Spinnability of Liquid. A Visco-elastic State. II. Spinnability and Visco-elastic Property

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Spinnability as a Visco-elastic State

From the statements and examples in the previous paper, it seems to be almost admissible that a sort of "elasticity" accompanying the thread-forming liquids is an important factor of the spinnability phenomenon. As was stated above, by analysing the η^*-P_R curves of anomalous-viscous liquids exhibiting spinnability, we estimated the value of the elastic constant specifying that elasticity, and assumed it to be probable that spinnability is a co-operation of a viscous flow specified by a relatively small coefficient of viscosity ($\eta = 10^0 \sim 10^1$) on the one hand, and an elastic deformation corresponding to a coefficient of elasticity $G = 10^1 \sim 10^2$ on the other hand. But the determination of G by the analysis of anomalous viscosity is an indirect way, and it will not always be permissible to use Philippoff's equation without any reservation. As was mentioned already, the elasticity of spinnable liquids is not a theoretical parameter, but a physical reality which is actually observed. When a liquid thread snaps, it springs back elastically; or when these liquids are left free after a violent agitation, an elastic returning in the liquid actually occurs.

Is a direct measurement of such elasticity impossible? In our case, as is easily understood, the usual statical methods, namely, the methods of observing a static elastic equilibrium between stress and strain are inapplicable because of a marked relaxation or a flowing which accompanies an elastic deformation. The author designed thereupon the following dynamic method, in which is observed a mechanical resonance of a body which is oscillated by an oscillatory force transmitted through a torsion wire and is suffering, from a surrounding liquid, viscous resistance proportional to the deformation velocity and elastic resistance proportional to the deformation rate.

Principle of the Method for a Measurement of Visco-elastic Constants —Forced Oscillation Resonance Method

Consider a device as is illustrated in Fig. 1.[1] We shall discuss the motion of the inner cylinder when it is forced into oscillation through a torsion wire. The sinusoidal rotational displacement

$$\Theta(t)=\Theta_0 \sin \omega t$$

($\omega=2\pi\nu$; ν; frequency)

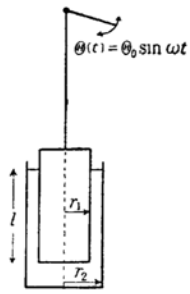

Fig. 1.

is given at the upper end of the torsion wire. The space between the inner and the outer cylinder is filled by a visco-elastic liquid.

Then

(inertial resistance of the cylinder)+(viscous resistance of the liquid)+(elastic resistance of the liquid)=(external elastic force from the torsion wire)

where

$$(\text{inertial resistance})=I\ddot{\theta}$$

I: moment of inertia of the inner cylinder

$$(\text{viscous resistance})=R_1\dot{\theta}$$

$$(\text{elastic resistance})=E_1\theta$$

$$(\text{external force})=k(\Theta-\theta)$$

k: torsion constant of the torsion wire

Therefore, the equation of motion of the inner cylinder is

$$I\ddot{\theta}+R_1\dot{\theta}+E_1\theta=k(\Theta-\theta) \qquad (1)$$

or

$$\ddot{\theta}+2\varepsilon\dot{\theta}+n_e^2\theta=L\sin\omega t \qquad (2)$$

where, $2\varepsilon\equiv R_1/I$

$n_e^2\equiv(k+E_1)/I$

$L\equiv k\Theta_0/I$

Since the transient term of the general solution of Eq. (2) damps soon, the singular solution is sufficient as long as we are concerned with a stationary state when the observation is made. The stationary state solution, therefore, is

$$\theta=\frac{L}{\sqrt{(n_e^2-\omega^2)^2+4\varepsilon^2\omega^2}}\sin(\omega t-\phi)$$

$$\equiv A\sin(\omega t-\phi) \qquad (3)$$

where, $\tan\phi=2\varepsilon\omega/(n_e^2-\omega^2)$

The amplitude of the forced oscillation of the inner cylinder is, therefore,

$$A=\frac{L}{\sqrt{(n_e^2-\omega^2)^2+4\varepsilon^2\omega^2}}\equiv L/\sqrt{f(\omega)} \qquad (4)$$

Condition of the amplitude resonance is

$$A=\max. \quad \text{or} \quad f(\omega)=\min.$$

namely $\dfrac{\partial A}{\partial\omega}=0$ or $\dfrac{\partial f}{\partial\omega}=0$

Calculation of this gives

$$\omega_{\text{res}}^2=n_e^2-2\varepsilon^2, \quad \text{or} \quad \nu_{\text{res}}=\frac{1}{2\pi}\sqrt{n_e^2-2\varepsilon^2} \qquad (5)$$

where ω_{res} and ν_{res} mean ω and ν at resonance respectively, and consequently

$$A_{\text{res}}=L/\sqrt{4\varepsilon^4+4\varepsilon^2\omega^2_{\text{res}}} \qquad (6)$$

where A_{res} means A when resonance.

