Spinnability of Liquid. A Visco-elastic State. I. Spinnability and Anomalous Viscosity

By Tsurutaro NAKAGAWA

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Introduction

It is well-known that some substances which are usually considered as "liquids" have a marked thread-forming property as is shown by Fig. 1. The so-called mucilaginous fluids, such as egg-white, vitreous humour of the eye, saliva, secretion of the various mucous membranes, mucus from seaweeds, extraction of the root of *Abelmoschus Manihot* Medicus (*Hibiscus Manihot* L.), mucus of a taro, mucus of "nattô" (fermented beans), and other rotten or fermented things, all possess this peculiar property; furthermore in the laboratory, we see the phenomenon in a raw rubber-benzene solution, aq. solution of mercury sulphosalicylic acid, and in some coacervates. When we raise a stirring rod from these liquids, or when the liquids are poured out of a beaker, a very long and fine thread is spun which sometimes reaches a length of 30~40 cm. or more.

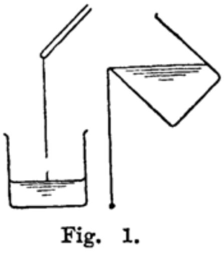

Fig. 1.

To what is this phenomenon attributed? One may ascribe it to the high viscosity which is characteristic of the solution of polymeric substances; but the impropriety of this assumption will be understood by the fact that the other high-viscous polymer solutions, for example, starch solution, gelatin sol, or agar-agar sol, pectin sol, etc. show no spinnability. Recognizing that the spinnability of liquid is not solely related to the viscous flow, what is the other factor to be added?

Inspection of the examples cited above gives us two general ideas; first, from the chemical point of view, they are high-polymeric solutions, and second, from the physical point of view, they are in the colloidal state. Mechanical properties of these high-polymeric or colloidal states consist of many non-ideal peculiarities: their deformation is non-Hookean, and their flow is non-Newtonian. From the standpoint of relaxation phenomena, the time of mechanical relaxation λ of these high-polymeric, colloidal and the so-called "amorphous" substances is finite. Deviations from the ideal behavior of the mechanical properties of these high-polymeric materials depend chiefly upon this finite relaxation time. Because of the fact that λ is comparable with the time of our observation $\mathfrak{T}$, the mechanical behavior of those amorphous substances usually appears as a relaxation phenomena. According to the relative magnitude of λ to $\mathfrak{T}$, the apparent mechanical behavior of the subject shows much variety; in other words, the time-effect is remarkable in the mechanical properties of high-polymers.

One of the phenomenological treatments to describe systematically these non-ideal, time-sensitive mechanical properties is the theory of the "visco-elastic or elastic-viscous state". By this method, various actual anomalies of the mechanical behavior are described quantitatively as a function of the "magnitudes" of η (viscosity coefficient) and G (elasticity coefficient) and of the "type" of coupling of η and G. Now that our spinnable (thread-forming) liquids are generally high-polymeric or colloidal solutions, the above-stated concept of a visco-elastic state will be applicable to this peculiar mechanical property. Supporting this view, we actually observe some elastic property in these spinnable liquids; a liquid-thread springs back elastically when it breaks, or these liquids in a vessel turn back in the opposite direction when we rotate it in one direction and then hold it.

In this essay, the spinnability of liquids is treated from these points of view.

Tammann and Tampke⁽¹⁾ measured spinnability by the maximum length of a liquid thread formed when a rod is raised from a spinnable liquid as is shown by Fig. 2. This method seems to be the most convenient and popular.

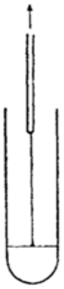

Fig. 2.

Jochims⁽²⁾ found out that viscosity is not the single factor which causes spinnability and determines the degree of spinnability, and that an elastic scaffolding existing in such a liquid is another important factor.

