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FLOW RETARDATION DURING DEFORMATION IN VARIOUS MODES

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Retardation of the flow of a polymer fluid during elongation in various modes is analyzed on the basis of theory and experiments.

It has been discovered in earlier studies [1, 2] that a polymer fluid (polyethylene melt) under tension with a constant deformation rate $\varkappa$ can exhibit two ranges of deformation as a solid almost (with essentially elastic strains developing). The usually observed first range is found during the beginning of the deformation process and extends over periods shorter than the relaxation time. The second loss of fluidity can already occur after the flow has developed. The tension force F(t), varying in time, was found to pass through two maxima. Both ranges of suppressed flow corresponded to an increase of force F. As the deformation rate $\varkappa$ was increased, both ranges eventually merged into one. An appraisal of the recurring flow based on the second increasing of the force suggests that this property is characteristic of polymers which crystallize (polyethylene) as well as of those which do not (polystyrene).

After the recurring solidification there either again develops a flow (low-density polyethylene at 125°C) or occurs a rupture of the elongated specimen (high-density polyethylene at 130°C). Thorough data on rupture of monodisperse polymer fluids can be found in another report [3], where it has been attributed to a loss of fluidity. It remains unclear, however, whether or not solidification had recurred in that study [3].

The loss of fluidity is, it seems, manifested differently in different polymer fluids. Thus, e.g., no loss of fluidity (no range of constant irreversible strain) was found in grade P-20 polyisobutylene elongated at 44°C within the same range of strain and strain rates as polyethylene had been earlier [1]. Here the force F(t), varying in time, passed through only one maximum and continued to decrease monotonically.

It is to be noted that polyisobutylene at 44°C and low-density polyethylene at 125°C have approximately the same viscosity, $\eta \sim 3 \cdot 10^5$ Pa·sec and modulus of high-elasticity $G_e \sim 10^3$ Pa. Their flow curves within the given range of shearing strain rates ($\varkappa < 1$ sec^{-1}) also do not differ much.

According to another study [4], a polymer fluid in the range of nonlinear deformation often cannot be described by the viscosities and the relaxation times alone. Describing the loss of fluidity requires still another parameter β^* ($0 \le \beta \le 1$), which characterizes the aptitude of the material for strain orientation. The

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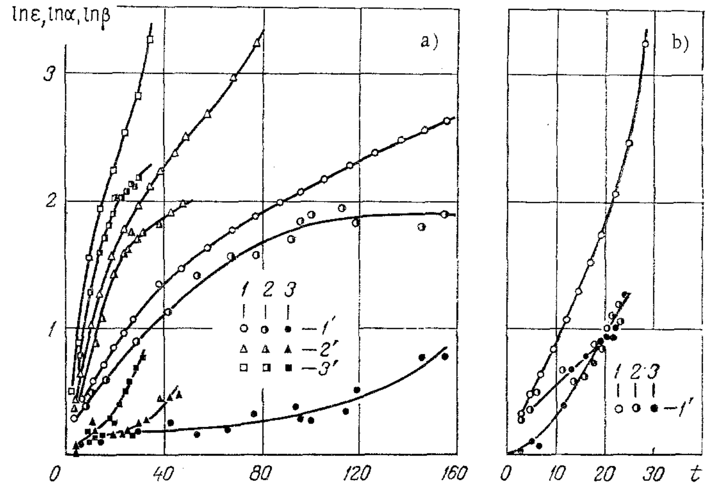

Fig. 1. Experimentally determined total strain (1), elastic strain (2), and irreversible strain (3) as functions of time for (a) polyethylene at $\sigma_0 = (1.0, 1.5, 2.0)\cdot 10^4$ N/m^2 (points 1', 2', 3') and (b) polyisobutylene at $\sigma_0 = 1.0\cdot 10^4$ N/m^2 (points 1').

higher the value of parameter β^* is, the sooner will loss of fluidity occur. Strain orientation appears earlier under tension than under shear [5]. Solidification of a fluid during shearing deformation can cause separation of the polymer from the walls of the capillary and thus result in a flow instability [3, 6, 7]. The authors of this report did not study experimentally the loss of fluidity by polyethylene and polyisobutylene during shearing.

