FLOW STRUCTURE OF AQUEOUS SOLUTIONS OF POLYETHYLENE OXIDE IN THE INLET REGION OF SHORT CAPILLARIES

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The article presents data on the visualization of the flow of aqueous solution of polyethylene oxide (PEO) in the inlet ection of a capillary. The times of structural relaxation in solutions of PEO are evaluated.

It was previously established that when solutions of high-molecular polymers flow through short capillaries, anomalously high "effective viscosity" (hydrodynamic resistance) [1-3] and pulsations of the speed of the incoming jet are observed although the Reynolds number is below the critical value [3]. The available integral characteristics of the flow of polymer solutions through short capillaries do not make it possible to explain the mechanism of the observed phenomena. In the solution of this problem data on the structure of such flows may be of the greatest importance. The experiments discussed below were therefore set up to shed light on the special features of the flow structure of a polymer solution in the inlet section of a short capillary.

In the experiments we used a flow viscometer with an entrance angle of 180° consisting of a cylindrical glass vessel with $2 \cdot 10^{-2}$ m diameter, a short capillary with $0.5 \cdot 10^{-3}$ m diameter, $0.21 \cdot 10^{-3}$ m long. The mean outflow velocity was determined at the time of discharge of a certain volume which was measured photoelectronically. The instantaneous outflow velocity, and also the onset of a fluctuating flow regime and its nature, were evaluated with the aid of a tensometric beam. The flow in the inlet section of the capillary was made visible by adding colored aqueous solution of PEO of the same concentration as the investigated one to the steam of jets, and at a speed equal to the flow velocity at the points where it was added. The diagram of the tensometric signal and the flow pattern were recorded simultaneously on video tape.

The "effective viscosity" of the polymer solutions was determined from calibrated graphs of the dependence of the time of their outflow on the pressure gradient obtained in the flow of glycerin solutions through a capillary; the viscosity of the solutions was measured with an Ubbelohde viscometer.

We investigated aqueous solutions of PEO with molecular mass $7 \cdot 10^6$ and concentration of 0.05% at 25°C. Aging of the solutions of PEO was practically prevented by additions of 0.05% potassium iodide [4].

In Fig. 1 the numbers indicate the points at which the flow was made visible in the inlet section of a short capillary. The pattern of the water inflow into the capillary is shown in Fig. 2, 1; it can be seen from it that the curving of the flow lines begins approximately on the boundary of a semisphere drawn from the center of the capillary. The flow pattern remained stable in the entire range of the investigated velocities. The dynamic head of the water jet emerging from the capillary does not change during the time of outflow. This is testified to by the rectilinear diagrams of the record of the velocity head of the water (see Fig. 3, 1 and 2).

In Fig. 2, item 3 shows the flow pattern of polymer solution with small pressure gradients at the end of the capillary. In this case, the flow lines are like those shown in Fig. 2, 1. Here the "effective viscosity" of the solution hardly differs from the viscosity of water. Further increase of the pressure gradient leads to increased discharge velocity, and in the flow patterns some change in comparison with the flow pattern of water becomes noticeable. In the direct vicinity of the entrance into the capillary the flow lines become curved, form-

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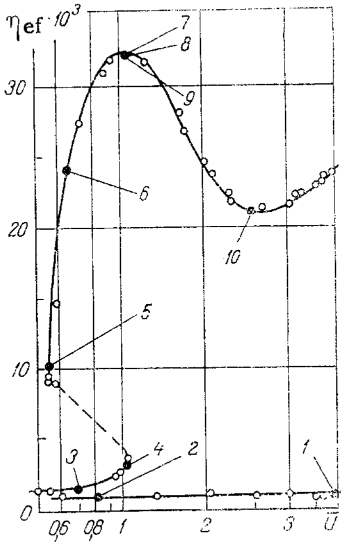

