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RHEOLOGICAL EQUATIONS OF STATE OF LINEAR POLYMERS AND THEIR MIXTURES

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A rheological governing relation for the solutions and melts of linear polymers has been obtained based on the microstructural ideas of the dynamics of a polymer chain. A relation for taking into account the influence of the polydispersity of polymers on the properties of the mixture has been proposed and the components of the complex shear modulus — the elastic modulus and the loss modulus — have been calculated. The performed comparison of the theoretical results obtained and the experimental data for the mixtures of two samples of polystyrene in different ratios demonstrates satisfactory agreement of theory and experiment.

Polymer materials are finding increasing use at present in various fields of science and technology, which entails a continuous improvement of the technology of the processes of manufacturing and processing of linear polymers. Therefore, modeling of the motion of polymer media in different units of production equipment becomes the most important practical problem, to solve which one must construct mathematical models of the mechanics of polymer liquids. For description of flows of the solutions and melts of linear polymers one often employs equations failing to take into account certain substantial features of the behavior of polymer liquids. It is well known that the solutions and melts of linear polymers display the gradient dependence of the elongation and shear viscosity, the first and second differences of normal stresses, and the retardation effects, i.e., they are nonlinear viscoelastic media. Therefore, it becomes necessary to take a more detailed account of the special properties of the material in constructing rheological relations which adequately describe combined nonuniform flows of polymer media.

To solve this problem we consider the motion of a set of Brownian particles of all macromolecules in the approximation of a continuous medium. For this purpose we introduce such macroscopic variables as the density $\rho(\mathbf{x}, t)$ and the momentum density $\rho\mathbf{v}(\mathbf{x}, t)$ that are determined in a standard manner [1, 2]:

$$\rho(\mathbf{x}, t) = \left\langle \sum_{\alpha,\nu} m\delta(\mathbf{x} - \mathbf{r}^{\alpha\nu}(t)) \right\rangle , \quad \rho\mathbf{v}(\mathbf{x}, t) = \left\langle \sum_{\alpha,\nu} m\mathbf{u}^{\alpha\nu}\delta(\mathbf{x} - \mathbf{r}^{\alpha\nu}(t)) \right\rangle . \tag{1}$$

The averaging is carried out over all kinds of realizations of the random force acting on a particle.

The equation of the dynamics of the Brownian particles is written in the form

$$m\frac{d}{dt}u_i^{\alpha\nu} = P_i^{\alpha\nu} + Q_i^{\alpha\nu} - 2T\mu A_{\alpha\gamma}r_i^{\alpha\nu} + \Phi_i^{\alpha\nu} . \tag{2}$$

Here and in what follows we will employ the agreement on summation over double indices.

To obtain the momentum equation from (1), using Eq. (2), we find the rate of change of the momentum of the unit volume of the liquid, formed by the Brownian particles:

$$\frac{\partial}{\partial t}(\rho v_k) = -\frac{1}{2}\frac{\partial}{\partial x_i} m \sum_{\alpha,\nu} (u_i^{\alpha\nu}u_k^{\alpha\nu}\delta(\mathbf{x} - \mathbf{r}^{\alpha\nu}(t))) - \frac{1}{2}\frac{\partial}{\partial x_i} m \sum_{\alpha,\nu} (r_i^{\alpha\nu}(Q_i^{\alpha\nu} - 2T\mu A_{\alpha\gamma}r_i^{\alpha\nu})\,\delta(\mathbf{x} - \mathbf{r}^{\alpha\nu}(t))) +$$

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$$+\frac{1}{2}\frac{\partial}{\partial x_i} m \sum_{\alpha,\nu} ((Q_i^{\alpha\nu} - 2T\mu A_{\alpha\gamma} r_i^{\alpha\nu})\,\delta\,(\mathbf{x} - \mathbf{r}^{\alpha\nu}(t))) + \sigma_k\,. \tag{3}$$

Let us separate the stress tensor in (3), for which purpose we must write the terms on the right-hand side in the form of the divergence of a certain tensor. The second term in (3) has already been written in the required form. In the third term, we expand formally the δ function in a Taylor series about the center of mass of the νth macromolecule $\mathbf{q}^\nu$ and restrict ourselves just to the first two terms of the expansion:

$$\delta\,(\mathbf{x} - \mathbf{r}^{\alpha\nu}) = \delta\,(\mathbf{x} - \mathbf{q}^\nu) - (r_i^{\alpha\nu} - q_i^\nu)\frac{\partial}{\partial x_i}\delta\,(\mathbf{x} - \mathbf{q}^\nu)\,. \tag{4}$$