H. Erbring⁽³⁾ first treated it systematically and extensively as a colloid-chemical problem; his general conclusion drawn out of his experiments is outlined as follows. He used Tammann and Tampke's principle (Fig. 2) to express the degree of spinnability quantitatively. From his measurements on an extract of flax-seeds, mucilage of quince, solutions of gum Arabic, mercury sulphosalicylic acid, acetyl cellulose, cotton-yellow, aluminium soap, polystyrene, sodium stearate, sodium silicate, polyvinyl alcohol, and viscose etc., some coacervates, for example, a gelatin-phenol coacervate and a gelatin-starch coacervate etc., Erbring gained the following general aspects on the spinnability phenomenon; (a) spinnability does not simply depend upon viscosity of liquid, (b) surface tension also is not an important factor, its influence being negligible for markedly spinnable liquids, (c) a sort of "elasticity" plays a principal rôle in this phenomenon, (d) spinnability is a phenomenon relating to a particular colloid-chemical "state" of a substance, and not to a special chemical species, (e) spinnability seems to be owing to some "structure" in liquid, both a proper fluidity (viscosity) and a proper consistency (structure) being important for the appearance of spinnability, (f) the existence of rod-shape or long-chain molecules in liquid seems to be necessary, (g) structural viscosity (non-Newtonian flow) is closely related to spinnability.

Measurement of Spinnability

As the first step, the author constructed an apparatus for observing quantitatively the degree of spinnability after the Tammann-Erbring method,⁽³⁾ in which the degree of spinnability is expressed by the maximum length of a liquid thread spun by a rod raised out of the liquid.

(A) **Apparatus**—Since the maximum length of a liquid thread depends appreciably upon the velocity of the ascending of a testing rod,

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(1) G. Tammann and R. Tampke, *Z. anorg. allgem. Chem.*, **162**, 1 (1927).

(2) J. Jochims, *Koll. Z.*, **61**, 250 (1932).

(3) H. Erbring, *Koll. Beih.*, **44**, 171 (1936); *Koll. Z.*, **77**, 32, 213 (1936); *ibid.*, **80**, 20 (1937); *ibid.*, **98**, 164 (1942) or *Chem. Abs.*, **36**, 6393 (1942).

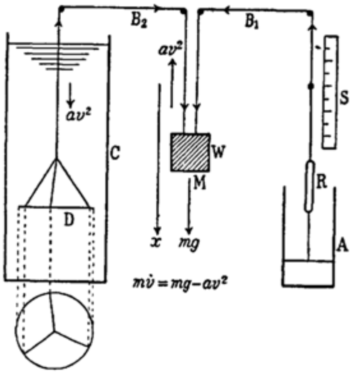

Fig. 3.

R, a velocity controlling device as is shown by Fig. 3 was constructed. The rod R is driven by a weight W and some pulleys, and acceleration of W is suppressed by a damper D moving in water, so that a constant terminal velocity is gained, which is voluntarily controlled if W is changed. The terminal velocity is attained soon after starting.

D is a disc of 16 cm. dia. Weight of W and D is 120 g. and 70 g. respectively, so that the effective driving weight of W is approximately 30 g., assuming empirically that the total frictional resistance at the mechanical contacts is equivalent to about 20 g. Then the velocity of R can be controlled in the neighbourhood of 5 cm./sec. Reproducibility is satisfactory. (Fluctuation of the measured maximum thread length is less than 5 mm.)

(B) Spinnability of simple high-viscous liquids: trivial case of spinnabiliy.—The most simple and trivial type of spinnability is one by very high viscosity of liquid, for then a liquid column is formed between the surface of the liquid and the tip of a rising rod because of the slowness of the liquid supply downward from a rod (Erbring's "Nachlieferungsvorgang"). From what value of viscosity does this simple spinnability due to the slow supply appear? The author experimented as follows.

As the comparatively high-viscous liquids whose flow are ideally Newtonian, exhibiting neither elastic property nor structural viscosity (anomalous viscosity), two solutions were taken, namely (a) conc. aq. solution of sucrose and (b) aq. solution of water glass (sodium silicate). Sucrose is suitable for preparing a high-viscous solution because of the difficulty of crystallizing out of a supersaturated solution.

Viscosities of these solutions at various concentrations and temperatures were measured by the falling-sphere method. The capillary method viscosimetry is not applicable on account of their high viscosity. In our case, η was calculated from the time t sec., necessary for a steel ball of radius 0.07875 cm. ($D=7.80$ g./cm.^{3}) to fall down 15 cm. along the central axis of a liquid column of radius 1.4 cm. and of height 30 cm. Thus, viscosities ranging in $2\sim600$ poises were measured.

