm{d} \log t}\right]_{t=\tau} \qquad (3)$$

The distribution functions, thus obtained, are shown in Fig. 5. As is seen clearly, they are of typical box type character. When seen in details, there appears a fairly broad flat region in the curve for the gel of 7.95% and a peak in the curve for the gel of 9.07%. The curve for the gel of 6.05% is regarded as the one in the rubbery flow region which follows after the flat region. The distribution functions of the gels described in the previous paper¹⁾ are shown together for comparison by dotted lines.

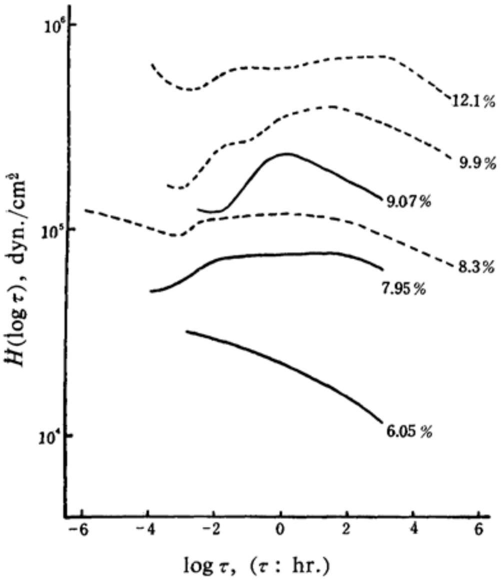

Fig. 5. Distribution functions of relaxation times.
—— Molecular weight, 8.5×10^4
---- Molecular weight, 1.1×10^4

When we see in detail the change in the shape of the curves with increase of concentration, it may certainly be said that the simple reduction rule concerning concentration which was proposed by Ferry et al.⁷⁾ and also the modified reduction rule by DeWitt et al.⁸⁾ on polymer solutions do not hold in this case, and that the circumstances are more complicated. However, when we seen all curves including dotted lines, it is found that the curves change their shapes continuously with the increase of concentration and that there is no marked difference among them in the tendency of the change in shape in spite of the fairly great difference in molecular weight.

The curve for the gel of 6.05% decreases monotonously. This corresponds to the rubbery flow region, and there appears a broad flat region in the curve of the gel of 7.95%, and the broad flat region is levelled up for the gel of 8.3%. Then there appears a peak in the flat region for the gel of 9.9%, and the peak shifts with the increase of concentration, accompanying the ascent of the curve.

Then it may be said that the difference in molecular weight has no marked effect on the distribution functions of relaxation times and that there are two or more mechanisms which behave differently with the increase of concentration.

In order to investigate the concentration dependence of distribution functions, the average values of $H(\log \tau)$ in the whole box type region, $\bar{H}$, which is regarded as the height of the idealized box type spectrum, are calculated and plotted in the form of $\log \bar{H}$ versus $\log C$, where C is concentration in weight %, in Fig. 6, including those for the case of molecular weight 1.1×10^4. Then we see in Fig. 6 that a linear relation holds between $\log \bar{H}$ and $\log C$ as follows,

$$\log \bar{H}=\alpha+\beta \log C \qquad \alpha=0.45,\ \beta=5 \qquad (4)$$

As is shown in the equation above described, the value of $\bar{H}$ is proportional to the fifth

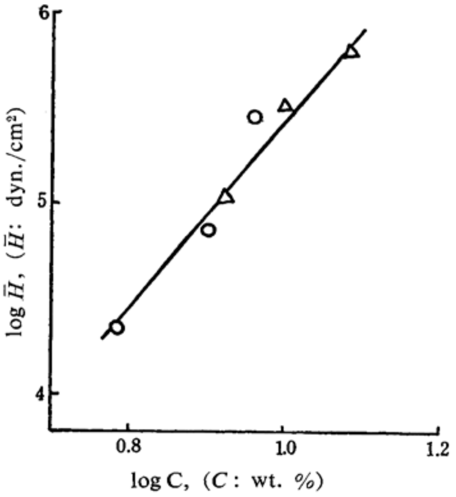

Fig. 6. Concentration dependence of average value of distribution functions of relaxation times in box type region.
○ Molecular weight, 8.5×10^4
△ Molecular weight, 1.1×10^4

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7) J. D. Ferry, ibid., 72, 3746 (1950).

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

power of concentration. Then it is said that in the case of thermo-reversible gels there exists much more sensitive dependence of distribution functions on concentration, compared with the case of concentrated polymer solutions[7,8].

Summary and Conclusion

A stress relaxation study was made for the gels of the polyvinyl alcohol-glycerin-water system using a chainomatic balance relaxometer, where the molecular weight of polyvinyl alcohol was 8.5×10^4. Relaxation Young's moduli under constant strain were measured up to two hours after sudden imposition of the strain for the gels of three different concentrations of polyvinyl alcohol: 6.05, 7.95 and 9.07% by weight. The relaxation curves at various temperatures were successfully superposed to a master relaxation curve for each concentration, and relaxation spectra were obtained from the master curves by Alfrey's approximation. The main results obtained are as follows.

1) The relaxation spectrum of the gel of the polyvinyl alcohol-glycerin-water system has a typical box type character.

2) The difference in molecular weight of polyvinyl alcohol has no marked effect on the relaxation spectrum of the gel.

3) The concentration dependence of the relaxation spectrum are fairly complicated in its details.

4) The average value of the distribution function of relaxation times in the box type region is proportional to the fifth power of concentration, rather than to the first or the second power.

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