MODEL OF ELASTIC DEFORMATION IN DESCRIBING THE STRETCHING OF POLYMER SOLUTIONS

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It is shown that the tension of solutions in the case of large elastic strains can be described by means of rheological equations for cross-linked rubber.

In [1-3, 6] the hypothesis was advanced that the strain orientation caused by large elastic strains which occur in the flow of viscoelastic liquids results in loss of fluidity by the liquids, which henceforth behave in a manner similar to a purely elastic medium. Using this hypothesis as a basis, below we examine the following phenomena: stretching of a stream of viscoelastic liquid from a container with 1) a free surface; 2) an open siphon.

The first phenomenon was initially studied in [4, 5], where certain suction devices were used to stretch-form a polymer stream from a tank. Similar experiments were conducted in [6] with a solution of polyethylene oxide (PEO), mainly of 0.5% concentration. However, here the liquid was withdrawn from a vessel by means of a rotating drum. A diagram of this experiment is shown in Fig. 1. In the case of the 0.5% solution of PEO, the maximum (Newtonian) viscosity of which at 22°C was $\eta \simeq 0.15$ Pa•sec and the relaxation time $\theta \simeq 0.7$ sec (evaluated from dynamic tests in the linear strain region), the length of the steadily stretched stream reached 0.5 m.

It is curious to note that a 40% solution of butyl rubber in transformer oil for which $\eta \simeq 10^3$ Pa•sec and $\theta \approx 1$ sec cannot be stretched by the above method.

Steady-state flow of a PEO solution with a strain rate decreasing along the stream can be realized only within a limited range of flow rates q. These flow rates are completely determined by the profile of the stream, i.e., by the dependence of the stream radius on the longitudinal coordinate (Fig. 2). The stream ruptures at low flow rates. At high flow rates, it becomes asymmetrical and the flow rate begins to fluctuate. It is also important to note that the velocity of the liquid stream near the rotating drum is generally lower than the drum speed, i.e., the stream slips relative to the drum.

The open siphon phenomenon [7] consists of the fact that a stream of polymer solution, under the influence of its own weight, will pull the remaining solution from a previously inclined vessel. One of the possible schemes of elastic siphoning is depicted in Fig. 4 and discussed below.

Drawing a Viscoelastic Liquid with a Free Surface from a Vessel. The following three regions of deformation can be distinguished in the steady-state stretching of a viscoelastic stream with a free surface (Fig. 1): I) region of nearly uniform tension, where the stream radius changes little along the z axis ($dr/dz \ll 1$); II) region close to the free surface, where the flow is not one-dimensional and the stream radius undergoes a sharp change; III) region under the free surface, where the flow is evidently close to radial.

In region I, the steady-state equations of conservation of mass and momentum, averaged over the stream cross section, have the form

$$Sv = q = \text{const}, \tag{1}$$

$$\frac{d}{dz}(\sigma S) = \rho g S - 2\sqrt{\pi}\,\sigma^* \frac{dS^{1/2}}{dz}, \tag{2}$$

where ρ = const; the z axis, which originates at the level of the free surface, is directed along the stream. Equation (2) is written in a noninertial approximation, which is acceptable if the following inequality is observed:

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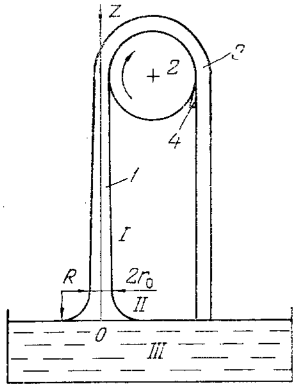

Fig. 1

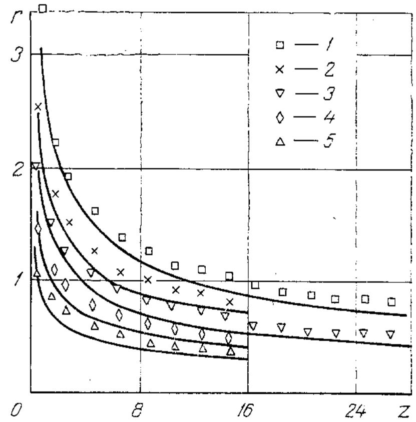

Fig. 2

Fig. 1. Diagram of withdrawal of a polymer solution from a container with a free surface using a rotating drum: 1) solution stream being withdrawn; 2) rotating drum; 3) stream flowing off drum; 4) scraper; I, II, III) regions of deformation of solution.