Fig. 1

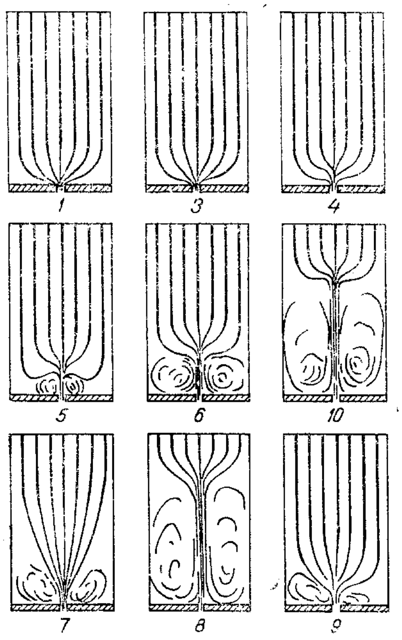

Fig. 2

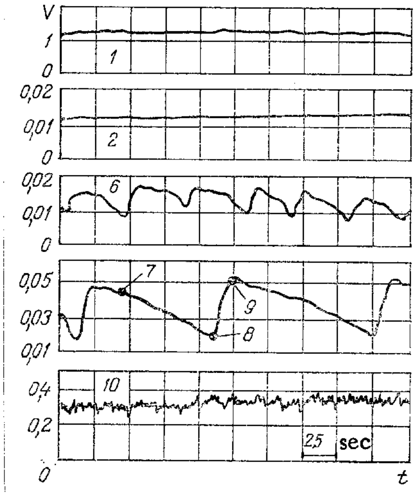

Fig. 3

Fig. 1. Dependence of the "effective viscosity" of aqueous solution of PEO with molecular mass $7\cdot 10^6$ and concentration of 0.05% on the mean outflow velocity through a capillary at 25°C. ν_{ef}, Pa·sec; $\bar{U}$, m/sec.

Fig. 2. Flow line pattern in the outflow of water and of aqueous solution of PEO from a capillary (the numbers below the patterns correspond to the points indicated in Fig. 1).

Fig. 3. Change with time of the tensometric signal which is proportional to the dynamic head of the emerging jet of aqueous solution of PEO (the numbers of the curves correspond to the points marked in Fig. 1). V, volts; t, sec.

ing the submerged entrance jet. This region is a cone whose apex lies in the plane of the entrance opening of the capillary. If the pressure gradient is increased even more, the expected increase of the mean velocity does not take place; on the contrary, the mean velocity becomes substantially lower than in the preceding experiment. In this case, the flow is of a more dissipative nature, testified to by the increased "effective viscosity" (see Fig. 1), and the flow pattern (Fig. 2, 5) begins to display a new characteristic region: the eddy torus surrounding the entrance cone, whose height somewhat increased.

It must be pointed out that the flow pattern in this velocity range is unstable in the sense that when the experiment was repeated with the same pressure gradient, the outflow velocity was sometimes higher, and the pattern of flowlines obtained was the same as the pattern shown in Fig. 2, 4, i.e., the flow pattern had a cone-shaped zone but without the toroidal eddy.

With increasing pressure gradient the "effective viscosity" increases but the mean outflow velocity increases imperceptibly. In the flow pattern (Fig. 2, 6) the height of the inlet cone increases, its taper in the direct vicinity of the entrance into the capillary decreases, and the inlet jet assumes the shape of a "cord." The circulation zone also increases, filling the space at the entrance into the opening of the capillary. The recorded diagram of the velocity head of the jet emerging from the capillary (see Fig. 3, 6) shows that the outflow here is of a pulsating (fluctuating) nature. The change in magnitude of the outflow velocity of aqueous solution of PEO from the capillary is imperceptible but the frequency is relatively high.

