RETARDATION OF A POLYMER FLUID FLOW UNDER LARGE ELASTIC STRAINS

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Data are presented on the homogeneous extension of low-density polyethylene. Retardation of the polymer flow under large elastic strains is noted.

Retardation of a polymer-fluid flow after flow development is examined in the example of homogeneous extension with a constant strain rate.

Homogeneous inertialess extension of a cylindrical specimen with $\varkappa$ = const is characterized by the following velocity components [1]:

$$v_x = \varkappa x;\ v_r = -\frac{\varkappa}{2} r;\ v_\varphi = 0. \tag{1}$$

Here r, x, and φ are cylindrical coordinates, and the x axis is directed along the specimen.

The complete longitudinal strain of an incompressible extensible specimen is

$$\varepsilon = \ln\frac{l}{l_0} = \ln\frac{r_0^2}{r^2} = \varkappa t. \tag{2}$$

Then the strain rate is

$$\varkappa = \frac{d\varepsilon}{dt}. \tag{3}$$

Used as a measure of the elastic and irreversible strain are

$$\varepsilon_l = \ln\frac{l}{l_r};\quad \varepsilon_f = \ln\frac{l_r}{l_0}. \tag{4}$$

Shrinkage occurs because of the elastic energy accumulated during extension of the polymer fluid.

The irreversible-strain rate is determined as follows:

$$e_f = \frac{d\varepsilon_f}{dt}. \tag{5}$$

The force F extending the specimen is measured in tension tests, and the constant cross-sectional stress is determined as follows:

$$\sigma = \frac{F}{S_0} e^{-\varkappa t}. \tag{6}$$

The main part of the experiments was performed on low-density polyethylene (grade 10203-003, molecular weight $\sim 10^6$) in the T = 105-150°C temperature band. The crystallization temperature is T_{cr} = 113°C. The transparent polyethylene in the melted state becomes cloudy below this temperature. The initial viscosity at 125°C is $\eta \sim 10^6$ P and the relaxation time is $\theta \sim 10^2$ sec.

Some qualitative experiments were also performed on high-density polyethylene and polystyrene.

The tension in the $\varkappa$ = const mode was executed on an apparatus with variable specimen length.* One end of the specimen is here fixed, while the other is displaced exponentially

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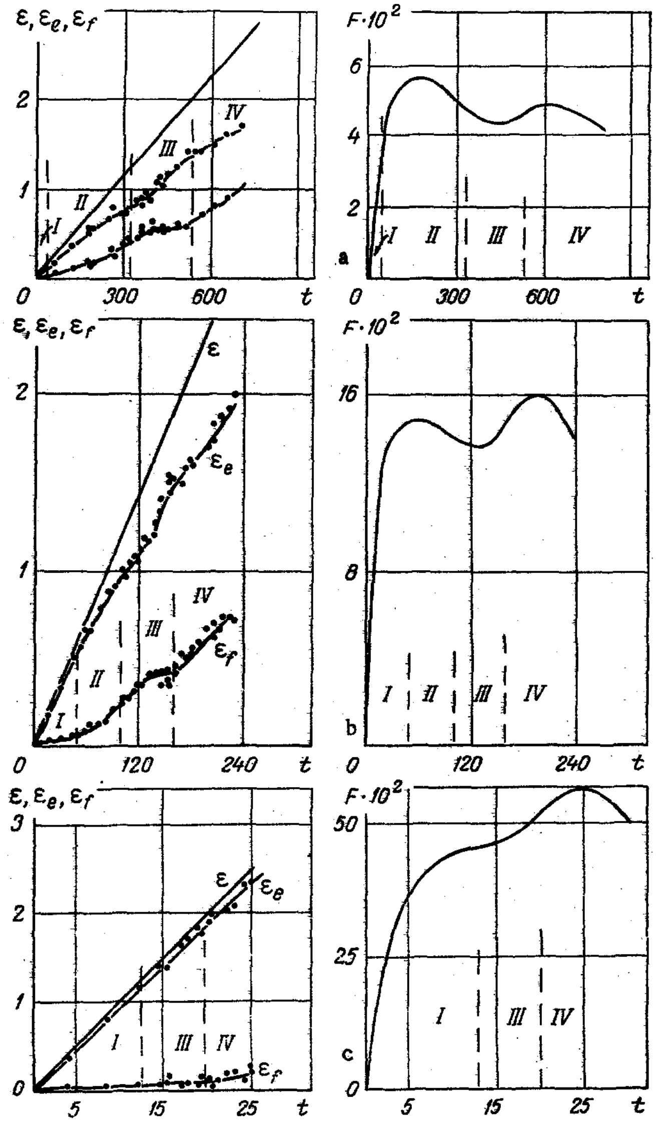

