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TRANSFER PROCESSES IN RHEOLOGICAL MEDIA

SPECIAL FEATURES OF NONLINEAR BEHAVIOR OF A POLYMER SOLUTION ON LARGE PERIODIC DEFORMATIONS

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Study of the behavior of polymer solution flows in the region of nonlinear viscoelasticity allows one to more accurately evaluate the adequacy of rheological models and to describe the rheological properties of a material in more detail. The nonlinear viscoelastic properties manifesting themselves in the process of studying the behavior of a polymer material on significant deformations were investigated with the aid of time dependences of shear stresses calculated at different amplitudes. The present work considers the applicability of the modified Vinogradov–Pokrovskii rheological model to describing the oscillating shearing of polymer fluids with a large amplitude. It has been established that on increase of the deformation amplitude, the shear stresses cease to be a true harmonic, and one observes the appearance of a "step" on their left front, which speaks of the substantial nonlinearity in the behavior of the sample. The obtained theoretical dependences are compared with experimental data for a 5% solution of polyethylene oxide in dimethyl sulfoxide. The comparison was made as by plotting the time dependences of normalized stresses, so by analyzing Lissajous figures. Despite the simplicity, the modified Vinogradov–Pokrovskii rheological model adequately describes the behavior of polymer materials on significant periodic deformations.

Keywords: *rheology, rheological model, nonlinear viscoelasticity, oscillations, shear, polymer solutions.*

Introduction. Many of the rheological models [1–7] are often used for describing the rheological characteristics of polymer materials in the case of stationary shear or comparatively small periodic shear deformations. However, in processing solutions and melts of polymers one encounters a situation, in which samples are subjected to nonstationary deformation taking on great values. Therefore transition from an analysis of the behavior of flows in the linear viscoelastic region to nonlinear effects is due to both practical considerations and to the appearance of more accurate measurement methods, for example, in the case of large periodic deformations [7–10]. This affords a possibility for a more reliable evaluation of the prognostic properties of rheological models due to the expansion of the region of their applicability for different types of deformation. In this connection, currently modeling of rheological characteristics in the region of nonlinear viscoelasticity becomes increasingly indispensable, since measurements in the case of large periodic deformations allow one to describe nonlinear rheological properties of a material in greater detail [7].

Dynamic shear oscillating tests are used widely in the rheology of fluids with specific properties such as solutions and melts of polymers, biopolymers, polyelectrolytes, suspensions, emulsions, gels, etc. [11–13]. In particular, measurements in the case of small-amplitude oscillating streams (SAOS) represent a classical method of obtaining relations of linear viscoelasticity of such fluids. This method has been studied most thoroughly from both theoretical and practical viewpoints [2]. As mentioned above, the majority of real processes proceed in the regions with appreciable deformation, and this requires the study of nonlinear dynamic properties of the systems studied. Often among such characteristics there is the dependence of stationary shear viscosity and of the first difference of normal stresses on the rate of shear. In this case, the dynamic properties do not manifest themselves or manifest them insignificantly, for example, such as nonmonotonic establishment of stress on simple shear.

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To obtain a more complete picture of nonlinear behavior of a polymer fluid use can be made of large-amplitude oscillations of shear vibrations (LAOS). From experimental point of view both SAOS and LAOS at the inlet are characterized by two parameters: the relative amplitude of sinusoidal shear vibrations γ_0 and their frequency ω. There are substantial differences, however, in studying the response of a polymer system to periodic effects determined by the specificity of the material itself. For SAOS the response is a sinusoid, and the amplitude of shear vibrations is directly proportional to γ_0. The main characteristics of SAOS are $G'(\omega)$ and $G''(\omega)$, which are the components of the dynamic shear modulus: elasticity modulus and loss modulus. For LAOS the response of the system is no longer a true sinusoid, and the amplitude of such vibrations increases with γ_0 not strictly proportionally. This is confirmed in experiments in [14–27].