Fig. 2. Theoretical (curves) and experimental (points) dependence of stream radius r (mm) on longitudinal coordinate z (cm) for a 0.5% water solution of polyoxyethylene: 1-5) q = 1.14, 0.58, 0.36, 0.17, and 0.09 $cm^3 \cdot sec^{-1}$, respectively.

$$\rho q \frac{dv}{dz} \ll \rho g S. \tag{3}$$

Let us assume that the behavior of the solution in region I of stream flow is similar to that of cross-linked rubber [1, 2]. In this case, the components of the elastic strain tensor X have the form: $x_{zz} = x,\ x_{rr} = x_{\varphi\varphi} = x^{-1/2}$.

Let us also assume that $x \gg x_{cr} \gg 1$, where x_{cr} is the critical value of elastic strain at which the solution loses fluidity. Then, allowing for the effect of surface tension on isotropic pressure, the stress σ, averaged over the cross section of the stream, can be written in the form

$$\sigma = \frac{4\mu}{n} x^n - \frac{\sigma^*}{r}\left(1 - r\frac{d^2r}{dz^2}\right). \tag{4}$$

The first term in Eq. (4) corresponds to the simplified two-parameter BST potential [8]

$$W = \frac{2n}{\mu} \operatorname{Sp}(\underline{\underline{x}}^n - \underline{\underline{\delta}}),$$

which is convenient for approximating empirical data. It should also be noted that Eq. (4) may also contain the term $3\eta_1 dv/dz$, describing the phenomenon of delayed elasticity. However, as can be shown on the basis of the results in [6], in this case

$$3\eta_1 dv/dz \ll \sigma.$$

Further, considering that at z > R (where R is the radius of the meniscus, see Fig. 1)

$$x = x_0 \frac{r_0^2}{r^2} = x_0 \frac{S_0}{S}, \tag{5}$$

Eq. (4) can be written as follows:

$$\sigma = G_*^0 \left(\frac{S_0}{S}\right)^n - \frac{\sigma^* \sqrt{\pi}}{S^{1/2}},\quad G_0^* = \sigma_0 + \frac{\sigma^* \sqrt{\pi}}{S_0^{1/2}}. \tag{6}$$

In deriving Eq. (6), it was assumed that

$$r\frac{d^2r}{dz^2} \ll 1. \tag{7}$$

The solution of Eq. (2), after the substitution of Eq. (6) into it, has the form

$$G_0^* \frac{n-1}{n}\left(\frac{S_0^n}{S^n}-1\right)-\sigma^* \sqrt{\pi}\,(S^{-1/2}-S_0^{-1/2})=\rho g(z-R). \tag{8}$$

To determine the initial values of stress σ_0 and stream radius r_0 at $z = R$, it is necessary to examine the behavior of the liquid in the regions II and III. Region III, as shown by the experiments in [6], is not essential to the subsequent analysis. This is because the stress in the stream is determined mainly by the weight of the liquid column above the free surface (in regions I and II) and, to a lesser degree, by surface tension. As regards the transitional region II, in a rough approximation it can be characterized by the dimensions R and r_0 (see Fig. 1). Assuming that the deformation of the liquid in region II is due mainly to its elasticity, we may write the following out of dimensional considerations:

$$R=\alpha(q\theta)^{1/3},\quad r_0=\beta(q\theta)^{1/3}. \tag{9}$$

The values of the constants α and β can be found empirically by measuring the meniscus, as was done in [6]. Here, too, we cite certain geometric considerations, making it possible to calculate α and β and obtain values close to the empirical values.

