EXPERIMENTAL VERIFICATION OF THE THEORY OF THIXOTROPY OF VISCOELASTIC POLYMER MEDIA

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Previous studies [1, 2] were devoted to the formulation of a phenomenological theory of the reversible changes (thixotropy) in the physicomechanical properties of viscoelastic media, in particular, polymer systems. The basis of this theory is the idea that the reversible changes in the structure and properties of viscoelastic thixotropic media under the influence of mechanical action are due to a change in their relaxation spectrum. In this case the behavior of the mechanical properties is entirely and uniquely determined by two material functions which completely characterize the given material: the relaxation time (frequency) distribution function, which describes the behavior of the material in the linear region of deformation, and the thixotropy function, which determines the nature of the changes (compression) of the relaxation spectrum on transition to the nonlinear region. The object of this approach is to reflect the effect of the change in supramolecular and molecular structures associated with the flow of polymer system, or in the bonds and orientation of the particles in disperse systems, on the viscoelastic and viscosity properties of the systems concerned. The essential validity of this approach was demonstrated in [3], where it was shown that at sufficiently high strain rates changes occur in the structure of the polymer leading to a change in mechanical properties. In [4] the basic structural functions were found. These, in conjunction with the proposed theory of thixotropy, characterize the behavior of a broad group of polymer systems in both the linear and the nonlinear regions of deformation. In this connection it should be noted that whereas for the linear region the accuracy of the laws obtained lies within the limits ± 100%, on transition to the nonlinear region the error may increase. Therefore, for the purposes of a rigorous quantitative verification of the theory we shall use not the universal functions obtained in [4], but the more precise characteristics of the specific material on which the experiments are performed, since those effects with respect to which it is desired to test the theory usually lie within the limits of 30% of the measured quantities.

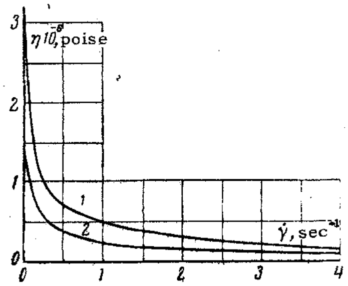

Fig. 1

The experimental and theoretical relations for the shear stress τ as a function of time t in simple shear were quantitatively compared for two cases: 1) for deformation at constant shear strain rate $\dot\gamma$ = const instantaneously developed at t = 0; 2) for stress relaxation after instantaneous interruption of steady-state flow with preservation of the constant strain γ = const. Two polymers were used to test the theory: P-20 low-molecular polyisobutylene with a weighted-mean molecular weight of 100 000 at room temperature and OP-30 polypropylene with a weighted-mean molecular weight of 700 000 at 230° C. The experimental procedure and the results of detailed studies of the rheological properties of these materials were published in [5, 6].

For $\dot\gamma$ = const the basic equations of the theory take the form [2]

$$\tau(t) = \dot\gamma \int\limits_{S(t)}^{\infty} \frac{N(s)}{s}(1 - e^{-st})\,ds, \qquad \varphi(S(t)) = \dot\gamma\,[1 - e^{-S(t)\,t}]. \quad (1)$$

Here s is the relaxation frequency, N(s) is the relaxation frequency function, φ(s) is the thixotropy function, S(t) is an auxiliary function describing the change in the spectrum during deformation.

For the case of stress relaxation after instantaneous interruption of steady-state flow at γ = const the basic relations of the theory take the form

$$\tau(t) = \dot\gamma \int\limits_{S(t)}^{\infty} \frac{N(s)}{s} e^{-st}\,ds, \qquad \varphi(S(t)) = \dot\gamma e^{-S(t)\,t}. \quad (2)$$

The experimentally determined relations for viscosity as a function of shear strain rate for the polymers in question (curve 1—polyisobutylene at 22° C, curve 2—polypropylene at 230° C) are represented in Fig. 1. The principal experimental difficulties are associated with the reliable determination of N(s) from which, using the relation

$$\eta(\varphi(s)) = \int\limits_{s}^{\infty} \frac{N(x)}{x}\,ds \quad (3)$$

(here η is the non-Newtonian viscosity), φ(s) can be uniquely determined. From relation (3) it is possible uniquely to determine any of the three functions $\eta(\dot\gamma)$, φ(s), N (s), if the other two are known. In [4] it was shown that for the universal structural functions $\varphi(s) \approx s$. Allowing for the possibility of accumulation of the error of this estimate in connection with the nonlinearity of relations (3), we set