Figure 2, 7-9 shows flow patterns relating to the same flow regime but at different instants of outflow. On the diagram of the dependence of "effective viscosity" of aqueous solution of PEO on its mean outflow velocity from the capillary, the region of maximum viscosity corresponds to this regime. The change of the flow patterns in time indicates that the instability of flow manifests itself here to a considerably greater extent. Turning to the diagram of the velocity head characteristic of the given regime of outflow (see Fig. 3, 7-9), we can easily see the peculiar nature of the change in outflow velocity. The experiment with simultaneous recording of the diagrams of outflow velocity and flowline patterns on video tape made it possible (in frame-by-frame playback) to compare the flow patterns and the corresponding instantaneous velocities of the solution emerging from the capillary. At the initial instant (Fig. 2, 7) the "cord" grows slowly, and the outflow velocity at the same time decreases slowly (Fig. 3, 7). At the same time the size of the eddy zone increases. After the "cord" has attained some maximum size (Fig. 2, 8), it "collapses" downstream, i.e., it is destroyed in a way (Fig. 2, 9). The outflow velocity at the same time increases abruptly (Fig. 3, 9), and immediately afterwards a new "cord" forms and its length increases. This process is periodic in time. The flow patterns repeat themselves with a period of hundredths of a second to tens of seconds, sometimes even more, in dependence on the flow regimes, the molecular mass of the polymers, and the temperature. It should be noted that the velocity pulsations in instable flow regime are mutually correlated in time, and that they are of a nonprobabilistic nature. An experiment showed that under the same conditions the recorded diagrams of the velocity head (Fig. 3, 6-9) are completely reproduced as to amplitude, shape, and frequency. It would be incorrect to say that the phenomenon under examination is of a turbulent nature; this, however, was assumed in [5].

The flow pattern corresponding to the point of the minimum on the dependence of the "effective viscosity" on the mean outflow velocity of the aqueous solution of PEO from the capillary (Fig. 1) is shown in Fig. 2, 10. The height of the "cord" in this experiment was greater than in the previous one. The diagram of the velocity head (Fig. 3, 10) indicates the pulsating nature of the velocity in these outflow regimes, but the pulsations became smaller. When the pressure gradient increases even more, the height of the "cord" decreases, and the "effective viscosity" somewhat increases (Fig. 1). In the process of recording the diagrams, the height of the "cord" changed somewhat, and it oscillated from side to side. The amplitude of the change in velocity head of the jet remained practically the same as in the case shown in Fig. 3, 10.

The obtained data on the flow structure make it possible to find the velocity distribution, and consequently also the velocity gradient in the entrance region of the capillary. Proceeding from the condition of continuity of the flow and regarding the flow velocity in the plane of pipe section as constant and equal to the discharge velocity in this pipe, we obtained the following expression for the longitudinal velocity distribution in the entrance region of the capillary:

$$U_y = U_0 \left(\frac{D}{D_y} \right)^2, \text{where} D = \frac{d}{D_0} d_0.$$

The y axis is the axis of symmetry of the flow, and it is correlated with the center of the inlet opening of the capillary; the direction is opposed to the direction of the flow.

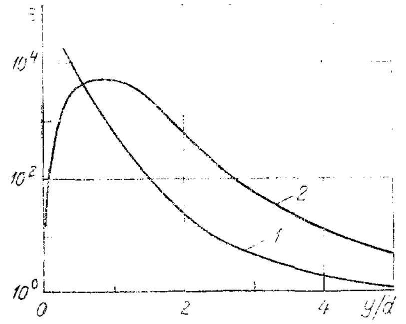

Fig. 4. Distribution of the velocity gradient on the flow axis in the entrance region of the capillary upon flow of water and of aqueous solution of polyethylene oxide [1) water; 2) aqueous solution of PEO, $\bar{U}$ = 2 m/sec; curve 2 is shifted relative to curve 1 by the length of the "cord"].