Fig. 1. Dependences of the total strain ε, the elastic strain ε_l, and the irreversible strain ε_f and tensile force F, N, on the extension time t, sec for T = 125°C and different strain rates $\varkappa$. a) $\varkappa = 3.84 \cdot 10^{-3}$ sec^{-1}; b) $\varkappa = 1.2 \cdot 10^{-2}$ sec^{-1}; c) $\varkappa = 10^{-1}$ sec^{-1}. The upper curve in a) is for ε, the middle for ε_l, and the lower for ε_f.

in the time [see (1)]. Silicone oil was used as the thermostat fluid. Strain rates from $3.84 \cdot 10^{-4}$ to 10^{-1} sec^{-1} and strains to $\varepsilon = 2.9$ were realized on the tension apparatus. The boundedness in ε is related to the length of the thermostat bath.

Cylindrical specimens of diameter $d \simeq 0.5$ cm were fabricated by extrusion from a capillary viscosimeter.

The tensile force F, elastic ε_l and residual ε_f strains were measured in the tests. The specimens were cut by shears to realize the retardation mode (to measure l_r).

Let us note that the preliminary (before the tension) prolonged action of the temperature could diminish the value of F(t) somewhat. The nature of the curves F(t) remained the same in principle here (heating lasted up to 2 h). It is established that practically no changes occur in F(t) for 15-30 min heating; this same time is completely adequate for heating the specimen before the test because the heating time is $t \sim d^2/\xi = 2.5 \cdot 10^2$ sec (for polyethylene $\xi \approx 0.1$ mm^2/sec for T = 125°C).

The spread in the experimental data in F did not exceed ±8% (an average line is drawn on the graphs), and the spread in ε_l is seen from the test points presented in the graphs.

Experimental dependences of the tensile force F (the dependences $\sigma(t)$ will be discussed in the analysis of Fig. 2), the elastic strain ε_l, and the irreversible strain ε_f on the time t are presented in Fig. 1 for 125°C. The dependence of the total strain $\varepsilon = \varkappa t$ is also shown by a straight line. Four strain domains are marked out for $\varkappa = 3.84 \cdot 10^{-3}$ and $1.2 \cdot 10^{-2}$ (Fig. 1a and b).

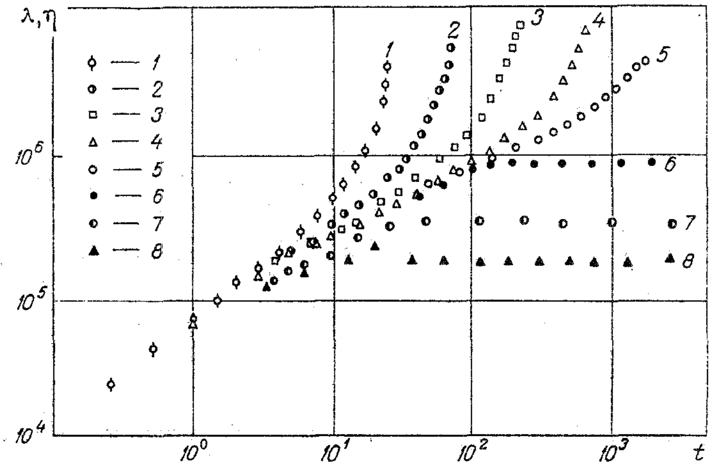

Fig. 2. Dependence $\lambda = \sigma/\varkappa$, Pa, under tension and $3\eta^* = 3\sigma/\varkappa$, Pa, under shear on the time t, sec, for different strain rates $\varkappa$, sec^{-1}, at T = 125°C. The following strain rates under tension correspond to points 1-5: 1) $\varkappa = 10^{-1}$; 2) $3.84\cdot10^{-2}$; 3) $1.2\cdot10^{-2}$; 4) $3.84\cdot10^{-3}$; 5) $1.2\cdot10^{-3}$ sec^{-1}. For points 6-8 under shear: 6) $\varkappa = 1.42\cdot10^{-3}$; 7) $1.125\cdot10^{-1}$; 8) $3.5\cdot10^{-1}$ sec^{-1}.