$$\varphi(s) = as, \quad (4)$$

where a is a dimensionless constant characteristic of the given material. A similar proposal, based on certain physical considerations, was made in [2]. The parameter a can be selected empirically or determined exactly if the value of the function N(s) is reliably known at least for some narrow frequency range. Substituting (4), with account for (3), into Eqs. (1), (2) and integrating parts, we get the following equations:

for the case $\dot{\gamma}$ = const

$$\tau(t) = \frac{\gamma^{\cdot} t}{a}\int_{0}^{\infty}\eta(x)\exp\frac{-xt}{a}\,dx \qquad \left(t \leqslant t^*, \quad t^* = \frac{a}{\gamma^{\cdot}}\right),$$

$$\tau(t) = aS(t)\,\eta(aS(t)) + \frac{\gamma^{\cdot} t}{a}\int_{aS(t)}^{\infty}\eta(x)\exp\frac{-xt}{a}\,dx \qquad (t > t^*), \tag{5}$$

$$t(S) = \frac{1}{S}\ln\frac{1}{1 - aS/\gamma^{\cdot}}, \tag{6}$$

for the case γ = const

$$\tau(t) = aS(t)\,\eta(aS(t)) - \frac{\gamma^{\cdot} t}{a}\int_{aS(t)}^{\infty}\eta(x)\exp\frac{-xt}{a}\,dx, \tag{7}$$

$$t(S) = \frac{1}{S}\ln\frac{\gamma^{\cdot}}{aS}. \tag{8}$$

Figures 2 and 3 show the theoretical and experimental relations $\tau(t)$ for the two cases of deformation considered at several values of the strain rate. The left branches of the curves, including the segments of constant stress, represent $\tau(t)$ for $\gamma^{\cdot}$ = const, the right drooping branches are the relaxation curves. The solid lines represent the experimental values, while the points through which the broken curves are drawn represent the theoretically calculated values. Figure 2 gives the curves for polyisobutylene, the value of a being taken as 3.5. Curve 1 corresponds to $\gamma^{\cdot} = 0.4$, curve 2 to $\gamma^{\cdot} = 1.2$ sec^{-1}. Figure 3 shows the corresponding curves for polypropylene (a = 4). Curves 1, 2, 3 correspond to $\gamma^{\cdot}$ = 0.24, 0.4 and 0.8 sec^{-1}, respectively. As may be seen from Figs. 2 and 3, there is perfectly satisfactory agreement between theory and experiment. However, in all cases the following differences between the theoretical and the experimental curves are observed: for the cases considered the theoretically determined maxima of values on the $\tau(t)$ curves are generally higher than those observed experimentally, while at large t stress relaxation is more rapid than predicted by the theory. Possible explanations include errors in the design of the experiments or in the calculations. We shall start by considering the first group of possible errors.

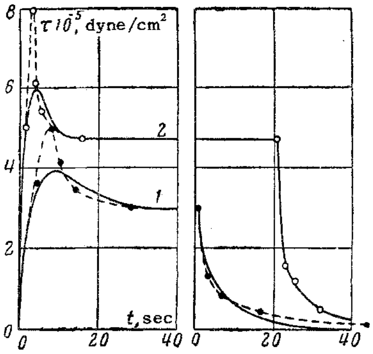

Fig. 2

As shown in [7], an important part in estimating the reliability of the results of measurements on instruments of the rotation type is played by the characteristics of the dynamometer device (rigidity and moment of inertia). Essentially, the experimental curves represent (correct to the scale) the curves of angular displacement of one of the measuring surfaces, which in the calculations was assumed to be strictly fixed. We note that in all the cases considered the maximum Reynolds number $R = \gamma\alpha^2 r^2\rho/\eta < 10^{-6}$ (the experiment was performed on a rotation instrument of the cone-plane type with an angle α = 0.0872 radian between the generators of the cone and the plane, maximum radius of the measuring surfaces r = 3.5 cm. The density of both material ρ did not exceed 1 g/cm^3). Therefore the inertia of the material may be neglected. Then the true strain rate is easily found from the expression

$$\gamma_0^{\cdot} = \gamma^{\cdot} - \frac{\omega_d}{\alpha} = \gamma^{\cdot} - \frac{1}{c\alpha}\frac{d\tau}{dt}. \tag{9}$$