If, therefore, A_{res} and ω_{res} are observed, ε and n_e are calculated from Eq. (6) and Eq. (5), so that R_1 and E_1 are known from Eq. (2).

We have, on the other hand, the next two relations[2],[3]

$$\begin{cases}\eta=\dfrac{R_1}{4\pi l}\left(\dfrac{1}{r_1^2}-\dfrac{1}{r_2^2}\right) & \text{poises}\\[2ex] G=\dfrac{E_1}{4\pi l}\left(\dfrac{1}{r_1^2}-\dfrac{1}{r_2^2}\right) & \text{dyn./cm.}^2\end{cases}$$

where η and G are the viscosity coefficient and the elasticity coefficient (rigidity, here) respectively of the fluid between the two cylinders, and r_1 and r_2 are radii of the inner and the outer cylinder respectively, l being an immersion depth of the inner cylinder.

Description of the Apparatus

An apparatus as is illustrated in Fig. 2 was constructed. A rotating disc A and another disc B which oscillates rotationally are connected to each other by a connecting rod R. R is combined to A by a pin; A is provided with several holes

(1) *Cf.* T. Kuyama. "*Kagaku*" (*Science*), **16**, 149 (1946); J. R. Van Wazer and H. Goldberg, *J. Appl. Phys.*, **18**, 207 (1947); T. Nakagawa, "*Kagaku*" (*Science*), **20**, 327, 469 (1950); T. Nakagawa, *J. Chem. Soc. Japan*, **72**, 759 (1951); T. Nakagawa, This Bulletin, **24**, 191 (1951).

(2) E. Hatschek, "The Viscosity of Liquids," G. Bell and Sons, Ltd., London, 1928.

(3) Th. Schwedoff, *J. de Phys.*, [2] **8**, 341 (1889).

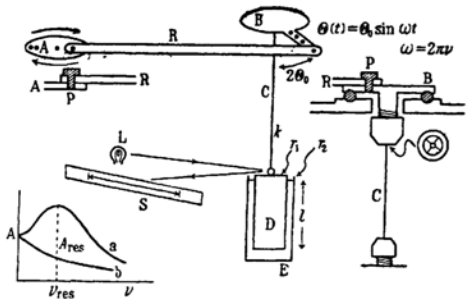

Fig. 2.

which are bored eccentrically at a distance of several millimeters to several centimeters from the center of the disc A, and is pinned by P to R by a certain suitable hole. The B—R coupling is made in a similar way by the holes bored eccentrically at the points several mm. to several cm. distant from the center of B, by using a pin P. A and B are both brass disc plates, 5~10cm. dia. and 5 mm.~1 cm. thick, R being also a brass square rod about 1 meter long. P are brass pins about 4 mm. dia. The under side of the disc B, as is shown in Fig. 2, is provided with a ball bearing to smooth its rotational oscillation. The upper and lower ends of the torsion wire C are each connected to the other body by a chuck whose head is divided in four (*cf.* Fig. 2). If the eccentricity at the A—R coupling is several millimeters, the one at the B—R coupling is several centimeters, and the length of R is about one meter, the rotational angular oscillation of B may be supposed to be almost perfectly sinusoidal. The torsion wire C is a properly selected piano wire, about 0.5 mm. dia. and about 30 cm. long. The inner cylinder D is a glass tube about 5 cm. dia. which is at the upper opening provided with a hard rubber plug to which is attached the above-stated chuck at the center, to be connected to the wire C, and this tube is filled with a proper amount of lead shot to prevent floating up on the one hand and to control the moment of inertia I on the other hand. Since ordinary piano wire has a habit of being bent, it is necessary to straighten it by giving an appreciable weight to D. The outer cylinder E is also a glass vessel about 6.5 cm. dia.

At the chuck which is the lowest end of the wire C, is attached a small galvanometer mirror which reflects a light from a lamp L onto the scale S, and we are able to observe the amplitude of rotational oscillation of D. It should be remembered here that the angle swept by light is double the actual angle of a deflection of the mirror or the body D. The disc A is driven by a phonograph motor, which is convenient to control the revolution speed.