Domain I from the time t = 0 is characterized by a moderate difference between the elastic strain ε_l and the total strain ε (less than 5%, for example). The strain time in domain I is considerably less than the relaxation time, and the polymer is deformed to almost a solid. The force grows in this domain.

The flow of the polymer medium develops in domain II (e_p grows). In this domain the force F(t) passing through a maximum starts to drop.

Domain III starts from the inflection point of the dependence F(t) on the descending section of the curve. This point corresponds to the inflection point of the ascending section of the dependence of ε_f. In this domain the irreversible-strain rate e_f starts to diminish as t grows and is made close to zero ($\varepsilon_f \approx \mathrm{const}$), i.e., the irreversible flow is suppressed on this section and the body starts to be deformed as a solid. The force grows repeatedly on the section $e_f \simeq 0$, which is also characteristic for the strain of solids under high elastic strains in the mode $\varkappa = \mathrm{const}$.

A duplicate flow ($e_f > 0$) again develops in the domain IV. Let us note that the polymer remains identically transparent and is deformed homogeneously in all four domains.

For $\varkappa = 0.1\ \mathrm{sec}^{-1}$ (Fig. 1c), the minimum in the dependence F(t) vanishes and after the first growth of the force the second growth (in practice there is no domain II) starts directly. Therefore, the elastic-strain domain merges with the duplicate solidification domain for times less than the relaxation time.

Let us note that after the duplicate growth of the force, its drop starts, accompanied by the development of a secondary flow in all the cases considered. The strain in the secondary-flow domain has practically no irreversible influence on the polymer. This was verified by comparing the dependences F(t) obtained on specimens prepared from the polymer after participation in the secondary flow and undeformed specimens.

Under tension the ratio $\lambda = \sigma/\varkappa$ grows monotonically in time for $\varkappa \geqslant 1.2\cdot10^{-3}\ \mathrm{sec}^{-1}$ on both the growth sections of the force and its drop (Fig. 2). Let us note that $\lambda(t)$, and therefore the stress σ do not grow more slowly than exp $\varkappa t$ [see (6)] on the section of force growth.

For $\varkappa < 1.2\cdot10^{-3}\ \mathrm{sec}^{-1}$ no dependence $\lambda(t)$ could be obtained successfully because of the large errors in measuring the tensile force.

The dependences $3\eta^* = 3\sigma/\varkappa$ obtained in a shear flow are shown by the points 6-8 in Fig. 2. As is usual, these dependences achieve stationary flow. For large $\varkappa$ they pass through a maximum before emerging into stationary flow. The shear dependence $3\eta^*$, obtained in the domain of linear fluid behavior, corresponds to the points 6.

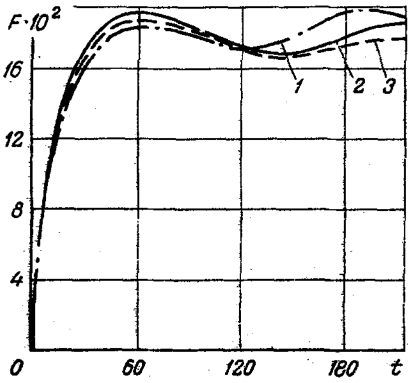

Fig. 3. Dependences of the tensile force F, N, on the reduced tension time t, sec, taking account of the temperature invariance: 1, 2, 3 correspond to T = 125, 145, 168°C; $\varkappa = 1.2 \cdot 10^{-2}$, $3.84 \cdot 10^{-2}$, 10^{-1} sec^{-1}.

Both the curves $\lambda(t)$ and $3\eta^*$ merge into one for small strain times.

Let us note that if the curve $\lambda(t)$ under tension with $\varkappa = 1.2 \cdot 10^{-3}$ (see Fig. 2) also merges into stationary flow under further tension (for $\varepsilon > 2.9$), then it is only for times considerably exceeding the relaxation time determined in the linear domain (see curve 5).