The LAOS method itself began to be used fairly recently. Already in early publications [15–25] relating to the years 1960–1970 basic concepts of the analysis of shear stresses at large oscillations were suggested. This is a direct analysis of the form of nonlinear viscoelastic response and application of the Fourier transform [16–23]. Initially this method was used to investigate solutions and melts of linear polymers [15], as well as filled systems [15]. Later it was applied to mixtures, gels, melts of polymers, biopolymers, polyelectrolytes, and suspensions [17, 24]. It is already at that time that researchers noted that as the amplitude of vibrations increased there occurred a decrease in the components of the dynamic shear modulus, which are the first harmonics of the signal investigated. Since the Fourier analysis required measurement of higher-order harmonics and many of the technical problems were not solved at that time and hampered the progress in this area, some of the researchers began to apply Lissajous figures for investigations of nonlinear viscoelastic behavior as they can easily be reproduced on the screens of oscillographs [22]. As is shown in [9], nonlinear viscoelastic properties manifesting themselves in investigation of the behavior of polymer material on significant deformations can be interpreted, for example, with the aid of Lissajous figures or directly by analyzing time dependences of shear stresses obtained at different degrees of deformation. Here a conclusion can be drawn on the increase in the nonlinearity of the response of the sample with increase in the amplitude of vibrations. From the mid-1990′s many technical difficulties of experimental character were overcome, and at the present time the LAOS method is a reliable instrument of both experimental and theoretical investigations [24, 25]. In particular, this method is important for checking the adequacy of rheological models in the nonlinear region of deformation rates.

At the present time, there exist many rheological models, with some being developed up to now, whereas others ceased to be crucial. Among the most known methods there are those of Giesekus [3], Pom–Pom [5], Leonov–Prokunin [4], and of Vinogradov–Pokrovskii (modified model) [1, 6, 11–14]. All of them yield a good description of the linear effects at small periodic deformations and nonlinear effects at large stationary deformations. In the present work, we investigate the change in the structure of material response on increase in the deformation amplitude. The aim of the work first of all is the checking of the adequacy of the modified Vinogradov–Pokrovskii rheological model.

Kinematics of the Process. We consider two plane parallel plates, with a polymer sample placed in between. The lower plate is at rest, whereas the upper one executes vibrations by the harmonic law with frequency ω and amplitude A. We arrange the coordinate axes *xyz* as shown in Fig. 1. As a result, there occur shear deformations in the sample, but no changes take place along the Z axis, i.e., $0Z$ is neutral with respect to deformation. In the case considered only one component of the tensor of velocity gradients ν_{12} differs from zero.

If we assume that $y = h$, then the law of the displacement of the upper plate or deformation of the sample will have the form $x = A \sin \omega t$. Then the equation for the deformation rate will take the form $V_x = dx/dt = A\omega \cos \omega t$. At the space between the plates comparable with the deformation amplitude, the distribution of the deformation rates in the space will have a linear character (Fig. 1) and the distribution of the rate in the sample along the $0x$ axis can be expressed as $V_x(y) = A\omega\,(y/h) \cos \omega t$. Evaluating the derivative with respect to the variable y, we find the gradient of the deformation rate, which will look like

$$\nu_{12} = \frac{dV_x}{dy} = \frac{A}{h}\,\omega \cos \omega t = \gamma_0 \omega \cos \omega t \,.$$

Dependence of stresses on the deformation rate ν_{12} is used in investigation of nonlinear rheological properties of polymer materials [1, 2].

Thus, if the deformation of the sample follows the sinusoidal law, the deformation rate will have the form of the cosine curve. For stresses in the process of deformation it is possible to observe the effect of the delay in the polymer system response from deformation or deformation rate (Fig. 2):

$$\sigma_{12}(t) = G'(\omega)\gamma_0 \sin \omega t + G''(\omega)\gamma_0 \cos \omega t = \gamma_0 \sqrt{(G'(\omega))^2 + (G''(\omega))^2}\, \sin (\omega t + \varphi) \,, \tag{1}$$

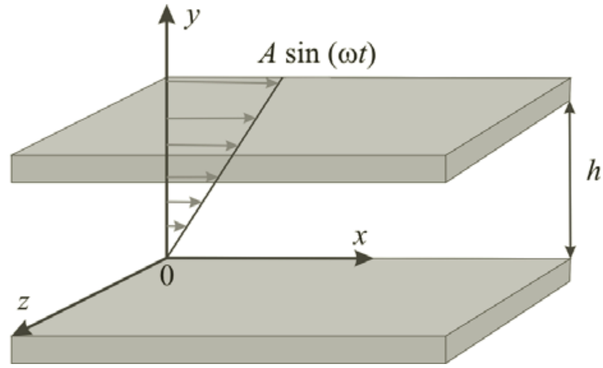

Fig. 1. Schematic representation of shear periodic deformations.