As already noted, the stress σ_0 at the beginning of region I (i.e., at $z = R$) is determined by the weight of the liquid column in region II and by the force created by surface tension. Using an exact expression for the stress from surface tension

$$P_{\sigma_*}=\frac{\sigma^*}{r}\left[\frac{1}{\sqrt{1+r'^2}}-\frac{rr''}{(1+r'^2)^{3/2}}\right]$$

and taking into consideration the approximate formula

$$r(z)\approx r_0+R-\sqrt{R^2-(R-z)^2},$$

describing the meniscus in region II (see Fig. 1), it is not difficult to obtain an expression for σ_0:

$$\sigma_0=\frac{F_0}{\pi r_0^2}=\rho gRm+\frac{2\gamma\sigma^*}{R},$$

$$\gamma=\alpha/\beta,\quad m(\gamma)=\gamma^2\left[\frac{2}{3}+\left(1+\frac{1}{\gamma}\right)^2-\frac{\pi}{2}\left(1+\frac{1}{\gamma}\right)\right]. \tag{10}$$

In (10), the first term on the right side is due to the force of gravity, while the second term describes the contribution of surface tension to the total force F_0.

The quantity σ_0, regarded as a function of R (see (10)), passes through a minimum min σ_0 at a certain value of R_0. The corresponding values min σ_0, R_0, and q_0 (based on Eq. (9)) have the form

$$\min\sigma_0=2\sqrt{2\rho g\sigma^* m\gamma},\quad R_0=\sqrt{\frac{2\gamma\sigma^*}{\rho gm}},\quad q_0=\frac{1}{\theta}\left(\frac{2\gamma\sigma^*}{\rho gm\alpha^2}\right)^{3/2}. \tag{11}$$

Since $R \sim q^{1/3}$ (see (9)), Eq. (10) gives the relation between the flow rate q and the initial tensile (stretching) stress σ_0. If $R < R_0$ ($q < q_0$), the relation $\sigma_0(R)$ (or $\sigma_0(q)$) is decreasing. As a result, it is evidently unstable. Thus, the values of R_0 and q_0 determined from Eqs. (11) can be regarded as certain critical values, below which the steady-state flow being studied no longer exists.

Having determined σ_0 and r_0 from (9) and (10) for the case when surface tension in region I is insubstantial ($\rho gRm \gg 2\sigma^*/r_0$), we can use Eq. (8) to find an expression for the stream profile

TABLE 1. Lower Critical Values q_0 and R_0 in Relation to the Surface Tension σ^*

σ^*, Pa·cm	6,0	6,2	6,4	6,6	6,8	7,0
R_0, cm	0,330	0,335	0,341	0,346	0,351	0,356
q_0, cm^3·sec^{-1}	0,0846	0,0889	0,0932	0,0976	0,1020	0,1066

$$\frac{r}{r_0} = \left(\frac{z}{cR} + \frac{c-1}{c}\right)^{-1/2n}, \quad c = \frac{n-1}{n} m. \tag{12}$$

At z >> R, Eq. (12), with allowance for (9), can be represented in the form

$$\frac{r}{r_0} \approx \left(\frac{cR}{z}\right)^{1/2n}. \tag{13}$$

It follows from (12) and (13) that n > 1, since only in this case will the stream radius decrease slightly with an increase in z. This ensures the existence of long streams, i.e., ensures the property of so-called spinability. With a change in flow rate or temperature (the effect of which is due to the strong dependence of θ on T), the corresponding profiles r(z) at z >> R will differ only by constant multipliers dependent on q and θ, as follows from (9) and (13).

At z >> R, the expressions for velocity v and the longitudinal component of the strain-rate tensor have the form

$$v(z) = v_0 (z/cR)^{1/n}, \quad v_0 = q/\pi r_0^2, \tag{14}$$

$$\varkappa = \frac{v}{nz} = \frac{v_0}{n}(cRz^{n-1})^{-1/n}. \tag{15}$$

We find from these formulas that v and ϰ are slightly dependent on q (specifically, as $q^{\frac{n-1}{3n}}$). Meanwhile, ϰ decreases with an increase in z.

