Rheological Properties of Thermo-reversible Gels

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In the preceding papers[1-3] the results of stress relaxation studies made on various kinds of thermo-reversible gels (for example, the gels of polyvinyl alcohol-glycerin-water system[1], the gels of polyvinyl alcohol-Congo red-water system[2], and the hydrogels of agar-agar[3]), were reported on.

In the present paper the author reports on the results of a more comprehensive study on the rheological properties of the thermo-reversible gels above described, including the results of a stress relaxation experiment on hydrogels of gelatin.

Experimental

A chainomatic balance relaxometer was used to measure the relaxation Young's modulus of hydrogels of gelatin, which was the same one as was used previously[1-3]. The intrinsic viscosity $[\eta]_{55^\circ\mathrm{C}}$ of a powder sample of gelatin in the presence of 0.15 M sodium chloride and at pH 7 was determined to be 0.21 (100 cc./g.) by means of a capillary viscometer of the Ostwald type, and the molecular weight M_n was estimated from the value to be about 2×10^4, according to the relation between M_n and $[\eta]_{55^\circ\mathrm{C}}$ which had been reported previously by Scatchard et al.[4] Cylindrical specimens of 17.5 wt.% were prepared and aged at about 0°C in liquid paraffin for more than two weeks. Before the experiment each specimen gel was brought to and kept at the temperature of measurement for five hours[5], and then the observation of the relaxation Young's modulus was started.

Results and Discussion

Stress Relaxation Data of Gelatin Gels.—The data of the relaxation Young's modulus of 17.5% gelatin gel under a constant compressional strain are given in Fig. 1. The amount of strain was 15% for all specimens. The mechanical behavior of the gel may be represented by a six-parameter model as shown in Fig. 2, and the relaxation Young's modulus $E_r(t)$ under constant strain is expressed by the following Eq. 1:

$$E_r(t)=E_1\mathrm{e}^{-t/\tau_1}+E_2\mathrm{e}^{-t/\tau_2}+E_3\mathrm{e}^{-t/\tau_3} \qquad (1)$$

in which

$$\tau_1>\tau_2>\tau_3$$

The values of the parameters obtained are given in Table I.

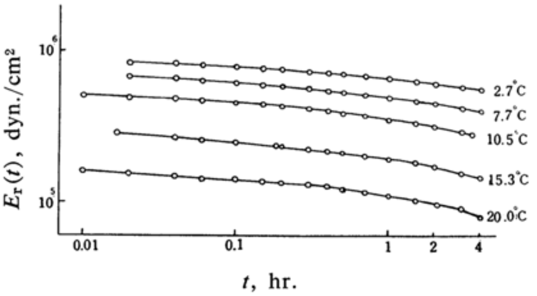

Fig. 1. Relaxation Young's modulus of 17.5% gelatin gel.

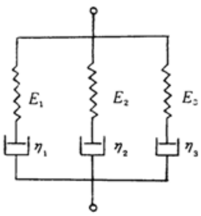

Fig. 2. Mechanical model.
$E_1/\eta_1=\tau_1,\ E_2/\eta_2=\tau_2,\ E_3/\eta_3=\tau_3$

Applcation of the Modified Time-Temperature Superposition Principle. — For the gels of the polyvinyl alcohol-glycerin-water system and those of the polyvinyl alcohol-Congo red-water system, the time temperature superposition principle[6] was applied successfully as has been reported previously[1,2] but the circumstances were found to be different in the hydrogels of agar-agar[3,7]; they were also found to be so in the hydrogels of gelatin, as is seen in Fig. 1.

Recently Nagamatsu, Takemura et al. have proposed the modified time-temperature superposition principle for crystalline polymers which include the vertical shift $\log b_T$ along

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

[2] K. Arakawa, ibid., **32**, 1248 (1959); **33**, 1568 (1960).

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

[4] G. Scatchard, J. L. Oncley, J. W. Williams and A. Brown, *J. Am. Chem. Soc.*, **66**, 1980 (1944).