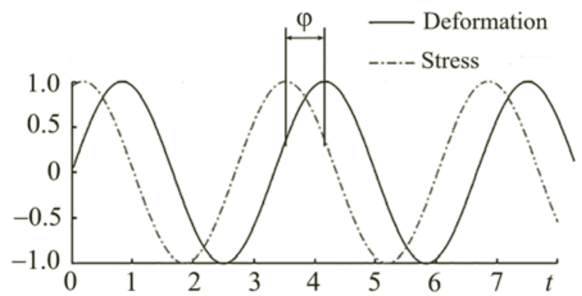

Fig. 2. Dependence of normalized stresses and deformation on time.

where the angle of the shift of phases or the angle of losses is $\varphi = \arctan(G''(\omega)/G'(\omega))$ [1, 2].

The frequency dependences of the components of the dynamic shear modulus have been studied rather adequately [1, 2, 13]. At different frequencies the viscous properties of the material can prevail over the elastic ones and vice versa. If we restrict ourselves only to the discussion of one relaxation process with characteristic time τ_0, then at $\omega << 1/\tau_0$ the loss modulus is much in excess of the elasticity modulus $G''(\omega) >> G'(\omega)$, and the material behaves as a viscous fluid. In this case, $\varphi \approx \pi/2$. When $\omega = 1/\tau_0$, the loss modulus is equal to the elasticity modulus $G''(\omega) = G'(\omega)$ and $\varphi \approx \pi/4$. If $\omega >> 1/\tau_0$, the loss modulus is much less than the elasticity modulus $G''(\omega) << G'(\omega)$, and the material behaves as an elastic body. In this case, $\varphi \to 0$.

A convenient method of visual representation of results is the rejection of the use of time as an argument and construction of the phase pattern of the dependence of stress on deformation. Such a pattern is called the Lissajous figure. For the region of the linear viscoelastic behavior of the Lissajous figures are ellipses, whereas in the case of nonlinear response of the sample they are transformed into figures of various shapes [7].

We can easily see this for the case of small oscillating vibrations. We write down the relationship between the normalized shear stress and deformation in a parametric form:

$$\begin{cases} y = \cos\varphi \sin\omega t + \sin\varphi \cos\omega t \, , \\ x = \sin\omega t \, . \end{cases}$$

From this, having replaced the variable t, we obtain

$$x^2 - 2\cos\varphi xy + y^2 = \sin^2\varphi \, . \qquad (2)$$

Thus, the phase trajectory is the curve of the second order $a_1x^2 + 2a_2xy + a_3y^2 = a_4$ [28] and, to determine its type, we will rotate the coordinate axes. To determine the turning angle we will make use of the expression [28]

$$\cot 2\alpha = \frac{a_1 - a_3}{2a_2} = 0 \, .$$

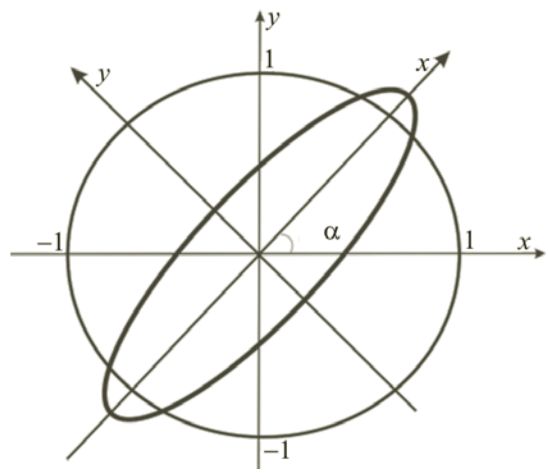

Fig. 3. Dependence of the normalized shear stress on normalized deformation.