For a rough description of the solidification developing after the recurrent flow during elongation (e.g., low-density polyethylene [1, 2]), in study [8] was taken into account the effect of two opposing mechanisms on the characteristic relaxation time θ, namely the initial increase and subsequent decrease of θ due to, for instance, strain orientation and thermally activated viscous flow and possibly irreversible accumulating ruptures of macromolecules. Strain orientation causes the initial increase of the relaxation time, thermally activated viscous flow causes its subsequent decrease. The main purpose of taking this dual mechanism into account was to study its manifestations during elongation in various forms.

In the theoretical analysis of elongation at a constant strain rate [8] it has been possible to describe all the experimental data on polyisobutylene and polyethylene. Only large elastic strains were taken into account in the case of polyisobutylene, but also strain orientation and the possibility of thermally activated flow in the case of polyethylene. Some of the items in this comparative analysis have just been enumerated. Here we will only add the curious difference in the viscous behavior of these two polymers and in the length of time required for their flow to become steady.

In the case of polyisobutylene this transient period of flow during elongation at $\varkappa$ = const decreases monotonically (the time is measured beginning from the linear deformation) as $\varkappa$ increases, while the viscosity during steady flow $\lambda = \sigma/\varkappa$ then smoothly increases to 3η [2, 9].

In the case of polyethylene this transient period of flow during elongation at $\varkappa$ = const increases sharply (possibly jumpwise) near the range of linear deformation. The same applies to the viscosity in this range. As $\varkappa$ increases further, both the transient period and the viscosity under these flow conditions begin to decrease [10, 11]. The initial increase of viscosity with its subsequent decrease has been predicted on the basis of the integral model [12].

It should also be noted that in studies [10, 11] the strain rate of irreversible flow increased monotonically with time, unlike in studies [1, 2], apparently due to a less pronounced recurrent solidification. Steady flow of polyethylene and of butadiene caoutchouc in the range of nonlinear deformation during elongation at $\varkappa$ = const was never reached in studies [1, 2, 13, 14] (in all probability, because of the limited test time). Nevertheless, the deformation time could very well have been longer than the time required for the flow to become steady in the linear range. A decrease of the viscosity during steady flow was for the first time observed in study [15].

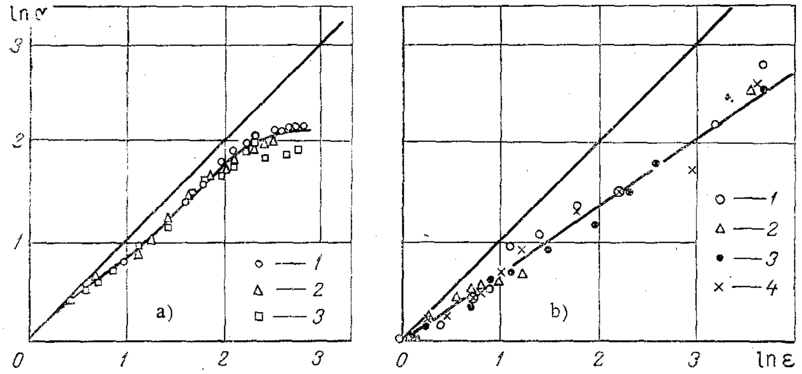

Fig. 2. Experimentally determined dependence of the elastic strain log α on the total strain log ε during elongation at a constant force: (a) polyethylene, points 1, 2, 3 correspond to $\sigma_0 = (1.0, 1.5, 2.0) \cdot 10^4$ N/m^2, respectively; (b) polyisobutylene, points 1, 2, 3, 4 correspond to $\sigma_0 = (1, 3.3, 6.3, \text{and } 11.7) \cdot 10^3$ N/m^2.

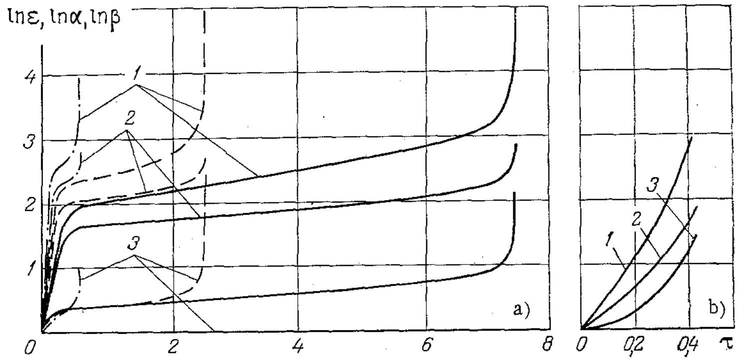

Fig. 3. Theoretically determined total strain (1), elastic strain (2), and irreversible strain (3) as functions of the dimensionless elongation time τ; solid, dash, and dash-dot lines refer to $\sigma_0 = (1.0, 1.5, 2.0) \cdot 10^4$ N/m^2 for (a) polyethylene, $\sigma_0 = 1.0 \cdot 10^4$ N/m^2 for (b) polyisobutylene.