It follows from (8) that in the case being examined, when $\frac{2\sigma^*}{r_0} \ll \rho g R m$, the tensile stress σ can be expressed as follows:

$$\sigma = \rho g\left(\frac{n}{n-1} z + Rm\frac{c-1}{c}\right). \tag{16}$$

It follows from (9) and (16) that the contribution to σ of the weight of the liquid column ceases to be dependent on the flow rate q as z increases. It should also be noted that the ratio $\eta^* = \sigma/\varkappa$ is often used as a measure of "viscosity" in experiments (especially in engineering trials). Within the framework of our scheme, this ratio has the following form at z >> R:

$$\eta^* = \frac{\rho g z}{v_0 (n-1)}\left(\frac{cR}{z}\right)^{1/n}. \tag{17}$$

Then Eqs. (9) and (17) show that $\eta^* \sim q^{\frac{n-1}{3n}}$ and increases without limit with an increase in z.

All of the properties noted above are in qualitative agreement with the experiments in [6]. Now let us proceed to a quantitative comparison of the theory with the same experiments, using a 0.5% water solution of PEO for this purpose. Here the density of the solution $\rho \approx 0.1$ Pa·sec^2·cm^{-2}, the surface tension $\sigma^* \approx 6$-7 Pa·cm, and the relaxation time $\theta \approx 0.7$ sec. As was shown in [6], in the region of flow rates for which steady-state flow exists, $\alpha = 0.87$ and $\gamma = \alpha/\beta = 2.6$. The lower critical values of q_0 and R_0, calculated in accordance with the above data, are shown in Table 1.

It can be seen that the calculated values of R_0 and q_0 agree well with the empirical data: $q_0 \approx 0.093$ cm^3·sec^{-1}, $R_0 \approx 0.035$ cm. In these experiments, it proved impossible to stretch a stream of the polymer solution at $q < q_0$ (or $R < R_0$).

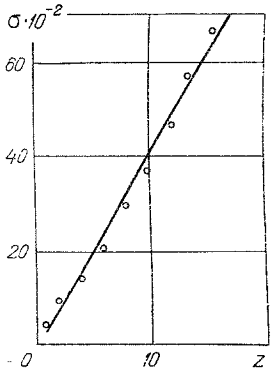

Fig. 3

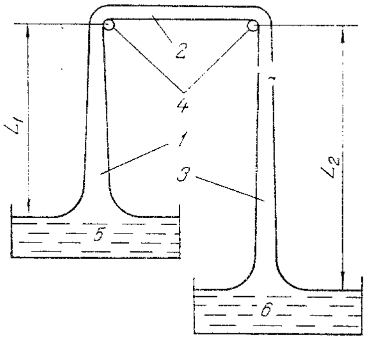

Fig. 4

Fig. 3. Dependence of stress σ (Pa) on longitudinal coordinate z (cm) for for $q = 0.38\ cm^3 \cdot sec^{-1}$. The solid line denotes calculated results; the points denote empirical results.

Fig. 4. Diagram of an open siphon: 1, 2, 3) parts of the stream of polymer solution; 4) wires across which the stream slides; 5, 6) containers with polymer solution.

As concerns the upper critical values q_* and R_*, in these experiments ($q_* \approx 1.14\ cm^3 \cdot sec^{-1}$, $R_* \approx 0.8$ cm), they are evidently connected with the development of instability in relation to nonaxisymmetric perturbations [6].

In accordance with the data presented in [8], the value of the constant n for natural cross-linked rubbers is equal to 1.64, while n = 1.34 for synthetic cross-linked rubbers. The second value of n (n = 1.34) will be used henceforth in our calculations. For convenience, numerical values of several of the constants encountered in Eqs. (8)-(17) are presented below:

n	m	$c = \frac{n-1}{n} m$	$1/c$	$1/n$
1,34	2,76	0,700	1,43	0,746

At these values for the constants, inequalities (3) and (7) are satisfied throughout the ranges of flow rates and lengths for the polymer streams withdrawn in the experiments. It should also be noted that the noninertial asymptote is an average.