[5] J. D. Ferry, ibid., **70**, 2244 (1948).

[6] J. D. Ferry, ibid., **72**, 3746 (1950); A. V. Tobolsky, *J. Appl. Phys.*, **27**, 673 (1956); C. A. Dahlquist and M. R. Hatfield, *J. Colloid Sci.*, **7**, 253 (1952).

[7] K. Arakawa, This Bulletin, **34**, 1233 (1961).

TABLE I. VALUES OF PARAMETERS OF 17.5% GELATIN GEL

T °C	E_1 10^5 dyn./cm²	E_2 10^5 dyn./cm²	E_3 10^5 dyn./cm²	τ_1 hr.	τ_2 min.	τ_3 min.
2.7	6.6	1.3	1.6	7.8	17	0.6
7.7	5.1	1.4	1.0	6.3	8	0.5
10.5	3.8	1.0_5	0.6_5	5.3	$8._3$	0.6
15.3	2.0_5	0.5_3	0.6_2	4.6	9	0.8
20.0	1.2_3	0.2_5	0.3_2	4.0	$8._4$	0.4

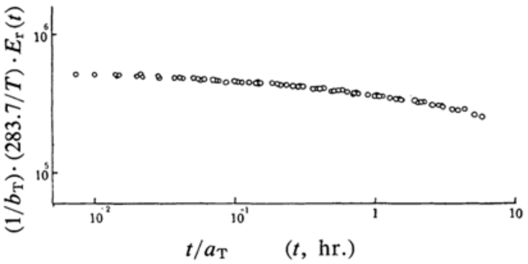

Fig. 3(a). Composite relaxation curve of 17.5% gelatin gel at 10.5°C.

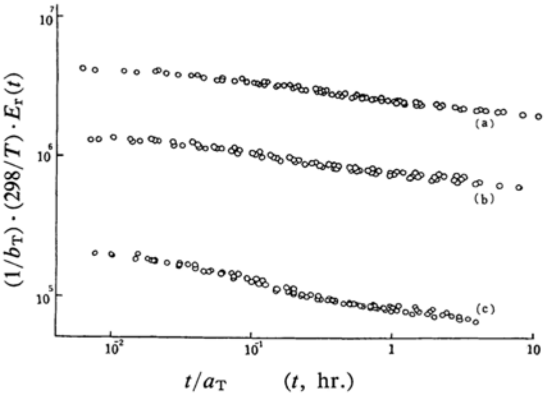

Fig. 3(b). Composite relaxation curves of agar-agar gel at 25°C.

(a) 4.1%, mol. wt. 8×10^3
(b) 2.6%, mol. wt. 4×10^4
(c) 1.0%, mol. wt. 8×10^3

TABLE II. SHIFT FACTORS $\log a_T$ AND $\log b_T$

17.5% Gelatin gel (mol. wt. 2×10^4)

T	$\log a_T$	$\log b_T$
2.7	0.44	0.22
7.7	0.16	0.13
15.3	−0.10	−0.26
20.0	-0.15_2	−0.50

2.6% Agar-agar gel (mol. wt. 4×10^4)

T	$\log a_T$	$\log b_T$
5.0	0.15_4	0.03_5
14.7	0.04_8	0.01_9
35.7	-0.12_7	-0.12_4
44.6	−0.27	-0.15_4

4.1% Agar-agar gel (mol. wt. 8×10^3)

T	$\log a_T$	$\log b_T$
1.3	0.22	0.07_5
14.4	0.13_5	0.05
38.2	−0.31	−0.04
46.8	−0.48	−0.16
55.5	−0.73	−0.25

1.0% Agar-agar gel (mol. wt. 8×10^3)

T	$\log a_T$	$\log b_T$
1.4	0.29	0.08
15.4	0.12	0.02_5
35.8	−0.10	-0.02_5
46.1	-0.18_5	-0.09_2
54.8	−0.25	−0.26
59.0	−0.28	−0.30

the $\log E_r$ axis as well as the usual horizontal shift $\log a_T$ along the log time axis[8].