Torsion constant k of the wire C is determined as follows from the observation of a natural frequency or a period T sec. of the free oscillation when a weight of a known moment of inertia I_{kn} is used in place of D.

$$k=4\pi^2\frac{I_{kn}}{T^2}$$

As a weight of a known moment of inertia, the author used a brass cylinder of several cm. dia. and height, whose moment of inertia is easily calculated by the formula

$$I=\frac{1}{2}Mr^2$$

(according to the rotation about the longitudinal axis)

where M and r are mass and radius of the cylinder respectively. It is recommended that several of these standard weights of various dimensions be prepared for the sake of calibrating a wide range of magnitude of torsion constant k. The standard weight, too, is provided with an above-stated fastening chuck to be easily connected to the wire. One of them, for example, which we used, has a value of $I=1.96\times10^3$ g. cm.^{2} ($M=791.2$ g., $r=2.23$ cm.).

With k thus determined, we are able to know the moment of inertia I of the inner cylinder D, by observing a period T sec. of its free oscillation, according to the formula

$$I=\frac{kT^2}{4\pi^2}$$

The procedure of the observation is as follows. A liquid to test is placed between D and E, and a dipping l is properly controlled. Oscillation is started. Inspecting the amplitude of a light spot on S, we vary a revolution speed of the motor or A, and consequeptly a frequency of oscillation of B. (In the case of a phonograph motor, we can easily perform this procedure by an accessory speed controlling arm.) As is shown in the curve (a) of Fig. 2, at a certain value of a frequency, the amplitude of the motion of D reaches a maximum which is of course greater than the amplitude of the driving disc B; in other words, a mechanical resonance of D occurs. Record the resonance frequency ν_{res} and the amplitude of a light spot on S at resonance. Then the above-mentioned analysis gives us the values of η and G of the sample; the amplitude of a light spot on S must be of course reduced to the value of the actual angular amplitude A_{res} of D. It must be remembered that when the dipping l, accordingly R_1, is too large, a maximum of the amplitude does not appear (*cf.* case (b) of Fig. 2).

Measurements were carried out under the following condition.

$k=1.89\times10^4$ dyn·cm.

I (of the inner cylinder) $=1.225\times10^3$ g. cm.^{2}

$\theta_0\fallingdotseq0.1$ radian

$r_1=2.4$ cm., $r_2=3.3$ cm.

$l=$ several cm.

The frequency of the free oscillation (for the determination of k or I), and the resonance frequency ν_{res} were all in the neighbourhood of

Table 1

Substance	Spinnability, cm.	η, poises	G, dyn./cm.^{2}	Conc., % wt.	Remarks
Rubber-xylene (I)	4.5	9.3	6.3		series coupling
Rubber-xylene (II)	11.0	51.	105.	3.6	series coupling
Extract of root of *Hibiscus Manihot* L.	1.0	11.3	27.6	2.9	series coupling
Hg sulphosalicylic acid aq. soln. (I)	5.5	4.2	27.8	4.2	series coupling
Hg sulphosalicylic acid aq. soln. (II)	4.5	4.2	35.0	3.1	series coupling
Starch paste	0	5.5	40.0		parallel coupling
Sucrose aq. soln.	0	11.9	0	68.	purely viscous
Water glass aq. soln.	0	16.6	0	61.	purely viscous

1 cycle per second. The resonance amplitude A_{res} was about 0.2 radian.

Experimental Results

In this way, Table 1 was acquired. As is seen in the table, the Newtonian liquids as a sucrose solution and a water glass solution do not exhibit spinnability even at the comparatively higher viscosities; that these purely viscous liquids require viscosity of 40~50 poises or more to become thread-forming, was already stated. Typically thread-forming liquids, on the other hand, as a rubber solution, an extract of a root of *Hibiscus Manihot* L., a solution of mercury sulphosalicylic acid etc. possess marked elasticity besides relatively low viscosity as is read in the table. Such co-operation of a simple viscous flow and an elastic deformation is responsible for the typical spinnability phenomenon. A thread-forming state is an elastic deformation like the elongation of a rubber string, superposed upon a viscous flow streaming down from above. This elastic deformation, however, is one which corresponds to a relatively small λ, time of relaxation. When this relaxation time is in the same order as our observation time $\mathfrak{t}$ (0.1~1 sec.) at the spinnability test, displacement is nearly elastic (reversible). But for a test of a sufficiently long period the displacement becomes viscous (irreversible). So that even in the typically spinnable liquids spinnability does not appear when they are treated by means of a very slow observation speed; a liquid thread will not be formed when a rod is raised up too slowly from a liquid.

Starch paste exhibits no spinnability in spite of its typically visco-elastic nature; this fact will be discussed later.

Spinnability (cm.), as was already described in the paper I, means the maximum length of the liquid thread spun between the surface of the liquid and the tip of the ascending rod, which is an arbitrary measure of the thread-forming ability of a liquid.

Discussions

(A) Optimum Values of η and G for Spinnability.—We have thus an idea that spinnability or the thread-forming property of some liquids is a superposition of a simple viscous flow and an elastic deformation, and determined experimentally the value of a viscosity coefficient specifying the degree of flowing and an elasticity coefficient specifying the extent of an elastic deformation. Now the next problem is to know the optimum values of η and G for thread-forming liquids to exhibit the most remarkable spinnability. To estimate these values, the author experimented as follows.