Taking these solutions, the author measured the degree of spinnability by the above-stated apparatus. The viscosity of a solution at the time when spinnability first appears is thus known.

In this way, the following conclusion was drawn out.

A solution of any concentration generally begins to exhibit spinnability at a temperature at which viscosity amounts to $40\sim50$ poises; in other words, at least $40\sim50$ poises of viscosity are necessary for a simple high-viscous liquid to produce spinnability. This critical viscosity is $4000\sim5000$ times as large as the viscosity of water.

It should however be noticed that, as will be stated below, typically spinnable liquids exhibit marked spinnability at the viscosity far lower than this.

(C) Spinnability of raw rubber solutions.—Solutions of raw rubber in xylene, toluene, and benzene etc. are, as egg-white and saliva, typically spinnable. Using the above-mentioned apparatus, spinnability (expressed by the maximum thread-length, L cm. before breaking) of a raw rubber—xylene solution at various concentrations was measured, by changing a lifting velocity, v of the rod R (*cf.* Fig. 4). As is clear from Fig. 4, spinnability—concentration relation has a maximum, showing that the $3\sim4\%$

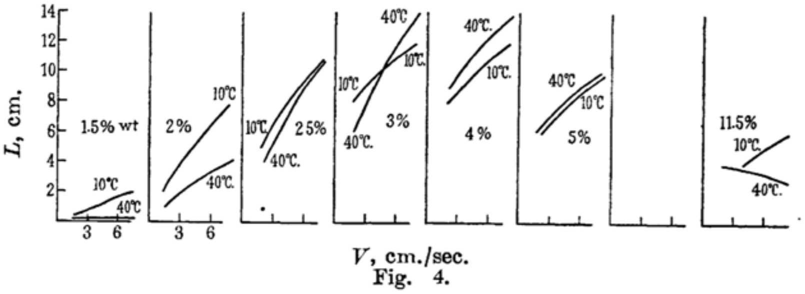

Fig. 4.

solutions exhibit the most remarkable spinnability. This result may be explained as follows by a concept of relaxation phenomenon. Spinnability increases with the increase of concentration or viscosity, but with too much increase of viscosity, a liquid becomes too rigid to follow the testing rod rising upwards with the velocity of several cm. per second, and the breaking occurs: in other words, spinnability is maximum when the time of relaxation of the solution is optimum in comparison with the time of observation or velocity of measurement. Optimum concentration, or the maximum in the concentration—spinnability curve thus takes place.

In marked contrast with sucrose solution in which at least 40∼50 poises of viscosity are necessary for it to exhibit spinnability, raw rubber solution, as illustrated in Fig. 4, shows marked spinnability even at 2 poises corresponding to a concentration of 2%. Saliva is also said to have obvious spinnability in spite of viscosity less than 1 poise. The foresight of Jochims,(2) Erbring(3) etc. seems to be correct, for they sought to attribute the remarkable spinnability of such typical spinnable liquids of comparatively low viscosity to a sort of "elasticity" coexisting with viscosity. The concept that spinnability is a co-operation of "viscous flow" streaming down from the tip of a rod and "elastic deformation" analogous to the elongation of a rubber string, appears to be correct.

Anomalous Viscosity (Structural Viscosity)

(A) Anomalous Viscosity. — Non-Newtonian flow is characteristic of most colloidal solutions, especially lyophile ones. In these cases, viscosity η is not a constant independent of shearing stress of flow, but generally decreases with the increase of the velocity gradient. The so-called Hagen-Poiseuille's law in the capillary flow does not hold.

When the Newtonian liquids are made to flow through a capillary of radius r and length L by means of a pressure p, and a volume v of fluid passes through it in a time t_0 sec., then viscosity η of a liquid is according to Hagen-Poiseuille's law

$$\eta=\frac{\pi p r^4 t_0}{8vL}=\text{const.}\times p t_0 \qquad (1)$$

$$(\text{provided } v=\text{const.})$$

In the ordinary Newtonian liquids, η or pt_0 is independent of p. In most of lyophile colloidal solutions, on the other hand, pt_0 is not independent of p, but generally decreases with the increase of p. Wo. Ostwald ascribed this effect to the destruction of an internal structure by the shearing stress of flow, and called it "structural viscosity"; but strictly, this effect might not always be attributed to this sole mechanism, and it will be rather safe simply to say anomalous viscosity or non-Newtonian flow (*cf.* Fig. 5).