These authors made an experimental and theoretical study of the behavior of polyisobutylene (at 44°C) and low density polyethylene (at 125°C) in a different mode of deformation, namely elongation by a constant force. In this case the deformable cylindrical specimen was fixed at one end and a constant force of tension was applied to it at the other (details of the test stand have been described in an earlier report [16]). A specimen was immersed in silicon oil, for thermostatization and weight compensation. The polyisobutylene specimens had been prepared by rolling between two plates [14], the polyethylene specimens had been prepared by extrusion from a capillary. Polyethylene being prone to thermomechanical breakdown, the specimens of this material had been prepared under stringently controlled conditions ($P = 2.75 \cdot 10^5$ N/m^2, $d = 2.8$ mm, $L = 10$ mm, $t_* \leq 20$ min).

In the experiments we determine the total strain $\log \varepsilon = \log l/l_0$, the elastic strain $\log \alpha = \log l/l_r$, and the irreversible strain $\log \beta = \log l_r/l_0$ as functions of time. The length l was measured visually with a ruler fastened along the vat. For the determination of its residual length l_r, a specimen after elongation was cut with scissors. This reading of l_r was taken after 20 min, a period much longer than the characteristic relaxation time. The length l_0 had been selected anywhere from 15 to 60 mm, depending on the amount l to which a specimen was to be elongated.

The maximum attainable strain $\log \varepsilon_{\max} = 2.8$ was determined by the length of the vat and the smallest length l_0 used. The tests were performed at the initial stresses $\sigma_0 = F/S_0 = (1.0, 1.5, 2.0) \cdot 10^4$ N/m^2.

The experimental results are shown in Fig. 1, viz., log ε, log α, and log β as function of the elongation time t for polyethylene (Fig. 1a) and for polyisobutylene (Fig. 1b). Despite the closeness of both η and θ in the data on the polymers (σ_0 and t are usually referred to these quantities, respectively, for putting the data in dimensionless form), the time to reach the maximum possible strain $\log \varepsilon_{\max} = 2.8$ is 6 times longer for polyethylene than for polyisobutylene at the same stress $\sigma_0 = 1.0 \cdot 10^4$ N/m². The log $\varepsilon(t)$ relation is characterized by an increasing strain rate $\varkappa(t) = d \log \varepsilon / dt$ for polyethylene, moreover, while for polyisobutylene $\varkappa(t)$ decreases within a wide range of ε and becomes approximately constant after a long time t. Still later $\varkappa(t)$ increases for both polyisobutylene and polyethylene ($\sigma_0 = 1.5 \cdot 10^4$ and $2.0 \cdot 10^4$ N/m²).

The curves of log α and log β as functions of time t follow entirely different trends for the two polymers, as shown in Fig. 1. The principal difference lies in polyethylene having a range in which it ceases to flow (log $\beta \approx$ const), i.e., deforming almost as a solid. The altitude of the log $\beta \approx$ const plateaus on the curves is approximately the same for all three initial stresses σ_0, while their length on the time scale increases with decreasing σ_0 but remains approximately the same on the curves of total deformation ε. Recurrent solidification causes an increase of the effective viscosity $\sigma/\varkappa(t)$ during development of subsequent flow. Recurrent development of irreversible strain log β causes an increase of the strain rate $\varkappa$. At the maximum total strain log $\varepsilon_{\max} = 2.8$ attained in this experiment ($\sigma_0 = 1.0 \cdot 10^4$ N/m²), moreover, the elastic component log $\alpha_{\max}$ is 1.7 times smaller in polyisobutylene than in polyethylene. This is, evidently, a consequence of recurrent solidification of polyethylene during elongation.

We note a jump approximately equal to 10% of the initial length of a specimen at the instant of load application to both polymers (not shown in Fig. 1).

The elastic strain over the range of fluidity loss is log $(\alpha_i/\alpha_f) \approx 0.7$ during elongation at either F = const or $\varkappa$ = const [1].