That is, the turning of the coordinate axes is to be made by π/4. Then, having made the replacement of variables (Fig. 3), for curve (2) we obtain the canonical equation of the ellipse:

$$\frac{x^2}{\frac{\sin^2\varphi}{1-\cos\varphi}} + \frac{y^2}{\frac{\sin^2\varphi}{1+\cos\varphi}} = 1 .$$

The semiaxes of this ellipse are defined by the following expressions:

$$a = \sin\varphi/\sqrt{1-\cos\varphi}\ , \quad b = \sin\varphi/\sqrt{1+\cos\varphi}\ ,$$

from which it is seen that $a \ge b$. When $\omega << 1/\tau_0$, $\varphi \to \frac{\pi}{2}$, $a \to 1$, and $b \to 1$, then the ellipse is degenerated into a circle (Fig. 3). When $\omega >> 1/\tau_0$, $a \to \sqrt{2}$ and $b \to 0$, and the ellipse is degenerated into a segment along the $0x$ axis.

The phase portrait in normalized stress–deformation rate coordinates is constructed analogously. Here, instead of (2) we obtain

$$\begin{cases} y = \cos\varphi\sin\omega t + \sin\varphi\cos\omega t\ , \\ x = \cos\omega t\ , \end{cases}$$

where y is the normalized stress and x is the normalized deformation rate. After analogous transformations we obtain

$$\frac{x^2}{\frac{\cos^2\varphi}{1+\sin\varphi}} + \frac{y^2}{\frac{\cos^2\varphi}{1-\sin\varphi}} = 1 .$$

This is also an ellipse with semiaxes $a = \cos\varphi\ \sqrt{1+\sin\varphi}$; $b = \cos\varphi/\sqrt{1-\sin\varphi}$, with $a \le b$. When $\omega << 1/\tau_0$, $a \to \beta$ and $b \to \sqrt{2}$, the ellipse degenerates into a segment along the $0y$ axis. When $\omega >> 1/\tau_0$, $a \to 1$ and $b \to 1$, and the ellipse degenerates into a circle.

Mathematical Model. The numerical calculations are based on the equations written on the basis of the modified Vinogradov–Pokrovskii rheological model [1, 6, 12]. To obtain this rheological determining relation, a microstructural approach was used allowing one to follow the relationship between the macro- and microcharacteristics of a polymer system. Of greater importance in the theory of polymer viscoelasticity is the monomolecular approximation, in the case of which one selected macromolecule moving in an effective medium formed by a solvent and other macromolecules is considered instead of the entire set of macromolecules in the volume [4–6]. In this case, the dynamics of the very selected macromolecule is modeled by the motion of an elastic dumb-bell — two beads connected by a spring. The characteristic feature of this model

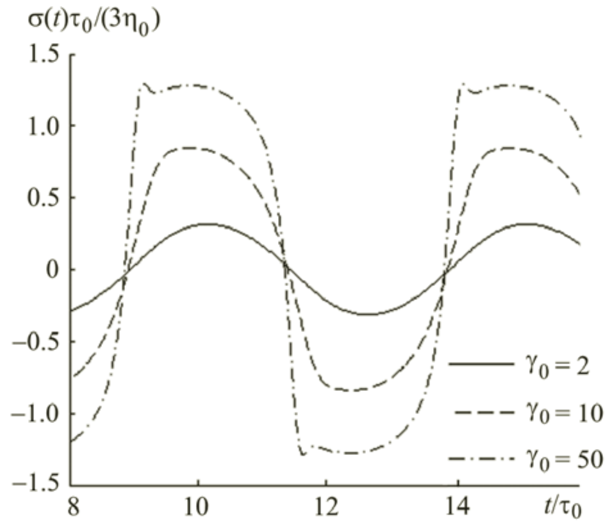

Fig. 4. Dependence of the dimensionless shear stress on time at different values of deformation amplitude.