As is shown in Fig. 4 of Part I, spinnability of a raw rubber—xylene solution has a maximum at a concentration of 3~4% by weight. Direct measurement of viscous elasticity of a 3.6% solution gives the following values (*cf.* Table 1)

$$\eta=51 \text{ poises}, \quad G=105 \text{ dyn./cm.}^2$$

These values will presumably indicate the order of the optimum values for spinnability. According to Maxwell's relation, the time of mechanical relaxation λ is

$$\lambda=\eta/G\fallingdotseq 0.5 \text{ sec.}$$

This value of λ is just the same order of the time-scale $\mathfrak{t}$ of our experimental investigation or the experimenting speed when we test the existence of spinnability. That the mechanical relaxation velocity of a system just coincides with the testing velocity, is a necessary condition for the appearance of the most remarkable spinnability. The case stated here just satisfies this condition.

(B) The Problem of the Coupling Type of η and G.—As was referred to previously, starch paste, a typical visco-elastic substance, does not exhibit spinnability. How is it explained?

The behavior of a material exhibiting a flow superimposed upon elasticity can be represented by means of mechanical models as follows (*cf.*

Fig. 3).[4],[5] Here the elastic mode of response to stress is indicated by a "spring", and the flow mechanism by a "dashpot" in which a

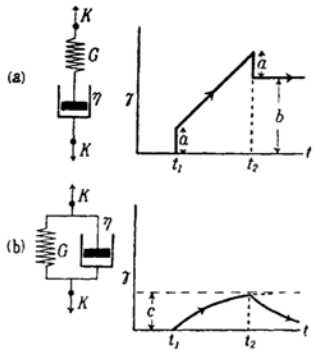

Fig. 3.

porous piston is assumed to move in viscous fluid. If stress is imposed, the ends can move either by a stretching of the spring, or by a flow in the dashpot. The response of the material to a stress can, in this way, be translated into the corresponding behavior of the mechanical model. As the simplest of such models of viscous elasticity, the next two types, as is illustrated by (a) and (b) of Fig. 3, are assumed. Take first the model (a). Impose a constant stress K at the ends, and plot the displacement γ against time t, then the behavior of the system will be as shown in the right-hand diagram of (a). When the stress K is applied at the time t_1, the spring instantaneously stretches to the amount a corresponding to (K/G), and at the time the dashpot begins to elongate steadily at the rate (K/η). When the stress K is removed at the time t_2, the spring instantaneously contracts by the amount a, but the dashpot remains in its elongated condition, and the amount of viscous flow b during the time (t_2-t_1) does not recover permanently.

Consider the second case (b). This device differs from that of the case (a) in that the spring and the dashpot are coupled in parallel, not in series. When the stress K is applied at t_1, the elastic stretching of the spring does not occur in phase with the stress, on account of the viscous damping resistance which is coupled in parallel with the spring. The equilibrium position of elastic deformation is reached asymptotically. And, moreover, unlike the case (a), total displacement does not exceed a value c corresponding to (K/G), even if the loading continues forever. When the load is removed at t_2, the ends return completely to the initial position of zero displacement through the same asymptotic path as above. Such a deformation type is called retarded elastic response, and such a time effect is called elastic after-effect.

Now the series mechanical model (a) is fit to symbolize the mechanical behavior of thread-forming fluids, for it is capable of elongating infinitely by a certain stress. The parallel model (b) is a case of a finite elongation for a certain stress, and the attempt to elongate it at a constant speed, seems to produce splitting or breaking into pieces, without forming a thread. When we call the former case (a) the series coupling and the latter (b) the parallel coupling of viscosity and elasticity, the mechanical behavior of starch paste may correspond to the latter *viz.* the parallel type of visco-elasticity.

Summary

According to the experiments and considerations presented above, a mechanical model as Fig. 4 is introduced for the thread-forming state of liquid. The thread-forming state is the "series" coupling of elasticity corresponding to $G=10^0\sim10^2$ dyn./cm.^{2} (some millionth of G for rubber) and viscosity which corresponds to $\eta=10^0\sim10^1$ poises (some thousands times η for water).

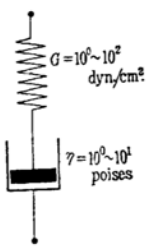

Fig. 4.

This is spinnability.

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(4) T. Alfrey, "Mechanical Behavior of High Polymers," Interscience Publishers, New York, 1948.
(5) R. Houwink, "Elasticity, Plasticity and Structure of Matter," Cambridge Univ. Press, London, 1937, p. 64.