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Abstract

Full Text

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HIGH ELASTICITY, SHEAR STRENGTH, AND THE DEVELOPMENT OF STEADY VISCOUS FLOW IN FLUID POLYMERS

Many works have been published on the study of the viscous properties of polymer melts. At the same time, very little is known about their elastic properties and the conditions of transition from highly elastic deformations to steady viscous flow. The present work is devoted to this question.

The study of polymer melts was carried out on a rotational cone-plate elastoviscometer (^{1}) in a shear-stress field (τ) of high homogeneity (98%) at various constant rates of deformation ($\dot{\gamma}$). The instrument is equipped with a dynamometer —a torsion brake of high rigidity, with a modulus of 140 kg $\mathrm{m} \cdot \mathrm{radian}^{-1}$. The experiments were carried out over a wide temperature range in vacuum (of the order of 10^{-4} torr), which excluded the influence of thermo-oxidative processes on the measurement results. Alkatin-2 and block polystyrene (manufactured by the Kuskov plant), with molecular weight of the order of $3 \cdot 10^5$, were chosen as the main objects of study.

Fig. 1. Three principal cases of the dependence of shear stresses on deformation time for polymer melts

At various values of $\dot{\gamma} = \mathrm{const}$, depending on the temperature and the nature of the polymer, curves of $t(t)$ and $\tau(\gamma)$ of three types are obtained. Since all experiments are carried out at a constant rate of deformation, the dependences $\tau(t)$ and $\tau(\gamma)$ are equivalent. For alkatin, typical curves $\tau(t)$ are presented by the graphs in Fig. 1. In Fig. 1, points I correspond to the beginning of deformation of the melt at constant rate, and points II to stopping of the rotating measuring surface and the beginning of relaxation of the polymer at constant deformation.

Curves of type A (Fig. 1) are observed at high temperatures, when relaxation proceeds at a high rate. After a constant rate of deformation has been imposed,

Fig. 2. Dependence of shear stresses on deformations at various temperatures and deformation rates for a high-pressure polyethylene melt

Figure 2: Fig. 2. Dependence of shear stresses on deformations at various temperatures and deformation rates for a high-pressure polyethylene melt

there is an almost instantaneous increase of the shear stresses to values corresponding to steady flow ($\tau = \tau_s$), and an equally rapid fall of the stresses when the moving measuring surface is stopped. Curves A in Fig. 1 were obtained at 240°. Under these conditions the polyethylene melt shows no signs of high elasticity.

Curves of type B are recorded at relatively low temperatures and deformation rates (in Fig. 1 they correspond to 120°). In this case, after

from the start of deformation, the shear stresses increase monotonically at a low rate until steady flow is reached; stress relaxation likewise proceeds at a low rate.

Curves of type **B** (for 114°) differ from curves by the appearance of a stress maximum ($\tau = \tau_m$) shortly after the start of deformation of the melt at a constant rate. Curves with a maximum are obtained at more or less considerable deformation rates and at low temperatures. After passing through the maximum, a steady flow regime is reached; moreover, constancy of the values τ_s at the values of $\dot{\gamma}$ used in the present work was observed for several hours. Under these conditions, after termination of the experiment and completion of stress relaxation, repeated testing of the melt can be carried out many times with high reproducibility. This applies to the character of the maximum, to the values τ_m, τ_s, and also to the deformations at which the maximum shear stresses (γ_m) and the steady flow regime (γ_s) are reached. The reproducibility of the maximum and of the steady-flow regimes in repeated tests of the melt indicates that, at low deformation rates, irreversible changes (degradation of the polymer macromolecules) are absent.

Fig. 2. Dependence of shear stresses on deformations at various temperatures and deformation rates for a high-pressure polyethylene melt

After the beginning of deformation of the polymer melt at a specified rate, the increase in shear stresses outpaces the rate of their relaxation. With a further increase in the deformation rate, a state is reached in which, owing to the presence in the melt structure of comparatively slowly relaxing elements, the shear stresses do not have time to dissipate at the proper rate even as τ rises to high values. Under these conditions, only a change in the structure of the system can cause the rapid development of the relaxation process. Two types of such structural changes are possible. First, destruction of the structural network in the melt, formed by junctions between macromolecules, whose existence is due to the action of intermolecular forces. This process is reversible; it can be repeated many times, as was described above. Second, at high deformation rates and relatively low temperatures, when reversible restructuring of the polymer structure is hindered, rupture of macromolecules that are in an especially unfavorable position and contain-

···delaying the development of the process of deformation of the melt. This process irreversibly changes the nature of the polymer. As the rate of deformation increases, the fraction of irreversible changes in the structure of the polymer increases. These changes occur over time and, at a constant rate of deformation, may be quite prolonged, which delays the attainment of steady flow.

The critical deformation regimes corresponding to the maxima on the curves $\tau(t)$ and $\tau(\gamma)$ record the change in that structure of the polymer melt which restrains the development of deformations. This is equivalent to reaching the shear-strength limit, i.e.

$$\tau_m = \tau_{sh}.$$

It follows from the above consideration of the question that the transition from curves of type A to curves of type and is determined by the combination of the basic conditions under which the experiments are carried out—the temperature and the deformation rate.