In the experiment with water (Fig. 4) the liquid in the central flow pipe begins to accelerate substantially in the direct vicinity ($2\text{-}3 \cdot 10^{-3}$ m) of the entrances to the capillary, and the longitudinal velocity gradient at the entrance to the capillary attains about $6 \cdot 10^4$ sec^{-1}. A completely different pattern is found when aqueous solution of PEO flows out of a capillary in which it had the same mean (in time) discharge velocity. In this case, with the approach to the opening, the velocity attains its maximum, however, not at the entrance to the capillary but at some distance equal to about $2 \cdot 10^{-2}$ m. On the pattern of flowlines this region corresponds to the place where the "cord" forms (see Fig. 2, 10). In the "cord" itself the velocity is practically invariable and equal to the mean (over the cross section) discharge velocity in the capillary. Thus the macromolecules in a convergent flow of liquid lead to the origin of a peculiar pipe with mobile and impermeable walls, the "cord." The existence of a circulating motion is obviously also due to the existence of such a pipe. It can be seen from Fig. 4 that upon approach to the source of the "cord" the polymer solution begins to be accelerated somewhat sooner than water, even when the source of the "cord" is made to coincide with the entrance to the capillary, and the maximum longitudinal velocity gradient is one order of magnitude smaller than in a flow without polymer additions ($\varepsilon_{max} \cong 5 \cdot 10^3 \text{ sec}^{-1}$).

The discovered differences in the qualitative flow patterns of water and solution of PEO and of the quantitative evaluations of the flow characteristics in the entrance region of the capillary require further study. However, even now the accumulated data are perfectly satisfactorily explained from the point of view of conformational changes of macromolecules under the conditions of an elongational flow. The specific rheological properties of dilute polymer solutions have to be due in the first place to the ability of macromolecular coils to change their shape under the effect of a hydrodynamic field. The question of the possibility of strong deformation of macromolecular coils under the effect of an elongational flow was dealt with by many authors [6-10, etc.]. We note that the deformation of a macromolecular coil in a longitudinal field is much stronger than in a shear field [10] because in longitudinal flow there arises a positive feedback between $[\eta]$ and $\dot{\varepsilon}$, and the process of scatter, which begins at relatively low critical $\dot{\varepsilon}_{cr}$, increases by a snowball effect. It can be easily proved that when the condition $\dot{\varepsilon}_{cr}\tau \cong 1$ [6] is fulfilled, the macromolecule goes over almost completely into the stretched conformation.

The fact that birefringence is observed when aqueous solutions of PEO flow into capillaries and slits shows that $\dot{\varepsilon}_{cr} \leqq \dot{\varepsilon}_{max}$ [11]. Then, adopting $\dot{\varepsilon}_{cr} = \dot{\varepsilon}_{max}$, we obtain the maximum relaxation time of PEO molecules (molecular mass $7 \cdot 10^6$) to be equal to about $2 \cdot 10^{-4}$ sec, which is of the same order of magnitude as that determined in accordance with Zimm's theory [12]: $\tau_Z = 4.3 \cdot 10^{-4}$ sec. If we take it that $\dot{\varepsilon}_{cr} = 1/\tau_Z$, then the time of effect of the longitudinal velocity gradient $\dot{\varepsilon} \geqq \dot{\varepsilon}_{cr}$ is ten times larger than τ_Z. Thus, the obtained data permit the assumption that the PEO molecules in the entrance region of a short capillary are subjected to the transition into the almost completely stretched state.

It can be seen from Fig. 4 that the longitudinal velocity gradient in the "cord" tends to zero, and then the PEO molecules that are there in stretched conformation are bound to coil because the internal tensile stress of the coil also tends to zero. Consequently, from the available experimental data we can also estimate the time within which the PEO molecules change from the stretched to the coiled conformation. It was shown above that with increasing pressure gradient the "cord" appears, and then grows. The outflow velocity of the PEO solution from the capillary also increases. The time for which the polymer is in the "cord" depends on its length and speed. Perfectly probable is a situation where the time of transition of the macromolecules from the fully stretched to the coiled conformation is equal to the time during which they are in the "cord." This regime obviously corresponds to the experiments which revealed intense pulsating outflow (see Fig. 2, 7-9). Apparently in this case the rate of growth of the "cord" is somewhat higher than the outflow velocity and, therefore, the length of the "cord" increases in time, and the time of dwelling of the polymer molecules in the entrance jet also increases. When a certain critical length is attained, the time of dwelling of the macromolecules in the "cord" becomes equal to the time of its twisting into a coil. At the entrance to the capillary the "cord" begins to "dissolve," and the solution again tends to the inlet opening of the capillary. Then, knowing the length and speed of the "cord" at the instant when the "cord" at the entrance to the capillary begins to "dissolve," we determine the time of coiling, which is $\tau_* = l/U_0 = 5\text{-}8 \cdot 10^{-2}$ sec, i.e., of the order of 10^{-1} sec. This time is almost three orders of magnitude longer than the maximum relaxation time of PEO molecules. Such discrepancy between the times of stretching and coiling of PEO molecules apparently cannot be explained from the positions of isolated macromolecules in the solution upon their longitudinal flow. The cause of such large τ_* may be the formation of some supermolecular structures (gels) under conditions of convergent flow, and these structures also determine the existence of the "cord." This agrees with the data obtained in [13].