Equation (12), obtained on the assumption that the effect of surface tension could be ignored, is valid only when $q \geqslant 0.36\ cm^3 \cdot sec^{-1}$. In this case, the term $(c - 1)/c$ can be ignored already at $z \approx R$, and Eq. (13) can be used. At $q < 0.36\ cm^3 \cdot sec^{-1}$, calculations performed on the basis of Eqs. (6) and (8)-(10) show that Eqs. (12) and (13) also remain valid, thanks to the fact that capillary effects on G_0^* are opposed by the total longitudinal force.

A comparison of the profiles calculated on the basis of Eqs. (12) and (13) with empirical profiles [6] for different values of q is shown in Figs. 2 and 3, along with the relation σ(z) for $q = 0.36\ cm^3 \cdot sec^{-1}$. The experimental values are represented by points, while the theoretical results are presented by lines. A similar comparison is shown for the relation r(z) in Table 2 at $z \geqslant 24$ cm and $q = 1.1\ cm^3 \cdot sec^{-1}$.

The deviation of the theoretical values from the empirical does not exceed 20% for the entire set. It should also be noted that all of the theoretical profiles are located above the empirical ones. The discrepancy between the theoretical and empirical relations can be reduced by changing either σ_0 or n. In the first case, it is necessary to consider the flow of the solution under the free surface in region III.

In conclusion, we should note that it might be possible to describe the phenomenon of spinability theoretically within the framework of a purely elastic asymptote and without the strain orientation hypothesis (i.e., the transition of the liquid to the highly elastic state at $x > x_{cr}$) if the stretching time t_* is less than the relaxation time θ. However, as was shown in [6], $t_* \approx \theta$ in the case of the PEO solution examined here. In connection

TABLE 2. Experimental and Theoretical Dependence of Stream Radius on the Longitudinal Coordinate at $z \geqslant 24$ cm ($q \approx 1.1$ $cm^3 \cdot sec^{-1}$)

z, cm		24	28	32	36	40
r, mm	Experimental	0,84	0,78	0,72	0,68	0,65
	Theoretical	0,79	0,74	0,71	0,68	0,65

with this, it is worthwhile to remember that in the nonlinear deformation of an elastic liquid, the behavior of which was described in [1], theoretical solution of the problem in question without allowance for strain orientation leads to an exponential decrease in r(z). Thus, at the values of r_0 and σ_0 determined from Eqs. (9) and (10), the length of the stretched stream will not exceed 0.1 cm. At this length, the stream radius will be about two orders less than r_0. This circumstance evidently explains the impossibility of using the above method to withdraw a stream of a transformer oil solution of butyl rubber. Good results were obtained in [9] in a rheological description of such a stream in simple shear on the basis of [1], without allowance for strain orientation.

Phenomenon of Open Siphoning. Finally, let us examine an open siphon scheme (Fig. 4) where a stream of solution 1 of length L_1, passing over two wires 4 and having a horizontal section 2, is stretched by the weight of a liquid column 3 of length L_2. The open siphon problem has a steady-state solution if it is possible to maintain the level of the liquid in vessels 5 and 6 at a constant level. We will use the results in the preceding section to construct such a solution. If the length of both streams is reckoned from the levels of their free surfaces, then at a given flow rate q determined by the initial conditions, both streams will have identical profiles at a length equal to L_1. This result follows at once from Eqs. (5) and (8) and the above-noted dimensional considerations. Here the length L_2 is determined by the relation

$$\pi r^2(L_1)\,\sigma(L_1) + F_{fr} = \pi r^2(L_2)\,\sigma(L_2),$$

where the value of L_1 is assigned and the functions r(z) and σ(z) are determined by Eqs. (15) and (18) [sic]. If stream friction against the wire $F_{fr} \approx 0$, then $L_2 \approx L_1$. It is interesting to note that, as follows from the analysis, in the case of an open siphon the polymer stream 3, flowing downward, expands as its descends. Such behavior can be described only on the basis of a rheological equation valid for rubbers. In the case of absence of the elastic siphon phenomenon, a stream of a viscoelastic liquid usually contracts as it falls.

