Visual observations show that unstable film motion is manifested in the form of rolls of clarified liquid, the height of which exceeds the film thickness by a factor of 2-3, following one another. Further, part of the suspension is drawn into the zone behind a roll, the stability of the sedimentation is destroyed, which is what leads to the noticeable decrease in the sedimentation rate of suspensions at angles of inclination of the plates exceeding 50° and $\rho_s = 1010\text{-}1015$ kg/m^3.

NOTATION

δ, thickness of the film, m; μ, dynamic coefficient of viscosity, N·sec/m^2; ρ_s and ρ_o, densities of the suspension and clarified liquid, kg/m^3; V_{av}, average velocity of motion of the film, m/sec; V_c and V_g, velocities of propagation of continuous and gravitational waves, m/sec; l and b, length and width of the flat tubes, m; h, distance along the normal between the plates, m; α, angle of inclination of the tubes to the horizontal, deg; A, a dimensionless grouping of constant.

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POSSIBLE MECHANISM FOR THE RETARDATION EFFECT IN THE FLOW OF POLYMERIC LIQUIDS

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The effect is examined theoretically taking into account the influence of both orientational as well as the thermal activation mechanism for viscous flow on the relaxation time and, possibly, irreversible accumulation of ruptures.

It was shown in [1] that in order to stretch melted polyethylene with a constant rate of deformation, a retardation is observed after the flow develops. In the region of retardation, the polymer deforms similarly to an elastic nonlinear body. Then, a flow develops again in the polymer. These facts were established by direct measurement of the reversible and irreversible parts of the deformation. In this case, the tensile forces can have two maxima as a function of time. The secondary increase in the force corresponds to the retardation in the flow, while the secondary drop corresponds to renewed development of the flow. A stationary flow was not achieved in the region of deformations investigated, while the testing time could easily exceed the relaxation time, which is determined by performing a shear experiment in the linear deformation range. We note that the stretching process, possibly, is accompanied by irreversible accumulation of ruptures of macromolecules.

Rheological equations [2], taking into account large elastic deformations and the orientation factor, are used in order to describe partially the effect of a retardation in the flow. The latter is determined by choosing a sharply increasing relaxation time as a

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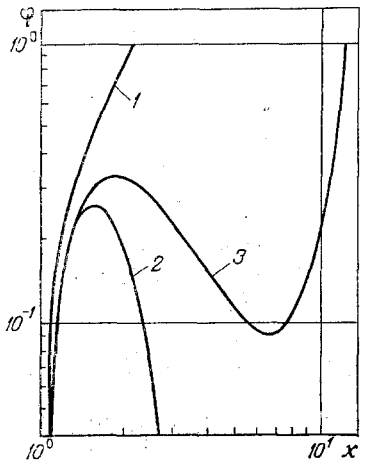

Fig. 1. Different forms of the function $\varphi(x)$: 1) $\varphi(x)$ for $\Phi(x) \equiv 1$; 2) $\Phi(x) = e^{-\beta w/2}$ and $\beta = 1$; 3) when $\Phi(x)$ is given by (3) for $\beta = 1$ and $\nu = 0.57$.

function of the elastic energy accumulated during deformation. The equations [2] applied to stretching [3] describe the retardation of the flow and the renewed growth in force. The renewed development of flow and the corresponding drop in force are not described by these equations. For a complete, but fairly rough, determination of the effect [1], in the present work, we kept in mind the influence on the characteristic relaxation time θ^* together with the orientation of the thermally activated viscous flow and, possibly, the irreversible accumulation of ruptures according to the Prandtl-Eyring mechanism (see [4]). In doing so, we do not consider the nature of the jumps and elements that lead to the indicated mechanism. A more detailed investigation of the latter requires special experiments on a microscopic scale.

We note that the mechanism for the retardation in the flow could be explained by the influence on the orientation of the heating due to the internal friction. An estimate of the influence of dissipation showed that over the testing time the temperature varies by not more than 0.1°C and this cannot be a reason for the reappearance of the flow.