is the account for the tensor character of the coefficient of friction of the beads determined by the induced anisotropy of the shear flow. This model has the form

$$\sigma_{ik} = -p\delta_{ik} + 3\frac{\eta_0}{\tau_0}a_{ik},$$
$$\frac{d}{dt}a_{ik} - \nu_{ij}a_{jk} - \nu_{kj}a_{ji} + \frac{1+(\kappa-\beta)I}{\tau_0}a_{ik} = \frac{2}{3}\gamma_{ik} - 3\frac{\beta}{\tau_0}a_{ij}a_{jk}. \quad (3)$$

Here $I = a_{jj}$ is the first invariant of the anisotropy tensor $\gamma_{ik} = (\nu_{ik} + \nu_{ki})/2$. In the equations of the dynamics of the macromolecule, the phenomenological parameters of the model κ and β take into account the dimensions and shape of the macromolecular ball and are connected by the relationship $\kappa = 1.2\beta$, which corresponds to the condition of independence of the asymptotic behavior of stationary shear viscosity from the molecular weight of the polymer [6, 12].

Earlier this rheological determining relation (3) was checked for the correspondence to the flows of real polymer fluids [3, 11–14]. Viscosimetry flows of polymer media were investigated, of which the most investigated are the simple shear and uniaxial stretching. Numerous experimental data on shear deformation of solutions and melts of linear polymers show that the shear viscosity is a decreasing function of the shear rate; the shear stress is an increasing function of the shear rate; the coefficients of the first and second difference of normal stresses are the decreasing functions of the shear rate. The results of calculations of the viscosimetrics function demonstrate qualitative correspondence of model (3) to the real behavior of solutions and melts of linear flowing polymers [6].

We also studied nonstationary effects on the basis of rheological model (3). For this purpose, the problem on establishing stresses on simple shear after instant application of shear deformation with a constant shear rate was solved. This can be done conveniently because there is possibility to compare the obtained results with both experimental data [10] and with calculations carried out on the basis of other models [7, 10].

Thus, model (3) can be selected as the initial approximation in describing nonlinear and viscoelastic properties of the solutions and melts of linear and branched polymers. Based on Eqs. (3), vibrations with both a large and small amplitude were modeled. It was assumed that the polymer sample was subjected to deformation with frequency ω by the harmonic law with the given amplitude γ_0. The response of the material is the dependence of stress on time. The calculations have shown that on deformation from the state of rest [$\sigma_{ik}(0) = 0$] a periodic regime of vibrations develops rather rapidly in the polymer system. The solutions of the obtained system of differential equations were found by the Runge–Kutta method.

At a small amplitude the shear stresses appearing in the material are directly proportional to deformation, i.e., represents a correct harmonic. At periodicity of deformation of the material with greater amplitude the response ceases to be a true harmonic. This is confirmed by both the results of modeling (Fig. 4) and experiments [7, 8].

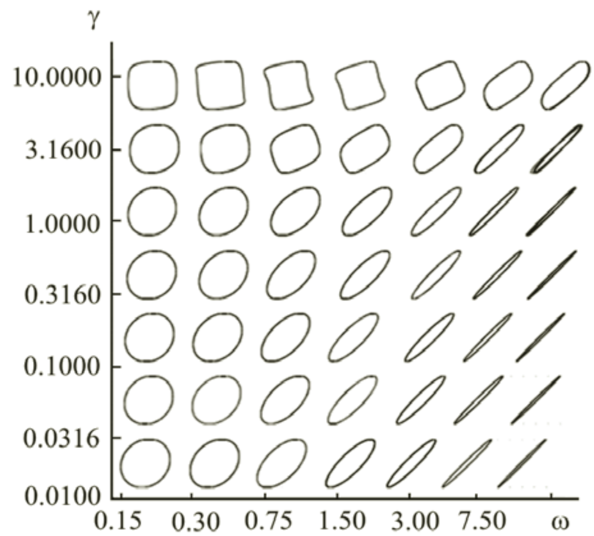

Fig. 5. Lissajous figures obtained on change of the amplitude and frequency of vibrations.