The dependence of log α and log ε for polyethylene and polyisobutylene respectively is shown in Fig. 2a, b.* The straight lines at a 45° slope in these graphs correspond to elongation of a purely elastic body ($\varepsilon \equiv \alpha$). The graphs indicate that the relation between log α and log ε does not depend on the elongating force and follows different trends for the two polymers.

Elongation of polyethylene is accompanied by a buildup of noticeable irreversible changes. The latter are revealed during recurrent elongation in the F = const mode (the $\varkappa$ = const mode is less sensitive to recurrent elongation) of already deformed specimens, upon a comparison of the data with those pertaining to only once deformed specimens. The total thermal history had been the same in both cases. A further evidence of irreversible changes is the decrease of the molecular mass during the elongation process, this mass having been determined from the characteristic viscosity.

It has not been clarified in this study whether or not the irreversible changes affect the mechanism of recurrent flow and if they do, then how. In order to determine this, it is necessary to set up a special experiment on the microlevel.

For a theoretical description of elongation at a constant force we will use the rheological equations of uniform elongation [8]. With the strain rate $\varkappa = 1/\varepsilon \, d\varepsilon/dt$ and the stress $\sigma = \sigma_0 \varepsilon$, disregarding the second relaxation mechanism (in the "fast alignment" approximation), these equations are

$$\begin{gathered}\frac{1}{x}\,\frac{dx}{d\tau} + \frac{(x+1)(x^3-1)}{6x}\,\Phi(x) = \frac{1}{\varepsilon}\,\frac{d\varepsilon}{d\tau},\ \frac{\sigma_0}{2\mu_1}\,\varepsilon = (x^2 - x^{-1}) + 3s\,\frac{1}{\varepsilon}\,\frac{d\varepsilon}{d\tau},\quad \sigma_x = 2\mu_1 (x^2 - x^{-1}),\\ \Phi(x) = \exp\left(-\frac{\beta^* w}{2}\right) \frac{\operatorname{sh}\left(\frac{\gamma}{RT}\,\sigma_x\right)}{\frac{\gamma}{RT}\,\sigma_x},\quad \tau = t/\theta,\ w = \frac{(x-1)^2 (x^2 + 4x + 1)}{x^2}.\end{gathered} \tag{1}$$

A theoretical analysis in the "fast alignment" approximation somewhat simplifies the equations corresponding to two parallel relaxators [8] without changing the qualitative pattern. Evidently, there are also not large quantitative changes incurred as a result.

The solutions to Eqs. (1) will be sought for given values of σ_0 and the initial condition

$$x|_{\tau=0} = 1. \tag{2}$$

The relation between elastic strains x and α has been established in an earlier study [8]. Here Eqs. (1) were solved for condition (2) on a digital computer by the Runge–Kutta numerical method. The following constants

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* The data on polyisobutylene have been taken from two earlier studies [2, 16] with the grade P-20 polyisobutylene somewhat different than that used in this study.

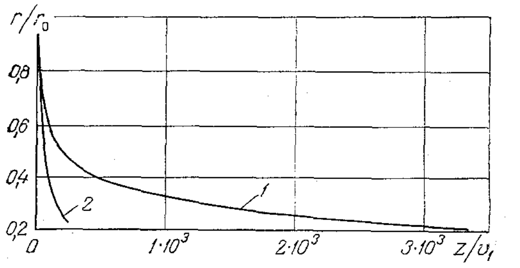

Fig. 4. Radius r/r_0 as a function of z/v_1 during nonuniform elongation of: 1) polyethylene and 2) polyisobutylene.

were used: for low-density polyethylene $\theta = 110$ sec, $\eta = 2.8\cdot10^5$ Pa·sec, $s = 0.36$, $\beta^* = 1$, $\gamma = 10^6$ cm^3/mole and for polyisobutylene at 44°C $\theta = 82$ sec, $\eta = 2.8\cdot10^5$ Pa·sec, $s = 0.25$, $\beta^* = \gamma \approx 0$. The values of θ, η, and s had been determined in the range of linear deformation, the values of β^* and γ had been determined in the range of nonlinear deformation [8]. The theoretical curves of log ε, log α, and log β as functions of τ for polyethylene and polyisobutylene are shown in Fig. 3. The higher σ_0 is for polyethylene, the steeper becomes the corresponding curve. A comparison of the graphs in Figs. 2 and 3 reveals a basic agreement between theory and experiment. A better qualitative agreement can be obtained by a slight change of the parameter γ.