In the case of the thermal activation mechanism for viscous flow, the equations that determine simple stretching for two parallel relaxation oscillators have the form

$$\frac{1}{x}\frac{dx}{d\tau} + \frac{(x+1)(x^3-1)}{6x^2}\Phi(x) = \Gamma; \quad k\frac{1}{y}\frac{dy}{d\tau} + \frac{(y+1)(y^3-1)}{6y^2} = k\Gamma; \tag{1}$$

$$\Gamma = \varkappa\theta_1; \quad k = \theta_2/\theta_1; \quad \tau = t/\theta_1;$$

$$\sigma = \frac{\theta_1}{\eta}(\sigma_x + \sigma_y); \quad \sigma_x = 2\mu_1(x^2 - x^{-1}); \quad \sigma_y = 2\mu_2(y^2 - y^{-1}); \tag{2}$$

$$\Phi(x) = \frac{\theta^*(x)}{\theta_1} = e^{-\frac{\beta w}{2}} \frac{\operatorname{sh}\left(\frac{\gamma}{RT}\sigma_x\right)}{\frac{\gamma}{RT}\sigma_x};$$

$$w = x^2 + 2x - 6 + 2x^{-1} + x^{-2}; \quad \theta^*(1) = \theta_1. \tag{3}$$

Here $\theta^*(x)$ is the characteristic relaxation time. Six independent material constants enter into (1)-(3): θ_1, θ_2, μ_1, μ_2, β, and γ. For derivation of Eqs. (1)-(3) for $\gamma = 0$ and $\mu_2 \to \infty$, see [3].

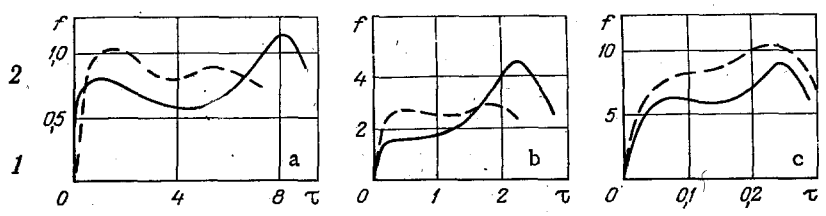

Fig. 2. The force f as a function of time τ: a) $\Gamma = 0.45$; b) 1.3; c) 11.

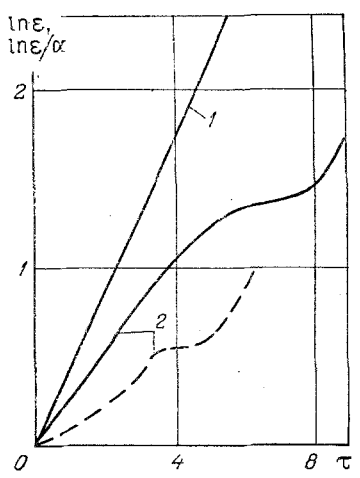

Fig. 3

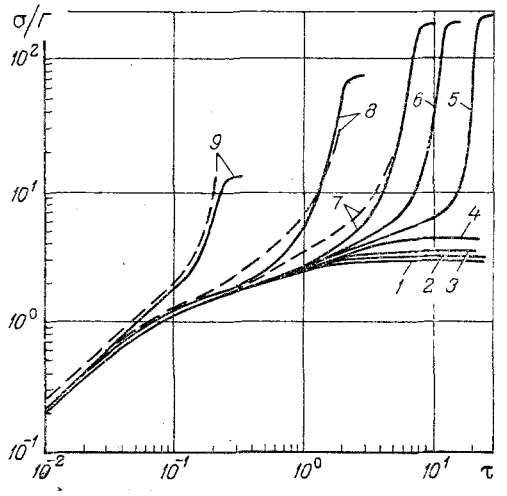

Fig. 4

Fig. 3. The total deformation lnε (1) and the residual lnε/α a function of time τ for stretching with Γ = 0.45.

Fig. 4. The ratio σ/Γ as a function of time τ. The curves 1-9 correspond, respectively, to Γ = 0.05, 0.1, 0.2, 0.3, 0.35, 0.4, 0.5, 1.3, and 11.

The use of two parallel relaxation oscillators (σ_x and σ_y) follows from a comparison of theory and experiment, carried out in [3, 5]. Such a representation permits describing quantitatively the effects related to the large elastic shearing and tensile strain for deformation rates varying by more than three orders of magnitude. In this case, it is assumed that the relaxation mechanisms do not interact with one another ($\theta_1 \gg \theta_2$ and $\mu_1 \ll \mu_2$). The derivation of Eqs. (1)-(3) is based on the classical potential of the network theory of Mackian elasticity. The effect of orientation and the thermal activation mechanism of viscous flow in the second relaxation oscillator is not taken into account. We emphasize once again that the orientation is taken into account by the first cofactor $\Phi(x)$, and the thermal activation mechanism by the second.