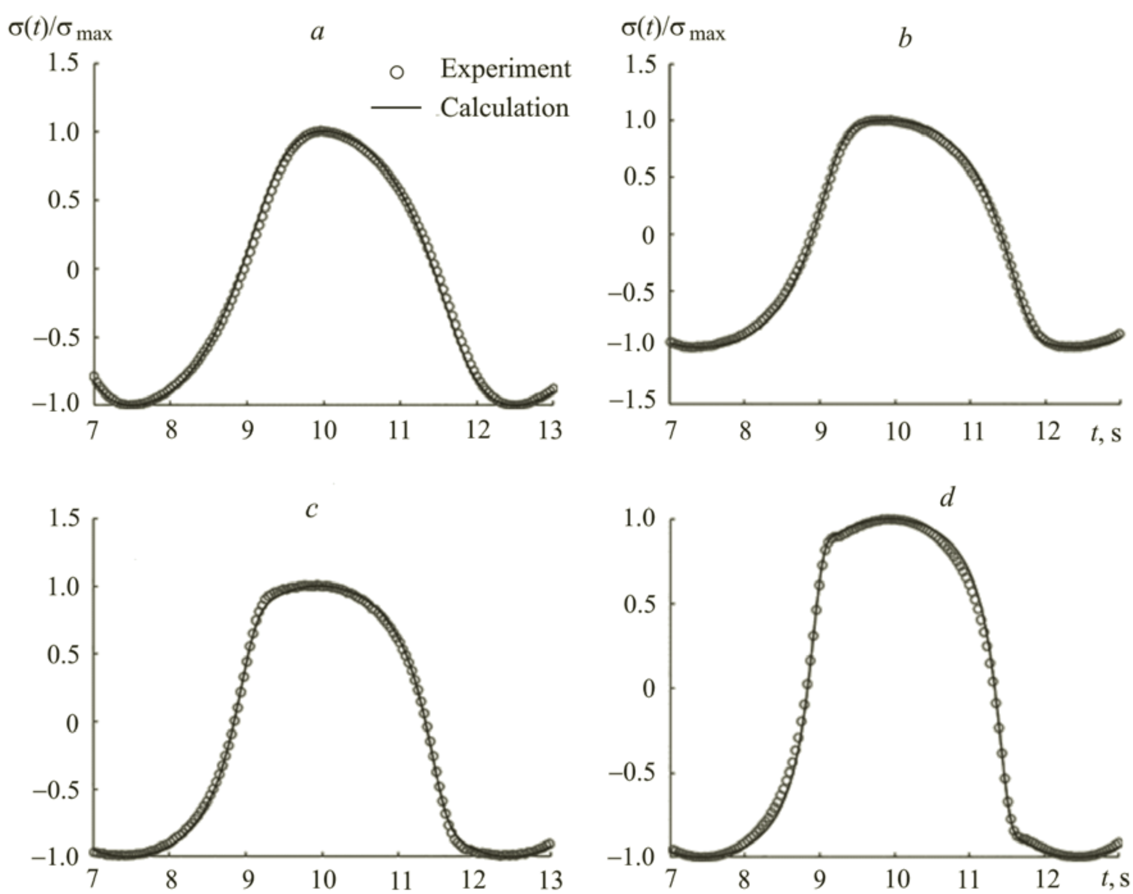

Fig. 6. Comparison of theoretical and experimental dependence for normalized shear stresses $\sigma(t)$ in an established regime at different relative deformation amplitudes: a) 5; b) 10; c) 20; d) 30.