In the earlier study [8] we considered the problem of elongation at $\varkappa = 1/\varepsilon d\varepsilon/dt = \text{const}$. We will add here that, since the function $\varphi(x) = \frac{(x+1)(x^2-1)}{6x}\Phi(x)$ passes through a maximum and after some dip continues to increase monotonically with x (Fig. 1 in [8]), there can, at a fixed $\varkappa < \max\varphi\theta^{-1}$ and depending on the initial conditions, occur two different modes of steady flow with the viscosity differing by two orders of magnitude. This conclusion must still be experimentally verified.

Let us also discuss the experiment with extrusion at a constant force performed on polyisobutylene of very high viscosity ($\eta = 10^{10}$ Pa·sec) in another study [17]. There log ε as a function of time t initially followed the same trend as here in Fig. 2b ($\varkappa$ increasing), but then continued with log ε increasing slower ($\varkappa$ decreasing). Meanwhile, log α decreased with time t. This trend of the function log ε (t) in study [17] can be explained with the aid of the data in study [4] pertaining to $\beta^* \ll 1$ [2, 16], but then the trend of log α (t) will remain unexplained.

We will now consider the retardation of flow during nonuniform elongation. Uniform and nonuniform elongation (at F = const in each case) are related as follows [18]

$$z/v_1 = \int_0^t \varepsilon(\xi)\,d\xi; \qquad r/r_0 = \varepsilon(t)^{-1/2}. \tag{3}$$

Here ε is the relative elongation at F = const (Fig. 2). With $\varepsilon(t)$ known, one can use relation (3) for constructing the profile r(z) of a nonuniform jet. Such a profile is obtained during extrusion, at a force F, of a polymer leaving a capillary (along the z-axis) at a mean velocity v_1. The effect of deformation inside the capillary on the r(z) profile is disregarded here, i.e., the loss of fluidity can be tracked without its distortion by the swelling effect [19]. The curves of r/r_0 as a function of z/v_1 calculated according to relation (3) for polyisobutylene and polyethylene with $\sigma_0 = 1.0\cdot10^4$ N/m^2 ($\sigma_0 = F/\pi r_0^2$ in the case of a capillary), on the basis of the data in Fig. 2, are shown in Fig. 4. It is noteworthy that the strain rate $dv_z/dz = \varkappa(z)$ during nonuniform elongation increases in the case of polyisobutylene and decreases in the case of polyethylene. This causes polyethylene to reach a certain radius r much farther along the z axis than polyisobutylene (Fig. 4) at the same mean velocity v_1.

The existence of long vertical filaments with a strain rate decreasing downward (spinning property) has been discovered [20] during extrusion of a polyoxyethylene concentrate with a free surface by means of a rotating drum. It is noteworthy that at a fixed flow rate a steady filament could not be extruded beyond a certain critical length. In all likelihood, loss of fluidity is the underlying cause of the spinning effect and the critical length of a filament is determined by either development of recurrent flow (as in the case of low-density polyethylene) or solid filament rupture (as in the case of high-density polyethylene).

In conclusion, we note that this analysis of elongation on the basis of data in studies [1, 4, 8] with the effects of strain orientation and thermally activated flow (possibly also irreversible accumulation of ruptures of macromolecules) has made it possible to combine a large amount of experimental data into a single pattern.

NOTATION

$\varkappa$, strain rate; F, tension force; η, viscosity; G_e, modulus of high-elasticity; t, time; θ, relaxation time; parameter β^* characterizes the proneness to orientation; λ, viscosity during elongation; $d = 2r_0$, diameter of the capillary; L, length of the capillary; P, pressure before the entrance to the capillary; t_*, time the polymer remains in the bomb of the capillary viscometer during preparation of specimens; $\varepsilon = l/l_0$, $\alpha = l/l_r$, and $\beta = l_r/l_0$, total strain, reversible (elastic) strain, and irreversible strain; l_0, l, and l_r, initial length, instantaneous length, and residual length of a specimen; α_i and α_f, initial and final elastic strain at $\log \beta \approx$ const, respectively; σ_0, stress at time t = 0; S_0, surface area at time t = 0; x, elastic strain; s, ratio of retardation time to relaxation time; parameter γ characterizes the intensity of the decrease of potential barrier under mechanical stress; $2\mu = \eta/\theta$, modulus of elasticity; R, universal gas constant; T, temperature, °K; σ_x, stress characterizing the elastic strain x; z, longitudinal coordinate; v_z, velocity along the z axis; r, local radius; v_1, mean velocity of the fluid leaving the capillary.

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