As experiments showed, the dependences $F(t)$ under tension and shear are subject to temperature invariance [2] at temperatures above the crystallization temperature. This means that upon compliance with the equality

$$\varkappa_k = \varkappa_0 \frac{\theta_0}{\theta_k}, \tag{7}$$

the correspondence

$$t_k/\theta_k = t_0/\theta_0 \tag{8}$$

is satisfied, and the dependences $F_0(t_0)$ and $F_k(t_k\theta_0/\theta_k)$ agree. (The subscript k denotes the different temperatures at which the test was performed; 0 is for some fixed test temperature.) For a polymer at temperatures above the crystallization temperature

$$\frac{\theta_k}{\theta_0} = \exp\left[\frac{E}{R}\left(\frac{1}{T_k} - \frac{1}{T_0}\right)\right]. \tag{9}$$

Here T_k is the temperature, °K, and E is the activation energy of the viscous flow.

Let us examine how the temperature invariance is verified experimentally.

For T = 145°C and $\varkappa = 3.84 \cdot 10^{-2}$ sec^{-1} the dependence $F(t)$ is represented by curve 1 in Fig. 3. Coincidences of one of the maximums of $F(t)$, e.g., were achieved in conducting the experiments by changing T and $\varkappa$ (different from T_0 and $\varkappa_0$). The second maximum (if it exists) hence automatically agrees in magnitude (but not in t). The ratio θ/θ_k is found by (7) from the correspondence found, and the viscous-flow activation energy from (9) is thereby $E \approx 15.6$ kcal/mole. Furthermore, using the time transformation (8), we obtain $F_0(t_0) \approx F_k(t_k\theta_0/\theta_k)$. The very same was done also for T = 168°C (see Fig. 3) and $\varkappa = 0.1$ sec^{-1}. The slight difference in the curves in Fig. 3 can be related to a somewhat different thermal prehistory of the tests. Let us also note that the values of E determined from the shear tests and by tension agreed.

Two maximums on the dependences $F(t)$ were also noted during tension of a high-density polyethylene melt (grade 20906-040). After the second growth of $F(t)$, rupture of the specimen with the preliminary formation of thinning similar to a neck was observed for this polymer. The duplicate growth of the force following directly after the first (analogous to Fig. 1c) was also observed in a noncrystallizing polymer, the polystyrene (grade D) melt. The elastic strain of these two polymers under tension was not measured.

Thus, it has been disclosed in this paper that a polymer fluid can have two domains during strain, in which it is deformed similarly to a solid. One of the domains is realized at a relatively low strain (the tension time is considerably less than the relaxation time), while the other is realized for large elastic strains. These domains can merge into one. Retardation of the flow (solidification) under tension with a constant strain rate is accompanied by a growth in the tensile force. The growth of stress in a finite section of the time does not absolutely indicate solidification being developed for significant elastic strains. After secondary solidification, either a secondary flow develops or rupture of the material occurs. A systematic study of the ruptures under tension of the melts is performed in [5]. We note that ruptures can, in principle, occur even in the domain of strain times less than the relaxation time, and cannot characterize the secondary-solidification domain. If secondary solidification is judged by the duplicate growth of the force, then it can be asserted that this property is characteristic for polymer fluids of different nature.

In conclusion, let us note that the property of solidification under large elastic strains is imbedded in the governing equations [4]. Under tension with $\varkappa$ = const this property results in $\varepsilon_f \to 0$ as t grows [5], i.e., starting with a certain time the polymer should be stretched as a solid. It is possible that the solidification considered in [4, 5] and the present paper is of the same nature (entropy). In this case, the main difference between theory [4] and experiment is that the experimental solidification being observed exists only in a bounded time interval. The development of a duplicate flow after solidification can be associated with distortion of the potential barriers governing the activation process, say, by the stress.

NOTATION

r, x, and φ, cylindrical coordinates; $\varkappa$, strain rate; ε, total strain; ε_f, irreversible strain; ε_l, elastic strain; e_f, irreversible-strain rate; $\theta(\theta_k)$, relaxation time; $t(t_k)$, time; F, tensile force; l_0 and l, r_0 and r, specimen length and radius in the initial and running times; l_r, length to which a piece of the stretched specimen of length l tends after instantaneous removal of the tensile stress from it; ξ, thermal diffusivity coefficient; $d = 2r_0$, initial diameter of the specimen being extended; σ, stress; S, specimen cross-sectional area; S_0, specimen cross section at $t = 0$; $\lambda = \sigma/\varkappa$; η, initial (Newtonian) viscosity; η^*, ratio between the stress and the strain rate under shear strain; E, activation energy; T, temperature; R, universal gas constant.

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