Here $\gamma^{\cdot}$ is the given shear strain rate, ω is the angular rate of displacement of the dynamometer, c = 10^{10} dyne/cm/radian is the rigidity of the dynamometer. As may be seen from Figs. 2 and 3, the maximum value of ω_d/α, corresponding to the maximum value of $d\tau/dt$, does not exceed $2 \cdot 10^{-5}$ sec^{-1} for all the materials and cases of deformation considered. Thus, with a very high degree of accuracy $\gamma^{\cdot}_0 = \gamma^{\cdot}$. Equation (9) may prove very useful in analyzing data obtained on an instrument with a so-called "soft" dynamometer, since (9) allows one to calculate the true dependence $\gamma_0^{\cdot}(t)$. For a very sharp change in stresses in the measured specimen an additional unallowed-for error may be introduced due to the inertia both of the dynamometer and of the secondary recording device (a EPP-09 potentiometric recorder). This error may lead to a serious underestimation of the measured quantity as compared with the true value, especially if there is a very sharp maximum. In measuring very small stresses (which is essential in a relaxation experiment at large t) the relative error becomes large, since the measured quantity itself is comparable with the instrument error.

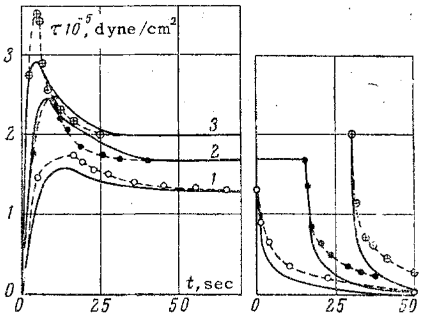

Fig. 3

Let us now turn to the second group of causes of possible errors. Of the three functions considered N(s), $\varphi(s)$, $\eta(\gamma^{\cdot})$ only the last (dependence of non-Newtonian viscosity on shear rate) was directly determined experimentally. In view of the large number of measurements the error associated with the experimental determination of $\eta(\gamma^{\cdot})$ may be considered small (at least, less than 6%) and without much influence on the results. The possibility of fundamental errors may be connected with the choice of the parameter a and, in general, with the determination of the function $\varphi(s)$. As may be seen from (5)-(8), a change in the parameter a leads to a corresponding compression or extension of the $\tau(t)$ curves along the t axis. It is characteristic that the maximum of the $\tau(t)$ curves observed at $t = t^*$ does not depend on a. In our work a was chosen in such a way that the position of the maximum on one of the theoretical curves roughly coincided with that observed experimentally. The following values of the parameter were taken: a = 3.5 for polyisobutylene, and a = 4 for polypropylene. The first of these values is also in accord with the results of high-frequency measurements of the dynamic properties of this material in which N(s) was determined [8]. In this case the N(s) computed from (3) for very high values of s (10^3 sec^{-1}) coincides with the N(s) determined from the results of dynamic measurements. Note also that at small s the relation $\varphi(s)$, and hence N(s), may prove more complex than assumed above; in particular, this may lead to serious errors at large values of t in the stress relaxation experiment. The error in determining N(s) and $\varphi(s)$ in the low-frequency region may also have a serious effect at the beginning of the process of destruction of the structure, i.e., in the neighborhood of the maximum of $\tau(t)$.

Of course, in making a quantitative comparison of the theoretical and experimental data one must not overlook the possibility of a further improvement in the theory.

It is of interest to compare certain basic theoretical results with previous experimental observations. Calculation shows that in the region $t < t^*$ (ascending branches of the $\tau(t)$ curves for $\gamma^{\cdot}$ = const) up to the maxima the deformation of the polymer proceeds without destruction of the structure; the thixotropic change in the viscoelastic properties takes place on the drooping branches of these curves—from the maximum values of the stresses corresponding to steady-state flow conditions. Precisely for this reason, the maximum value of the stress on the $\tau(t)$ curves observed for $\gamma^{\cdot}$ = const may be produced by the ultimate shear strength, while the region beyond the maximum up to transition to steady-state flow conditions is a region of structural stress relaxation. During relaxation, in accordance with the results of the calculations, the destroyed elements of structure are restored, which is determined, in accordance with (8), by a decrease in the function S(t). In this case the almost complete restoration of the structure continues much longer than the observed stress relaxation. These results correspond very well with the results of direct observations of the thixotropy effect in polymer melts described in [3].

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