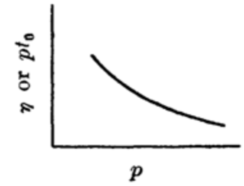

Fig. 5.

Philippoff(4) assumed a sort of elasticity in the non-Newtonian colloidal liquids, and presented the following formula,

$$\left.\begin{aligned}\eta^*&=\eta_\infty+\frac{\eta_0-\eta_\infty}{1+2P_R^2/(3G^2)}\\ P_R&=rp/(2L)\end{aligned}\right\}\qquad (2)$$

where η^* is the apparent viscosity gained from Eq. (1) into which we insert the experimental data mechanically (though, strictly speaking, it is nonsense to use Eq. (1) for non-Newtonian liquids). P_R means the shearing stress at the wall of a capillary, whose radius and length are r cm. and L cm. respectively, when pressure p dyne/cm.^{2} is given on the end of a capillary; this is also a formal diversion of the relation which holds only in the Newtonian flow, in which shearing stress changes linearly from zero at the central axis of a capillary to a maximum value at the wall of it as is given by the under formula of Eq. (2). η_0 and η_∞ are constants and correspond to $[\eta^*]_{P_R\to 0}$ and $[\eta^*]_{P_R\to\infty}$ respectively. G is a coefficient of the so-called fluid-elasticity, and in the case of the capillary flow, means a torsional elastic constant or rigidity. Thus, if we adopt the standpoint of Philippoff, it is possible to estimate the magnitude of an elastic constant of a sol by means of an experimental η^*—P_R curve.

(B) Anomalous Viscosity of the Spinnable Solutions.—The author studied elasticity of the typically spinnable liquids following Philippoff.

Since η must be plotted as a function of pressure p, the common Ostwald's viscometer

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(4) W. Philippoff, *Koll. Z.*, **71**, 1 (1935); *ibid.*, **75**, 142, 155 (1936); *ibid.*, **83**, 163 (1938).

is inapplicable. As the most suitable type for such experiments, the author used Tsuda's horizontal capillary viscometer.⑸ A voluntarily changeable pressure p is applied from the two large glass vessels which are connected to each other and each is filled with a certain amount of water, and then p equals the difference of the water-head of the two vessels.

Strictly speaking, all capillary type viscometers are in principle improper for the study of anomalous viscosity, because, in the capillary flow, the shearing stress P varies with the radial distance from the center of a capillary, so that the shearing stress at the wall is maximum and is zero at the center of a tube. This fact is not consistent with our aim to know η in relation to the shearing stress P. Couette's rotational viscometer is the most rational, for in this case the shearing stress P is almost constant, independent of the radial distance as long as the gap between the two cylinders is small as compared with radii of the two cylinders. Nevertheless Tsuda's horizontal capillary viscometer is preferable to the rotation type from the practical point of view; the latter is accompanied with some faults, namely, the structural complexity and the difficulty in controlling temperature.

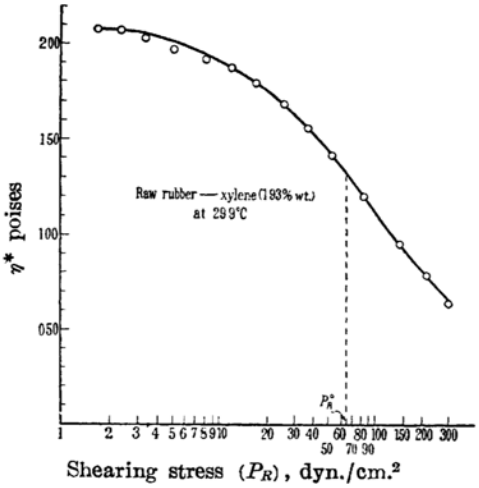

Fig. 7.

