Colloid Chemical Studies on Starching Materials. III. Dynamic Viscosity and Dynamic Rigidity of Starch Solutions

By Masayuki NAKAGAKI* and Kazuko MURAGISHI

(Received August 18, 1960)

In recent years, anomalous flow properties of colloidal systems have been investigated extensively in the field of rheology, in which the flow property is explained by a combination of rigidities and viscosities. Examples of the combination frequently used are so called Maxwell's model and Voigt's model. Even for fluid, it is required to presuppose some rigidity element to explain its flow property on the basis of these models. The existence of a kind of rigidity may be understood by considering the fact that the so-called structural viscosity of a solution can be explained by assuming a kind of yield value, as shown in a previous paper of this series on dilute solutions of polyvinyl alcohol[1].

In the present paper, starch solutions, also known to show structural viscosity, are examined by a rheometer to obtain the frequency dependencies of dynamic rigidity and dynamic viscosity, and an attempt is made to explain these by Maxwell's and Rouse's model.

Experimental

Rheometer.—A top-drive coaxial rheometer was used. Details of the rheometer were described by Nakagawa and Seno[2]. The sample to be studied was put in the gap between the coaxial internal and external cylinders. The radius of the internal cylinder r_1 was 2.00 cm. and that of the external cylinder r_2 was 2.50 cm. The depth l of the immersion of the internal cylinder was 15.0 cm., which was equal to the height of the cylinder. The moment of inertia I of the internal cylinder was 3005 g. cm². The internal cylinder was hung by a quenched steel wire whose diameter was 1.0 mm., and whose length was 92.5 cm. The torsional constant of the wire determined from the period of the free torsional oscillation, k, was 0.90×10^5 dyne cm.

At the top of the wire, a sinusoidal torsional oscillation was applied and the oscillation of the internal cylinder was recorded on a photographic paper as a Lissajous' figure obtained by combining perpendicularly the oscillation of the internal cylinder and the oscillation at the top of the wire. The Lissajous' figure thus obtained was an ellipse.

The dynamic viscosity η and the dynamic rigidity G are calculated by the equations:

$$\left.\begin{aligned}\eta&=\frac{R}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)=47.8\times10^{-5}\times R(\text{poises})\\G&=\frac{K}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)=47.8\times10^{-5}\times K(\text{dyne/cm}^2)\end{aligned}\right\}\tag{1}$$

where R and K are the quantities to be determined experimentally by using the equations:

$$\left.\begin{aligned}R&=k\sin\phi/\omega p\\K&=k(\cos\phi/p-1)+I\omega^2\end{aligned}\right\}\tag{2}$$

Here, the lag angle ϕ and the amplitude ratio p are to be obtained by the analysis of the photographic picture, and ω is the angular frequency. The latter is defined by

$$\omega=2\pi/T_{\mathrm{f}}\tag{3}$$

where T_{f} is the period of oscillation. All experiments were made in a thermostat at 30°C.

A Check of the Rheometer by Using Distilled Water.—Distilled water is an example of so-called Newtonian liquid, for which $G=0$ and $K=0$. All the Lissajous' figures obtained for distilled water by the present rheometer were linear, which give $\sin\phi=0$ and $R=0$. This means that the viscosity of distilled water was too small to be detected by this apparatus, that is $\eta\fallingdotseq0$. Since $\sin\phi=0$ and $\cos\phi=1$ for distilled water, Eq. 2 can be simplified to

$$1/p=1-(I/k)\omega^2\tag{4}$$

Therefore the relation between $1/p$ and ω^2 should be expressed by a straight line which intersects with the ordinate at $1/p=1$ and has an inclination of -0.0333 according to the values of I and k given above. In Fig. 1, the experimental values are shown by open circles, while the theoretical relation give by Eq. 4 is shown by a straight line. The agreement is fairly good. Apparent values of the rigidity G of distilled water calculated from the experimental values of p will give the experimental error. The error in the worst case was about 18 dyne/cm² (for $\omega=11.5$).

Materials and Preparation of Pastes. — The materials used were potato starch, sweet potato starch, and rice starch of pharmaceutical grade. The starch, dried in a desiccator and weighed accurately, was put in a flask, water was added, and it was heated at 90°C for 30 min. stirring with a glass rod inserted through a hole in a rubber stopper fitted loosely to the flask. For the heating, the temperature of a water bath was raised gradually from room temperature to boiling, and kept boiling

---

* Present address: Faculty of Pharmacy, Koyto University, Sakyo-ku, Kyoto.