Let us consider the curves $\tau(\gamma)$ obtained at different temperatures and deformation rates in experiments with alkathene (Fig. 2). Similar results were recorded for polystyrene. The characteristics of the experimental conditions described by the individual curves in graphs A– (Fig. 2) are given in Table 1.

As is seen from Fig. 2, with increasing deformation rate (at constant temperature), monotonic curves $\tau(\gamma)$ are transformed into curves with a maximum, the sharpness of whose appearance increases with increasing $\dot{\gamma}$.

Table 1

Values of the deformation rate $\dot{\gamma}$ (sec^{-1}) at different temperatures for a high-pressure polyethylene melt

Curve no. in Fig. 2	A at 114°	at 140°	at 195°
1	0.028	0.21	0.56
2	0.056	0.56	0.75
3	0.075	0.75	2.1
4	0.21	2.1	2.8
5	0.28	2.8	5.6
6	0.56	5.6	21
7	0.75		
8	2.1		

Figure 4

Figure 3: Figure 4

Fig. 3. Dependence of the deformations γ_m and γ_s on the deformation rate $\dot{\gamma}$ and temperature

The dependences $\tau_m(\dot{\gamma})$ and $\tau_s(\dot{\gamma})$ have a similar character. In a narrow range of variation of the variables they are described by a power-law function. As a measure of the sharpness with which the maximum is expressed on the curves $\tau(\gamma)$, one may take the quantity τ_m/τ_s. In the experiments considered with alkathene and polystyrene, the values of τ_m/τ_s did not exceed 1.4.

At not very high deformation rates, steady flow regimes are always attained at $\tau = \tau_s$ and $\dot{\gamma} = \dot{\gamma}_s$. For clarity, the transition to steady flow regimes on the curves $\tau(\gamma)$ is shown by crosses. An increase in $\dot{\gamma}$ somewhat accelerates the attainment of steady flow regimes, but leads to a sharp increase in γ_s. At different temperatures,

$$\gamma_s = A + B \lg \dot{\gamma},$$

where B has a value of about 2. The values of γ_m increase with increasing $\dot{\gamma}$ much more slowly than γ_s.

The values of γ_s and γ_m increase with increasing $\dot{\gamma}$ as the temperature is lowered. With decreasing temperature, γ_m reaches several hundreds, and γ_s—several thousands of percent. This is explained by the data presented in Fig. 3.

In the process of deformation of the polymer, from values of γ close to γ_m up to $\gamma = \gamma_s$, a change in the structure of the polymer takes place, and there may occur···

degradation of macromolecules [2]. At high rates of deformation this process proceeds for a more or less prolonged time. If the temperature and rate of deformation are specified, then, in order to reduce the mechanodestruction of the polymer in the melt, it is important to reduce the duration of the mechanical action. Under short-term action, even very high rates of deformation under conditions where large shear stresses and $\dot{\gamma}$ values close to $\dot{\gamma}_m$, or exceeding this value, are attained, the mechanodestruction of the polymer may be insignificant.

Fig. 4. Dependence of the shear moduli of high-elastic deformation on $\dot{\gamma}$ for a melt of block polystyrene.

With increasing temperature (at a constant rate of deformation), the resistance of the polymer to deformation rapidly decreases, the values of τ_m, τ_s, $\dot{\gamma}_m$, $\dot{\gamma}_s$ decrease, and the $\tau(\dot{\gamma})$ curves become monotonic. This means that, with increasing temperature, the development of the process of steady viscous flow is greatly facilitated and accelerated, the sharpness of the transition through the strength limit and the structural changes in the polymer accompanying this transition are reduced. To avoid mechanodestruction of polymers or to reduce its intensity, it is advisable to process thermoplastics at the highest possible temperatures, when their thermal destruction is still absent and antioxidants still retain their effectiveness (or the processing is carried out in an inert gaseous medium).

At the rates of deformation used in the present work, the activation energy for the transition through the strength limit is somewhat higher than the activation energy of viscous flow (alkathene-2), or these activation energies have practically identical values (polystyrene). It may be assumed that, in those cases where the activation energies of the processes considered have close values, degradation of macromolecules during the transition through the strength limit is practically absent, and this transition is accompanied only by reversible changes in the structure of the polymer melt.

From the conditional coefficients tangent to the $\tau(\dot\gamma)$ curves at $\tau = 0$, one can find the shear moduli G. At relatively low values of the rates of deformation,

$$G = a + b \lg \dot\gamma.$$

In the case of alkathene, for various temperatures $b = 4$. For polystyrene the value of b decreases from 8 to 2.5 as the temperature is raised from 160 to 210°. With increasing $\dot\gamma$, within a comparatively narrow interval of $\dot\gamma$ values, a sharp change occurs in the character of the dependence $G(\dot\gamma)$. In the region of those $\dot\gamma$ values at which the $\tau(\dot\gamma)$ curves acquire a sharply extremal character and the ascending branch of these curves becomes rectilinear, over a considerable interval of variation of $\dot\gamma$ and τ the value of G does not depend on $\dot\gamma$. It is precisely under these conditions that the high elasticity of polymer melts is sharply manifested. The dependence $G(\dot\gamma)$ for polystyrene is illustrated by the data of Fig. 4.

The transition from the Newtonian branch to the structural branch on the flow curves occurs at rates of deformation significantly lower than those at which the strength limit is detected.

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Note: Figure translations are in progress. See original paper for figures.