A confirmation of these assumptions may be an experiment involving the "cutting of the cord" at the instant of its stable existence. If the "cord is cut" sufficiently quickly with the aid of a platinum thread at the entrance to the capillary, its stability is lost and it is destroyed. The outflow velocity then greatly increases, and immediately afterwards a new "cord" forms and grows again. The situation here is in many respects the same as in Kachal'skii's well-known experiment [10]. A fiber of polyvinyl alcohol, on which a load is suspended, does not dissolve when it is lowered into boiling water, but it suffices to cut the fiber, i.e., remove the load, and it instantly dissolves.

Attention should be drawn to the fact that the system water—PEO under conditions of elongational flow with certain flow regimes is a self-regulating system with negative feedback. This last manifests itself in the following: increasing longitudinal velocity gradients lead to deformation of the macromolecular coils, and this in turn causes a change of the structure of flow in such a way that the longitudinal velocity gradients decrease.

NOTATION

$\bar{U}$, mean discharge velocity in flow through a capillary; U_0, velocity at the entrance to the capillary; U_y, velocity determined in cross sections of the flow pipe; D, diameter of the flow pipe at the entrance to the capillary; D_y, diameter of the flow pipe determined in its cross sections; d, diameter of the flow pipe in the unperturbed part of the flow; D_0, diameter of the measuring cell in which the flow was made visible; d_0, diameter of the capillary; $\dot{\varepsilon}$, longitudinal velocity gradient; $[\eta]$, characteristic viscosity; τ, maximum relaxation time, τ_*, time of transition of macromolecules from the stretched to the coiled conformation; $\underline{l}$, length of the "cord"; τ_Z, relaxation time determined in accordance with Zimm's theory.

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HEAT TRANSFER IN FLUIDIZED BEDS

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We propose a simplified model of external heat transfer in a fluidized bed. We compare calculated and experimental data, and recommend a computational procedure in polydisperse beds.

Recent research on the combustion and gasification of low-grade solid fuels in a fluidized bed indicates considerable practical interest in the development of models of external heat transfer in high-temperature beds with a high variation of particle sizes. In developing such a model it is quite natural to consider a fluidized bed as a layer of large particles, taking account of their special features, in particular the important role of the convective heat transfer component [1].

With this approach, for all practical purposes it is valid to assume that the temperature drop between the heat-transfer surface and the bed core occurs mainly in the layer of particles nearest the surface. This in turn makes it possible in the first approximation to consider mechanistically heat transfer between the surface and a layer of fluidized particles as a problem of heating a packet consisting of a gaseous layer of thickness l_0 and a quasihomogeneous medium (the fluidized bed). Unlike models proposed earlier (e.g., [2]), it is assumed that the whole packet is penetrated by gas filtering through it.

This problem can be formulated mathematically as follows:

$$\lambda_f \frac{d^2T_f}{dy^2} - \frac{c_f\rho_f u (T_f - T_0)}{H\varepsilon} = 0, \quad 0 \leqslant y < l_0, \tag{1}$$

$$\lambda_s \frac{d^2T_s}{dy^2} - \frac{c_f\rho_f u (T_s - T_0)}{H} = 0, \quad l_0 < y \leqslant l \tag{2}$$

with the boundary conditions

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