[1] M. Nakagaki and A. Shimazaki, This Bulletin, **29**, 60 (1956).

[2] T. Nakagawa and M. Seno, ibid., **29**, 471 (1956).

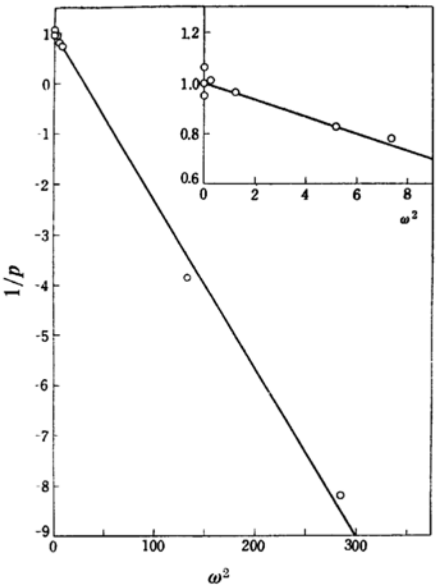

Fig. 1. Distilled water.

for 30 min. The temperature in the flask was 90°C when the bath water was boiling. Then, the flask was placed in cold water for cooling. The paste was used for the measurement immediately after it was cooled, and the measurement was finished in the same day.

Results and Discussion

The values of the dynamic viscosity η and the dynamic rigidity G thus obtained are shown in the following figures. Fig. 2 is for 3% potato starch paste, Fig. 3 is for 5% potato starch paste, Fig. 4 is for 5% sweet potato starch paste, and Fig. 5 is for 5% rice starch paste. In these figures, the abscissa is $\log \omega$, while the ordinate is $\log \eta$ for open circles and is $\log G$ for closed circles.

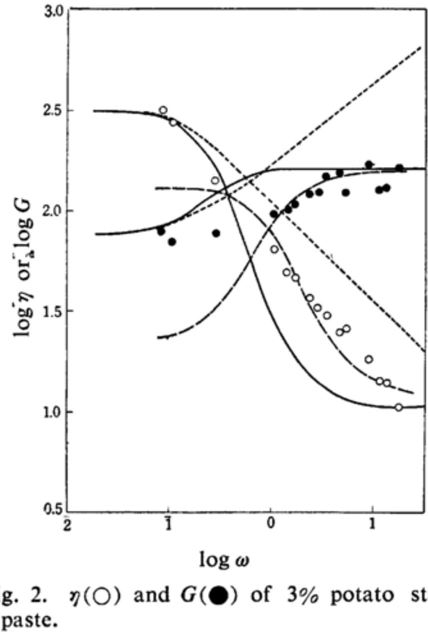

Fig. 2. η(○) and G(●) of 3% potato starch paste.

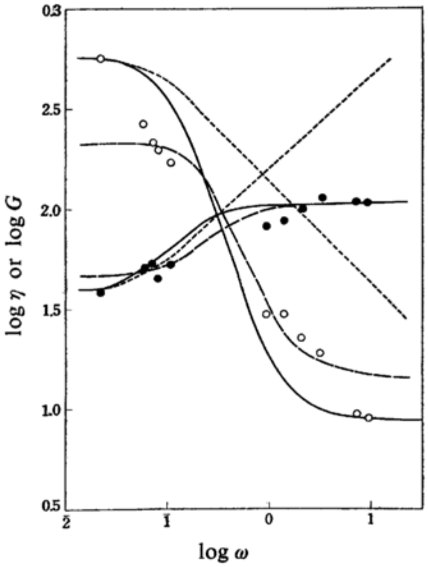

Fig. 3. η(○) and G(●) of 5% potato starch paste.

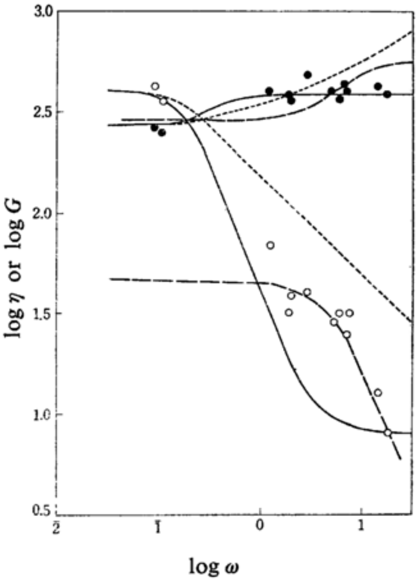

Fig. 4. η(○) and G(●) of 5% sweet potato starch paste.