The composite relaxation curve of 17.5% gelatin gels which has been obtained from the relaxation curves shown in Fig. 1 by the application of the modified superposition principle described above is shown in Fig. 3(a). Those of hydrogels of agar-agar which have been obtained according to the same procedure from the data previously reported[3,7] are also shown in Fig. 3(b). The values of the two kinds of shift factors $\log a_T$ and $\log b_T$, are tabulated in Table II.

Structure of Thermo-reversible Gels.—Concerning those thermo-reversible gels which make the sol-gel transition reversibly, it may be generally said that the junctions supporting the network structure in the gels are of a secondary nature, rather than of a primary nature (covalent bond) as in swollen gels, for example, the swollen gels of vulcanized rubber. Therefore, it may be also said that in the stress relaxation experiment of thermo-reversible gels, scission of network chains occurs at the junctions rather than along the network stands.

In a rubber network with N_0 moles of effective network chains, the relaxation Young's modulus $E_r(t)$ under constant strain is proportional to the moles of effective network chains $N(t)$ at the time t as follows:

$$\frac{E_r(t)}{E_r(0)}=\frac{N(t)}{N_0} \tag{2}$$

and with the assumption that the rate of bond cleavage at network junctions is of a first order:

$$-\frac{\mathrm{d}N(t)}{\mathrm{d}t}=kN(t) \tag{3}$$

in which k is the rate constant of the bond cleavage reaction. Then we obtain from Eqs. 2 and 3:

$$E_r(t)=E_r(0)\mathrm{e}^{-kt} \tag{4}$$

Therefore, the reciprocal of k is found to be

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[8] K. Nagamatsu, T. Yoshitomi and T. Takemoto, *Memoirs Fac. Eng. Kyushu Univ.*, **30**, 259 (1958); K. Nagamatsu, T. Takemura, T. Yoshitomi and T. Takemoto, *J. Polymer Sci.*, **33**, 515 (1958); T. Takemura, ibid., **38**, 471 (1959).

equal to τ_1, which is obtained graphically[3] from the experimental curve according to Eq. 1, and then the activation energy $\Delta\overline{H}$ as an average, which is obtained from the the $\log \tau_1$ vs. $1/T$ relation, may be regarded as the activation energy of the bond cleavage reaction at the junctions. An example[2] the $\log \tau_1$ vs. $1/T$ relation is shown in Fig. 4.

$$\Delta\overline{H}=R\frac{\partial \ln \tau_1}{\partial(1/T)} \tag{5}$$

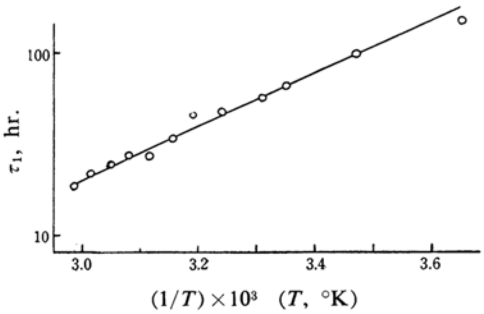

Fig. 4. τ_1, vs. $1/T$ relation of polyvinyl alcohol-Congo red-water gel.
Mol. wt. of PVA, 4.9×10^4
Composition: PVA, 17.5 wt. %
1.75 wt. %

TABLE III. VALUES OF ACTIVATION ENERGY $\Delta\overline{H}$

PVA-glycerin-water gel

Mol. wt. of PVA	Concn. of PVA %	$\Delta\overline{H}$ kcal./mol.
1.1×10^4	8.3	4.6
	9.9	4.0
	12.1	4.6
8.5×10^4	7.95	4.8
	9.07	4.0

PVA-Congo red-water gel

Mol. wt. of PVA	Concn. of PVA, %	Concn. of C. R., %	$\Delta\overline{H}$ kcal./mol.
8.5×10^4	15.0	1.50	7.9
	17.5	1.75	8.5
3.5×10^4	17.5	1.75	7.5
4.9×10^4	17.5	1.75	7.0
9.8×10^4	17.5	1.75	7.0