The solution of Eqs. (1)-(3) is examined for the case of stretching with a constant rate of deformation ($\Gamma = \text{const}$) with the following initial conditions:

$$x|_{\tau=0} = y|_{\tau=0} = 1. \tag{4}$$

In problem (1)-(4), qualitatively different behavior of the solutions depends on the form of the function (see (1))

$$\varphi(x) = \frac{(x+1)(x^3-1)}{6x^2}\,\Phi(x).$$

Figure 1 shows three qualitatively different versions of the function $\varphi(x)$. Curve 1 denotes the function $\varphi_1(x)$, when $\Phi(x) \equiv 1$, i.e., the influence of only large elastic stresses on stretching are taken into account. Curve 2 ($\varphi_2(x)$) determines the orientational effect. The influence of the thermal activation mechanism of viscous flow in this case is not taken into account, i.e. $\Phi(x) = e^{-\beta w/z}$. When all three factors are considered (see $\Phi(x)$ in (3)), three qualitatively different curves for $\varphi(x)$ can exist. For $2\nu/\beta \gg 1$ ($\nu = 2\mu_1\gamma/RT$), the function $\varphi(x)$ is qualitatively similar to $\varphi_1(x)$, while for $2\nu/\beta < 1$ it is similar to $\varphi_2(x)$. The case examined in the present work is realized for $2\nu/\beta \gtrsim 1$. Then, the curve $\varphi_3(x)$ has the form of curve 3.

The stationary solution of the problem being examined exists for $\varphi_1(x)$ with arbitrary stretching rates Γ. For $\varphi_2(x)$ a stationary solution exists only for $\Gamma \max \varphi_2(x)$. For larger Γ the solution is a monotonically increasing function, which is close to the elastic asymptote. The case of $\varphi_3(x)$ is an intermediate situation. Here, a stationary solution exists for arbitrary Γ. Near $\min \varphi_3(x)$ (stationary flow is not achieved), for $\Gamma > \max \varphi_3(x)$ $\Gamma \approx (1/x)(dx/d\tau)$, i.e., in this vicinity the solution is close to the elastic case.

Equations (1)-(3) with condition (4) was solved numerically on a computer using the Runge—Kutta method. In order to make comparisons with experiment, the ratio $\sigma(\tau)/\Gamma$ and the force per unit area of the initial section were computed:

$$f = \sigma e^{-\Gamma\tau}. \tag{5}$$

We note also that for $|\Gamma| < 1$ ($y \approx 1$) and $\tau > k$ the second equation in (1) can be represented as

$$y^2 - y^{-1} = 3k\Gamma. \tag{6}$$

The system of equations describing stretching taking into account (6) has the form

$$\frac{1}{x}\frac{dx}{d\tau} + \frac{\Gamma(x+1)(x^3-1)}{6x^2}\Phi(x) = \Gamma;$$
$$\sigma = (1-s)(x^2 - x^{-1}) + 3s\Gamma; \quad s = \eta_2/\eta; \quad (1-s) = \eta_1/\eta. \tag{7}$$

In order to make the following comparison with experiment, we will also determine the magnitude of the resilience (deformation) $\alpha = l/l_r$.

For the simplified Eq. (7), the elastic deformations α and x are connected by the expression

$$\alpha = \exp\int_1^x U(\xi)\,d\xi; \quad U(\xi) = \left[\xi + \frac{s(1+\xi)}{2(1-s)}\Phi(\xi)\right]^{-1}.$$

Here x is the elastic strain that accumulates with stretching up to the time τ. The scheme for solving the problem of determining α is the same as in [3], where the function $\alpha(x)$ is obtained for $\Phi(\xi) \equiv 1$.

The calculations were carried out for T = 398°K and for the constants of the liquid having the following values: $\eta_1 = 1.8\cdot10^5$ Pa·sec, $\eta_2 = 10^5$ Pa·sec, $\theta_1 = 1.1\cdot10^2$ sec, $\theta_2 = 6$ sec, $\beta \approx 1$, and $\gamma = 10^6$ cm^3/mole. The first four constants are obtained from experiments performed in the linear range of behavior of the liquid in the presence of shear with a constant rate of deformation (according to the value of the largest Newtonian viscosity and the stress as a function of time). We obtain the constants β and γ in the region of nonlinear deformation from the correspondence between theoretical and experimental functions $f(\tau)$, obtained with stretching for $\Gamma = 0.45$-11.