For all these pastes, the dynamic viscosity decreased and the dynamic rigidity increased with the increase of the frequency. This is, as is well known, the usual viscoelastic behavior. To describe the viscoelastic behavior, Maxwell's four element model is often used. By this model the frequency dependence of

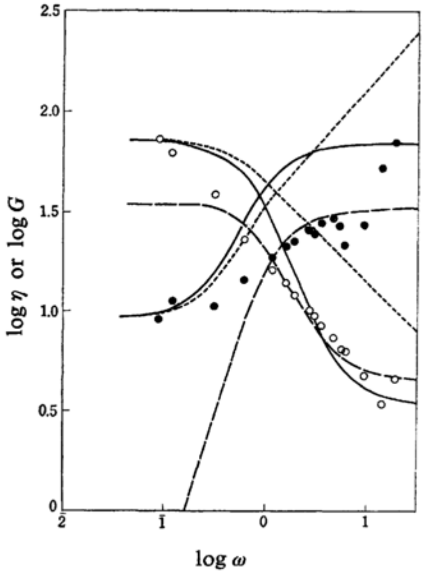

Fig. 5. η(○) and G(●) of 5% rice starch paste.

the dynamic viscosity and the dynamic rigidity are expressed by the equations,

$$\eta=\eta_2/(1+\tau_2{}^2\omega^2)+\eta_3 \tag{5}$$

$$G=G_1+G_2\tau_2{}^2\omega^2/(1+\tau_2{}^2\omega^2) \tag{6}$$

where, η_2, η_3, G_1 and G_2 are constants, and τ_2 is also a constant called relaxation time, and is given by the relation,

$$\tau_2=\eta_2/G_2 \tag{7}$$

An attempt was made to see how well these equations can explain the experimental results.

In order to find out the values of the parameters, G_1, G_2, η_2, η_3 and τ_2, attaching importance equally to both η and G, the following procedure was at first used. By using Eqs. 5, 6 and 7,

$$\left.\begin{aligned}\eta&=B-\tau_2G\\ B&=\eta_3+\eta_2+\tau_2G_1\end{aligned}\right\} \tag{8}$$

can be derived. Therefore, if one plots experimental values of η and G of the same ω value on the ordinate and the abscissa, respectively, one should obtain a linear relationship and one can determine the value of B and τ_2. Then, by plotting experimentally obtained η and $(B-\tau_2G)$ on the ordinate (these quantities are not necessarily equal with each other because of experimental errors and any deviation from Maxwell's model), and $1/(1+\tau_2{}^2\omega^2)$ on the abscissa, one should again obtain another linear relationship which gives the value of η_2 and η_3. The parameter G_1 is obtained from these values on the basis of the second equation of Eq. 8. Thus, one should be able to determine the values of all the parameters, η_2, η_3, G_1, G_2, and τ_2. However, the experimental data seemed not to agree with Maxwell's model in the present case, because two expected linear relationships were not exactly satisfied. By trying, however, to draw straight lines to satisfy the experimental plots as far as possible, the values of the parameters were determined, as shown in lines called I in Table I. Calculated values of $\log\eta$ and $\log G$ by using these values are shown in Figs. 2—5 with broken curves. It is seen that these curves partially satisfy the experimental plots but not in the whole range of the frequency.

The second method to determine the parameter values of Maxwell's four element model was used as follows, according to the experience that most curves in the previous case were already almost horizontal in the larger and smaller range of $\log\omega$. Eqs. 5 and 6 show that

$$\left.\begin{aligned}\eta(\tau_2\omega\langle\langle 1)&=\eta_2+\eta_3\\ \eta(\tau_2\omega\rangle\rangle 1)&=\eta_3\\ G(\tau_2\omega\langle\langle 1)&=G_1\\ G(\tau_2\omega\rangle\rangle 1)&=G_1+G_2\end{aligned}\right\} \tag{9}$$

On the basis of these equations, it was assumed that the experimental values of η and G for the smallest ω are $(\eta_2+\eta_3)$ and G_1, respectively, and those for the largest ω are η_3 and (G_1+G_2). The values of the parameters thus obtained

TABLE I. PARAMETERS IN MAXWELL'S FOUR ELEMENT MODEL
(in c. g. s. units)