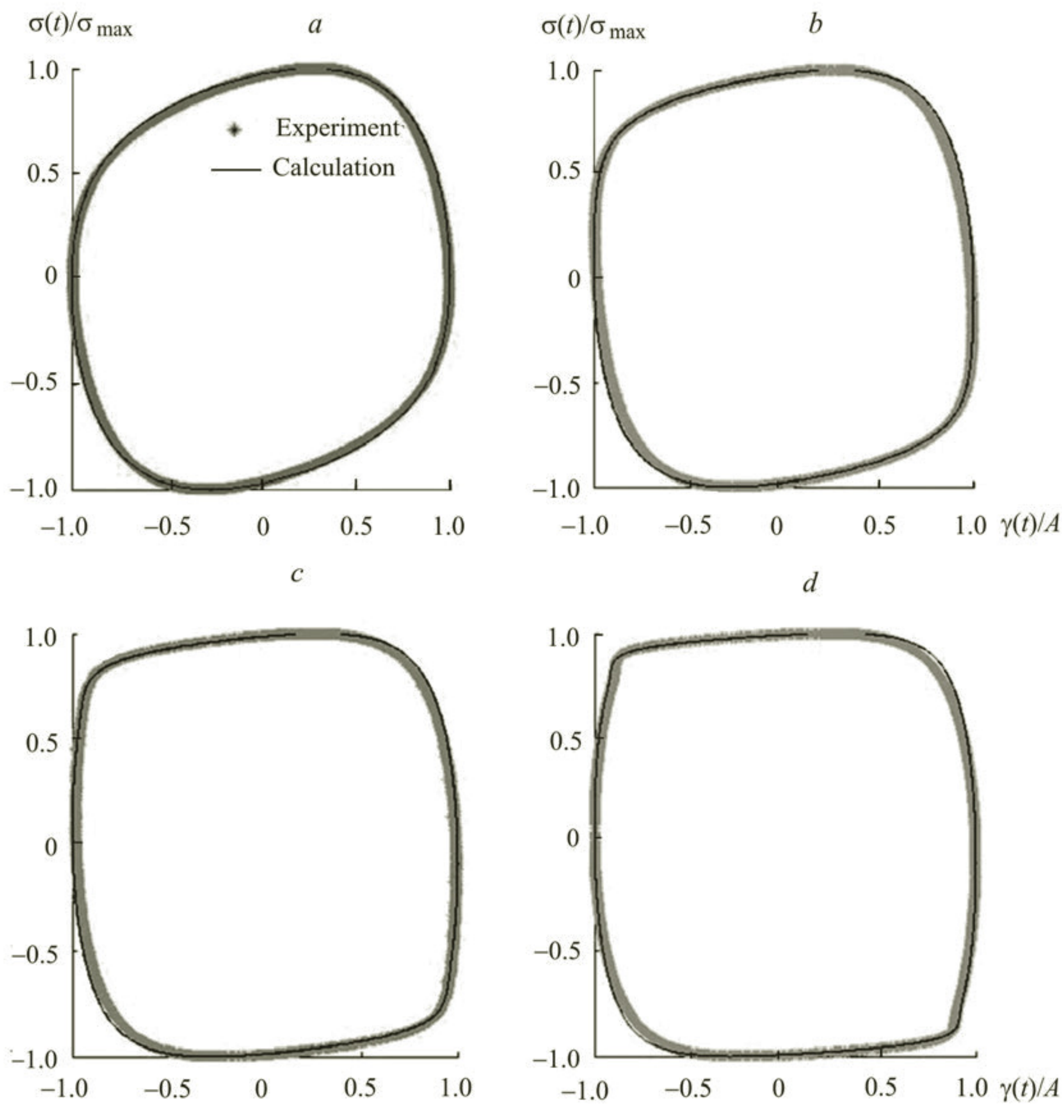

Fig. 7. Lissajous figures for theoretical dependences and experimental data for normalized shear stresses $\sigma(t)$ in an established regime at different relative deformation amplitudes: a) 5; b) 10; c) 20; d) 40.

Figure 5 presents the Lissajous figures constructed in the normalized stresses–shear deformation coordinates at different values of amplitude and frequency. At small values of the relative amplitude of shear vibrations the phase trajectories have the shape of an ellipse with the sizes of semiaxes calculated in the previous section. The nonlinearity of the mechanical behavior at large deformations is reflected in the nonellipticity of the Lissajous figures. It is seen from Fig. 5 that on increase of the frequency, they narrow, which corresponds to the increase of the elastic properties of the sample in comparison with viscous ones. On increase in amplitude, the Lissajous figures transform closer to a rectangular or hysteresis shape.

Comparison of Modeling Results with Experiment. A great number of works, the references to which can be found in [6–8], are devoted to investigation of transient and stationary rheological characteristics at large periodic deformations. Let us consider the experimental data of work [8] where deformation of a 5% solution of polyethylene oxide in dimethyl sulfoxide was investigated. The polymer solution was subjected to harmonic deformation at a large amplitude γ_0 that successively attained the values 50, 100, 500, 1000, 2000, and 4000% at the frequency $\omega = 0.2$ Hz.