We note that the number of monomeric links (computed from the known value of γ), participating in the jumping act, is $z \approx 60$. This value is somewhat greater than for flows without the influence or orientation [7].

In Figs. 2-4 the solid lines are the computed curves.

The tensile stresses f (see (5)) as a function of time τ are shown in Fig. 2. Curve 1 in Fig. 2a shows the solution to Eqs. (1)-(3); curve 2 shows the solution to the approximate equations (7). For $\tau > 0.1$, these solutions are no longer distinguishable. For the values of Γ presented in Fig. 2, the function $f(\tau)$ have a double-hump form. When Γ decreases, the second maximum, corresponding to large τ in the functions $f(\tau)$, degenerates (not shown in Fig. 2).

Figure 3 shows the total deformation $\ln\varepsilon$ and the residual deformation $\ln\varepsilon/\alpha$ (see [6]) as a function of τ for $\Gamma = 0.45$. For stretching with $\Gamma = \text{const}$, the total deformation is $\ln\varepsilon = \Gamma\tau$, which follows from the kinematics of uniform stretching (see [6]). The dependence of $\ln\varepsilon/\alpha$ as a function of τ after the initial increase flattens out (the flow lags) and subsequently increases further. We note that the time at which the plateau appears in the function $\ln\varepsilon/\alpha$, corresponds to the beginning of renewed growth in force (see Fig. 2a). In the region where the force decreases again (Fig. 2a), the flow reappears (see Fig. 3).

The dependence of the ratio σ/Γ as a function of τ is shown in Fig. 4. Stationary flow is achieved, as already noted above, for deformation with arbitrary Γ. The quantity σ/Γ for stationary flow is the ratio of the effective viscosity on stretching to the maximum viscosity $\eta = \eta_1 + \eta_2$.

For small Γ, stationary flow is attained after a time $\tau^* \sim \theta_1$, and $\sigma/\Gamma = 3$. With increasing Γ, the ratio σ/Γ for the stationary flow at first increased and reached 200. At the same time, the time τ^* also increases considerably. With further increase in Γ, both the ratio σ/Γ for the stationary flow as well as the time it takes to achieve the stationary flow τ^* begin to decrease.

We note that taking into account the influence of only large elastic stresses ($\Phi(x) \equiv 1$) in the range of Γ being examined leads to a single maximum in the function $f(\tau)$, monotonic decrease in τ^*, and a weak increase in σ/Γ (with increasing Γ) in the presence of a stationary flow.

The dashed lines represent the experimental dependences taken from [1]. It is evident from Figs. 2-4 that there is a semiquantitative correspondence between theory and experiment. The experimental dependences σ/Γ as a function of τ (Fig. 4) do not attain stationary flow. This is apparently related to the limitations of the apparatus in obtaining large deformations.

In conclusion, we note that the discovery of the theoretical existence of stationary flow and the passage of effective viscosity as a function of the deformation rate through a maximum require additional experimental verification using the apparatus of the type in [8] with which large deformations can be attained.

NOTATION

x and y, elastic deformations in each of the relaxation oscillators; σ_x and σ_y, stresses in each relaxation oscillator; σ, dimensionless tensile stress; $2\mu_1 = \eta_1/\theta_1$ and $2\mu_2 = \eta_2/\theta_2$, elastic moduli; η_1, η_2, θ_1, and θ_2, viscosity and relaxation times; $\eta = \eta_1 + \eta_2$, largest newtonian viscosity; $\varkappa$ and Γ, dimensional and dimensionless deformation rates; t and τ, dimensional and dimensionless times; R, universal gas constant; T, temperature, in °K; β, dimensionless parameter that characterizes the flexibility of a molecular chain ($0 \leqslant \beta \leqslant 1$); γ, a parameter that characterizes the magnitude of the decrease in the potential barriers under the action of mechanical stresses; $\nu = 2\mu_1\gamma/RT$; s, ratio of the retardation time to the relaxation time ($0 \leqslant s \leqslant 1$); θ^*, some characteristic relaxation time; ε, total longitudinal deformation; α, elastic deformation (elastic jump); l, instantaneous length of the stretched specimen; l_r, length that the stretched specimen of length l approaches after the stress is removed from it for $\tau \to \infty$; z, number of monomeric links participating in the jumping act; τ^*, time required to attain a stationary flow; f, dimensionless ratio of the tensile force and the initial cross-sectional area.

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