Starch	Concentration	No.	G_1	G_2	η_2	η_3	τ_2
Potato	3%	I	22.5	129	120	13.0	0.933
		II	78.5	83.1	303	10.6	3.65
Potato	5%	I	45.3	60.0	200	15.0	3.33
		II	38.8	66.2	550	8.82	7.55
Sweet potato	5%	I	290	287	43.2	3.17	0.150
		II	268	120	411	8.01	3.43
Rice	5%	I	0.32	32.6	30.5	4.60	0.937
		II	9.21	59.6	67.6	3.41	1.13

are cited in line II of Table I. By using these values, solid curves in Figs. 2—5 were obtained. Comparing these curves with experimental plots, it is seen that $\log\eta$ decreases with the increase of $\log\omega$ more slowly in experimental plots than in Maxwell's model, and that $\log G$ increases at greater values of $\log\omega$ in experimental plots than in Maxwell's model. Moreover, it is by no means guaranteed experimentally that $\log\eta$ and $\log G$ curves are almost horizontal in the larger and smaller ranges of $\log\omega$.

Considering that these two attempts were not successful, it may be concluded that the viscoelastic behavior of starch paste can not be explained by Maxwell's four element model. Then, Rouse's model was examined. Rouse[3] studied the viscoelastic properties of high polymer solution and obtained theoretical equations. Neglecting the viscosity of solvent, η_s, because it is far smaller than the viscosity of paste, the equations are:

$$\left.\begin{aligned} &\eta=\eta_0 f_1(\tau\omega)\\ &f_1=(6/\pi^2)\sum_{p=1}^{N}[p^2/(p^4+\tau^2\omega^2)]\end{aligned}\right\}\qquad(10)$$

and

$$\left.\begin{aligned} &G=(6/\pi^2)(\eta_0/\tau)f_2(\tau\omega)\\ &f_2=\sum_{p=1}^{N}[\tau^2\omega^2/(p^4+\tau^2\omega^2)]\end{aligned}\right\}\qquad(11)$$

The values of f_1 and f_2 are given in Rouse's paper. These equations are essentially a modification of Maxwell's theory. On comparing these equations with experimental data, it turned out to be necessary to introduce a constant G_0 into Eq. 11 to give

$$G=G_0+(6/\pi^2)(\eta_0/\tau)f_2(\tau\omega)\qquad(12)$$

Referring the results of the second method of Maxwell's four element model (the line II in Table I), the value of η_0 should be equal to $(\eta_2+\eta_3)$ and G_0 to G_1 in order to satisfy the experimental values for small ω values. If it is further assumed that the value of τ is equal to τ_2 of the second method, the dotted curves in Figs. 2—5 are obtained. Values of both $\log\eta$ and $\log G$ thus calculated from Eqs. 10 and 12, respectively, are in all cases greater than experimental values. If the value of τ is to be changed to improve the agreement between the calculated values and the experimental values, the value of τ should be larger for $\log\eta$ (to shift the theoretical curves toward the left), and smaller for $\log G$ (to shift the curves to the right). Therefore, Rouse's equation can not explain both $\log\eta$ and $\log G$ simultaneously by using a common set of η_0, G_0, and τ. The other feature of Rouse's curves to be mentioned here is that $\log\eta$ decreases with the increase of $\log\omega$ too slowly and $\log G$ increases too rapidly, if they are compared with the experimental data. This difficulty will be removed if one assumes that there are large aggregates of polymer molecules with large values of η_0 and G_0 in a paste under small frequency and that the aggregates change to smaller ones of smaller η_0 and G_0 with the increase of the frequency. Such an assumption of the structural change of paste with the frequency will be discussed in detail in a following paper of this series.

Comparing the values of parameters in the line II of Table I, it is seen that the rigidity of sweet potato starch paste is much greater than potato starch paste, and both the rigidity and viscosity of rice starch paste are smaller than those of potato and sweet potato starch pastes. These are comparisons for pastes prepared by heating at 90°C for 30 min. The viscoelastic properties of starch paste would change by changing the method of preparation, so that the above stated results do not exclude an expectation that rice starch paste would have larger η and G values than potato starch paste if the pastes are cooked at a higher temperature for a longer time.

The authors wish to thank Dr. Tsurutaro Nakagawa for his kind advice concerning the construction of the rheometer. The authors also thank Dainihon Ink Manufacturing Co. for supporting this project.

Summary

The frequency dependences of dynamic viscosity and dynamic rigidity of (3 and) 5% starch pastes were measured by using a top-drive coaxial rheometer for potato starch, sweet potato starch and rice starch at 30°C. The results were compared with Maxwell's four element model and Rouse's model. Neither fit the experimental results. A structural change of the paste depending on the frequency was suggested.

Faculty of the Science of Living
Osaka City University
Nishi-ku, Osaka

---

[3] P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).