In the calculations use was made of the following values of the parameters of the model: $\tau_0 = 0.21$ s; $\eta_0 = 2.76$ Pa·s; $\beta = 0.037$; $\kappa = 0.0453$. The effectiveness of application of the modified Vinogradov–Pokrovskii rheological model was checked by optimizing the parameters of the model in the linear region (at small periodic deformations). Thereafter the behavior of the model with found parameters was compared with experimental results obtained at large periodic deformations. Figure 6 contains a comparison of the established dependences of the normalized response with experimental data from work [8].

Attention should be paid to the fact that the left and right fronts of forced vibrations are deformed differently with increase of the relative amplitude. At the left front, with increase of the amplitude at the graph of experimental dependences one observes the appearance of a "step." With increase in γ_0, the first front deviates from the harmonic without the appearance of a step. The model provides a good description of this effect (Fig. 6).

We will consider now the Lissajous figures for the dependences obtained (Fig. 7). The noted nonlinearity of the viscoelastic properties of a polymer melt manifests itself more vividly as deviation of the closed phase trajectory from the ellipsoidal form. As is seen from the graphs given in Fig. 7, an increase in the nonlinearity of the response of the sample on increase in the amplitude of vibrations manifests itself not only in the deformation of the initial ellipse, but also in the appearance of inflection points on the phase portraits. This is confirmed by both experimental data and by the theoretical dependence. Since measurements were carried out at a small frequency $\omega = 0.2$ s^{-1} < $1/\tau_0$ s^{-1}, it is possible to note the predominance of viscous properties of the solution over the elastic ones, which is confirmed by the large width of the figures obtained (Fig. 7).

Comparing the obtained results with experimental data, it can be concluded that the model allows one to rather accurately describe the behavior of polymer materials at large periodic deformations.

Conclusions. In the course of the work we carried out modeling of nonlinear viscoelasticity of a polymer material in the case of its large periodic deformations with the aid of modified Vinogradov–Pokrovskii rheological model. A comparison of the results was carried out with experimental data for a 5 wt.% solution of polyethylene oxide in dimethyl sulfoxide investigated at harmonic deformations with a large amplitude attaining 40 relative units, which were measured at 35° and frequency 0.2 Hz.

The nonlinear properties of the investigated sample manifest themselves in the distortion of the material response. The response ceases to be a true harmonic, on increase in the amplitude the appearance of a step is observed on the left front, with the absence of response deformation on the right front. On increase in the amplitude, one can observe the deviation from the ellipsoid form on the Lissajous figures and the appearance of deflection points. The considered model allows one to model the nonlinear effects appearing on increase in the amplitude of material deformation. It is also possible to use this model for modeling more complex flows of polymer media.

Curiously, the simple model (3) that takes into account only one relaxation process gives such good correspondence with experimental data. In describing the gradient dependence of shear viscosity and of the first difference of normal stresses, this model demonstrates only qualitative correspondence of computational dependences and experimental data [13, 14].

In further investigations we are planning to adapt the considered model to the multimode case to increase the accuracy of the results obtainable in various regimes of deformation.

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NOTATION

A, amplitude of deformation; a_1, a_2, a_3, a_4, coefficients in the general equation of the second-order curve, ellipse semiaxes; a_{ik}, symmetrical tensor of anisotropy of second rank; G', elasticity modulus; G'', loss modulus; h, distance between plates; p, hydrostatic pressure; t, time; V_x, deformation rate; 2α, angle of rotation of coordinates; γ_{ik}, symmetrized tensor of velocity gradients; γ_0, relative amplitude of deformation; ν_{12}, gradient of deformation rate; η_0, initial value of viscosity; κ and β, phenomenological parameters of the model; ν_{ik}, tensor of velocity gradients; σ_{ik}, tensor of stresses of a polymer system; $\sigma_{12}(t)$, shear stresses; τ_0, initial value of relaxation time; φ, angle of shift of phases; ω, frequency of oscillations.

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