Agar-agar gel

Mol. wt. of agar-agar	Concn. of agar-agar, %	$\Delta\overline{H}$ kcal./mol.
8×10^3	1.0	4.8
	2.6	5.8
	4.1	4.5
4×10^4	2.6	6.6

Gelatin gel

Mol. wt. of gelatin	Concn. of gelatin, %	$\Delta\overline{H}$ kcal./mol.
2×10^4	17.5	5.8

The values of $\Delta\overline{H}$ thus obtained for various kinds of thermo-reversible gels are tabulated in Table III. Those for the gels of the polyvinyl alcohol-glycerin-water system[1,9] and the gels of the polyvinyl alcohol-Congo red-water system[2] are calculated from the data previously reported[1,2,9] by the six-parameter model analysis and Eq. 5, while those for the agar-agar gels are quoted from a previous paper[7]. The value for the gelation gel is calculated from the values of τ_1 given in Table I.

It is clearly seen in Table III that the values of $\Delta\overline{H}$ for the gels of the polyvinyl alcohol-glycerin-water system, those for the hydrogels of agar-agar, and the value for the gelatin gel are all substantially equal with each other irrespective of the difference in chemical species and, of course, of the differencce in molecular weight. It is also seen that the values of $\Delta\overline{H}$ of the gels above described are substantially equal to the activation energy for the hydrogen bond between water molecules, 4.5 kcal./mol.[10], and to the one for the hydrogen bond between ethyl alcohol molecules, 6.2 kcal./mol.[10] The values $\Delta\overline{H}$ for the gels of the polyvinyl alcohol-Congo red-water system are found in Table III to be a little larger than those values for the hydrogen bonds described above, and to be nearly equal to the value for the hydrogen bond in the micelle of neutral cellulose[11], for example.

Therefore, in the gels of the polyvinyl alcohol-glycerin-water system in which no ions or ionic groups are present, it may be said that the hydrogen bonds play the principal part as the linkages between chain molecules.

In the hydrogels of agar-agar and those of gelatin, considering that the relaxation curves behave like those of other crystalline polymers concerning the application of the modified superposition principle as described above, and that the values of $\Delta\overline{H}$ are substantially equal to those of polyvinyl alcohol-glycerin-water gels, it may be also tentatively said that the hydrogen bonds in the micelles play a more important part as the linkages in the network than ionic groups do.

In the gels of the polyvinyl alcohol-Congo red-water system, Congo red molecules are supposed to play an important role in the formation of the network structure[12]. Probably in this case the hydrogen bond is also important.

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[9] K. Arakawa, This Bulletin, **34**, 1549 (1961).

[10] L. Pauling, "The Nature of Chemical Bond", Cornell University Press, Ithaca, N. Y. (1940), Chap. 9.

[11] N. Saito, "High Polymer Physics (Kobunshi Butsurigaku)", Shokabo, Tokyo (1958), p. 8.

[12] C. Ditmar and W. J. Priest, *J. Polymer Sci.*, **18**, 275 (1955).

Summary

From the stress relaxation data of various kinds of thermo-reversible gels obtained by means of a chainomatic balance relaxometer, it has been found that:

1) The modified time-temperature superposition principle which includes the vertical shift along the $\log E_r(t)$ axis as well as along the log time axis can be successfully applied to the hydrogels of agar-agar and gelatin, and composite relaxation curves are obtained with good coincidence;

2) The activation energy $\Delta\overline{H}$ which is obtained from the τ_1 vs. $1/T$ relation and which is regarded as the activation energy of the bond cleavage process at the junctions in the network is substantially equal to the value of the hydrogen bond in water and ethyl alcohol for the gels of the polyvinyl alcohol-glycerin-water system and for the hydrogels of agar-agar and gelatin; the value of $\Delta\overline{H}$ is, however, a little larger for the gels of the polyvinyl alcohol-Congo red-water system.

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