Experimental results on anomalous viscosity of xylene solution of raw rubber ("pale sheet") are illustrated in Fig. 6 and Fig. 7. For reference, the η^*—P_R curves for sucrose solution aq. and vanadium pentoxide sol are added in Fig. 6. Take three sets of (η^*, P_R) values, then from Eq. (2) three constants G, η_0 and η_∞ can be determined. Using, for example, from the lower curve about raw rubber—xylene system in Fig. 6, the following three points

$$\left\{\begin{array}{lll} \text{A} & (P_R=\ 2.43, & \eta^*=0.933), \\ \text{B} & (P_R=17.2, & \eta^*=0.791), \\ \text{C} & (P_R=85.6, & \eta^*=0.497), \end{array}\right.$$

we obtain

$$G=21.6 \text{ dyn./cm.}^2, \qquad \eta_0=0.935 \text{ poise}$$
$$\eta_\infty=0.450 \text{ poise}$$

Or, since the inflection point of Eq. (2) can be determined from the condition

$$\frac{\mathrm{d}^2\eta^*}{\mathrm{d}P_R{}^2}=0, \tag{3}$$

it is obtained from Eq. (2) and Eq. (3), the next formula, provided P_R° means a value of P_R at the inflection point.⑷

$$G=\sqrt{\frac{2}{3}}\,P_R^\circ=0.815\,P_R^\circ$$

Using, for example, $P_R^\circ=60\sim70$ from Fig. 7,

$$G \doteqdot 50 \text{ dyn./cm.}^2$$

This is another procedure of determining G.

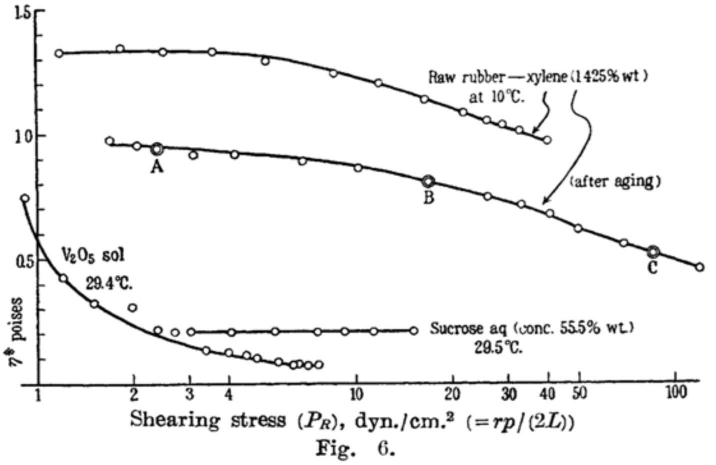

Fig. 6.

Maxwell's classical formula relating the time of mechanical relaxation λ

$$\lambda=\eta/G$$

becomes

$$\lambda=\eta_0/G$$

in the case of Philippoff's formulation of anomalous viscosity. From the above-gained

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⑸ S. Tsuda, *Koll.—Z.*, **45**, 325 (1928): Wo. Ostwald and H. Malss, *Koll.—Z.*, **63**, 61 (1933).

$\eta_0 = 0.935,\ G = 21.6,$

$$\lambda \doteqdot 0.04\ \text{sec.}$$

Since, on the other hand, our observation time, when we speak of the appearance of spinnability, is supposed to be 0.1～1 sec., the rubber solution of such a low concentration (1.5%) has a relaxation time much less than our observation time. Accordingly, the tendency to flow down is much stronger than the tendency to elongate to a liquid-thread, so that spinnability is not yet remarkable, as illustrated above (Fig. 4). However, as will be discussed later again in Part II, in a 3～4% rubber solution λ becomes the order of 0.5 sec., so that marked spinnability is observed on account of the fact that the relaxation time λ is comparable with our observation time. With the increase of the concentration moreover, λ of the fluid becomes presumably far larger than the observation time $\mathfrak{T}$. This situation, that the deformation of fluid can not follow the testing velocity, results in the snapping or breaking of a thread rather than extending or elongating it; spinnability decreases in this way (*cf.* Fig. 4).

Summary

Simple viscous liquids become thread-forming first at the viscosity of 40～50 poises or more.

Spinnability of typical thread-forming liquids is characterized by the co-operation of the far smaller viscosity and some "elasticity."

Department of Chemistry, Faculty of
Science, Tokyo University, Tokyo