The results obtained indicate that in certain cases the rheological behavior of liquid polymer streams can be described within the framework of a purely elastic asymptote. However, the range of applicability of this approach is sharply limited. For example, this approach is useless for examining the stretching of a stream vertically downward, as was confirmed by the results obtained above. The approach also proves fruitless in the case of a viscoelastic stream stretched in the horizontal direction, when the forces of gravity are insignificant. Actually, in the latter case, simple calculations within the framework of a "stream" approximation lead to the following results: In the case of a purely elastic stream, nonuniform steady stretching is impossible; with allowance for delay phenomena, stable, steady, nonuniform stretching is possible, but only if the parameter n in the simplified BST potential satisfies the inequality $n < 1$. However, as shown above, this inequality is incompatible with the possibility of stretching long streams in accordance with the scheme in Fig. 1.

NOTATION

η and θ, maximum Newtonian viscosity and relaxation time; r, stream radius; z, coordinate reckoned along stream; S, area of stream cross section perpendicular to z axis; v and σ, longitudinal velocity and stress, averaged over the stream cross section; σ^*, surface tension; ρ, density; g, acceleration due to gravity; X, elastic strain tensor; δ, unit tensor; $x_{rr} = x$, $x_{\varphi\varphi}$ and x_{zz}, components of the tensor X in tension in a cylindrical coordinate system; x_{cr}, critical strain, at which the solution begins to harden; μ, modulus of elasticity; W, elastic potential; n, constant; η_1 retardation viscosity; x_0, σ_0, r_0, S_0, elastic strain, stress, radius, and cross-sectional area at $z = R$; R, radius of meniscus; G_0^*, effective modulus; α, β, γ, constants characterizing the meniscus; ϰ, strain rate; $\eta^* = \sigma/\varkappa$; c, m, constants; T, temperature; t^*, time of passage of a fixed section from z = R to the drum; L_1 and L_2, lengths of the stream being stretched and the falling stream; F_{fr}, friction; q, flow rate.

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THE SPREADING OF A NON-NEWTONIAN LIQUID OVER A HORIZONTAL PLANE WITH INTENSIVE HEAT-TRANSFER AND MASS-TRANSFER PROCESSES ON THE SURFACE OF THE LAYER

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We investigate the flow of a layer of highly viscous non-Newtonian liquid over a horizontal plane, accompanied by intensive heat-transfer and mass-transfer processes.

We consider the behavior of a layer of viscoelastic liquid with a free surface on a solid horizontal plane. The coordinate system is so chosen that the axes OX and OY lie in this plane and the axis OZ is directed upward. In what follows, we shall consider the behavior of large liquid masses, and therefore we shall disregard capillary forces. For a highly viscous liquid the hydrodynamic problem is simplified. In the first place, the Reynolds numbers are small and the inertial terms may be neglected in the equations of motion. In the second place, the characteristic time scale of the flow is much longer than the relaxation time of the liquid (small Debora numbers), and the rheological equations of a nonlinearly viscoelastic liquid reduce to the rheological differential equation [1, 2] that is valid for slow flows:

$$\mathbf{T} = \eta \mathbf{A}_1 + \beta \mathbf{A}_1^2 + \nu \mathbf{A}_2. \tag{1}$$

Here T is the excess-stress tensor; $\mathbf{A}_1 = \left.\frac{D\mathbf{C}_t(\tau)}{D\tau}\right|_{\tau=t}$; $\mathbf{A}_2 = \left.\frac{D^2\mathbf{C}_t(\tau)}{D\tau^2}\right|_{\tau=t}$ Rivlin–Eriksen tensors [1, 2]; $C_t(\tau)$, Cauchy deformation tensor [1, 2]; coefficients η, β, ν depend on the second

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