Assuming that all the macromolecules are equal and that their coordinates of the center of mass are statistically not connected with the remaining coordinates, with account for relation (4) we write the expression for the stress tensor in normal coordinates:

$$\sigma_{ik} = -\,nT\delta_{ik} + nT\sum_\alpha \left(2\mu\lambda_\alpha\left(\langle\rho_i^\alpha\rho_k^\alpha\rangle - \frac{1}{2\mu\lambda_\alpha}\,\delta_{ik}\right) - \frac{1}{2T}\left(\langle\rho_i^\alpha \mathrm{T}_k^\alpha\rangle + \langle\rho_k^\alpha \mathrm{T}_i^\alpha\rangle\right)\right). \tag{5}$$

Next, it is convenient to pass to dimensionless covariances according to the formulas

$$x_{ik}^\alpha = \frac{2\mu\lambda_\alpha}{3}\langle\rho_i^\alpha\rho_k^\alpha\rangle\,, \quad u_{ik}^\alpha = \frac{1}{3T}\langle\rho_i^\alpha \mathrm{T}_k^\alpha\rangle\,.$$

Then expression (5) will take the form

$$\sigma_{ik} = -\,nT\delta_{ik} + 3nT\sum_\alpha\left(x_{ik}^\alpha - \frac{1}{3}\,\delta_{ik} - \frac{1}{2}\,(u_{ik}^\alpha + u_{ki}^\alpha)\right). \tag{6}$$

Earlier (in [3]), we have found the expressions for x_{ik}^α and u_{ik}^α:

$$\begin{aligned}
&\frac{D}{Dt}x_{ik}^\alpha - x_{ij}^\alpha\gamma_{jn}c_{nk}^\alpha - x_{kj}^\alpha\gamma_{jn}c_{ni}^\alpha = -\frac{1}{2B\tau_\alpha^{\mathrm{R}}}\left(\left(x_{ij}^\alpha - \frac{1}{3}\,\delta_{ij}\right)b_{jk}^\alpha + \left(x_{kj}^\alpha - \frac{1}{3}\,\delta_{kj}\right)b_{ji}^\alpha\right);\\
&\frac{D}{Dt}u_{ik}^\alpha - c_{ij}^\alpha\gamma_{jn}u_{nk}^\alpha + \frac{1}{2B\tau_\alpha^{\mathrm{R}}}c_{ij}^\alpha u_{jk}^\alpha = -\frac{1}{\tau}u_{ik}^\alpha - \frac{\psi}{\tau}\left(\left(x_{ij}^\alpha - \frac{1}{3}\,\delta_{ij}\right)f_{jk}^\alpha - 2B\tau_\alpha^{\mathrm{R}}x_{ij}^\alpha\gamma_{jn}d_{nk}^\alpha\right).
\end{aligned} \tag{7}$$

The system of equations (6)–(7) represents the rheological equation of state of a nonlinear anisotropic viscoelastic liquid for mathematical modeling of different flows of a polymer medium. This system was employed earlier for description of the linear and nonlinear properties of the solutions and melts of linear polymers with a narrow molecular-mass distribution in simple shear and uniaxial tension [2].

Based on the system of equations (6)–(7), we obtained in [3] the model of zero approximation by the available small molecular parameters

$$\begin{aligned}
&\sigma_{ik} = -\,nT\delta_{ik} + 3\,\frac{\eta_0}{\tau_0}\,a_{ik}\,;\\
&\frac{d}{dt}a_{ik} - \nu_{ij}a_{jk} - \nu_{kj}a_{ji} + \frac{1 + (\kappa - \beta)\,a_{jj}}{\tau_0}\,a_{ik} = \frac{2}{3}\,\gamma_{ik} - 3\,\frac{\beta}{\tau_0}\,a_{ij}a_{jk}\,.
\end{aligned} \tag{8}$$

The equations obtained are the rheological governing relation with four scalar parameters: $\eta_0 = nT\tau_0$ and τ_0 are the initial values of the shear viscosity and the relaxation time and κ and β are the phenomenological parameters of the model which take account of the size and shape of a coiled molecule in the equations of macromolecular dynamics. When $\beta = 0$, Eqs. (8) yield the well-known structural-phenomenological model of Pokrovskii and Vinogradov [2].

Based on the rheological model of zero approximation (8) we numerically investigated in [2–4] the stationary viscosimetric functions: the viscosity, the first and second differences of normal stresses in simple shear, and the viscosity in uniaxial tension as functions of the constant velocity gradient. We found the ratio of the stationary viscosity in uniaxial tension to the stationary viscosity in shear as a function of the first invariant of the tensor of additional stresses. In [5, 6], based on the model (8) written in cylindrical coordinates we: (a) obtained a correction to the Poiseuille law; (b) investigated flows in cylindrical regions with the rotating end and bottom of a cylinder with a free surface for a polymer liquid. The influence of the molecular weight and the polydispersity of a polymer sample on the shear and longitudinal viscosities was investigated in [7, 8], and the superposition of a simple shear flow on periodic deformations with small amplitudes was investigated in [9].

Let us compare results of the calculations from the system of equations (8) to experimental data for simple oscillating shear flow, when $\nu_{12}(t) = \nu_{12} \exp -(i\omega t)$. In this case the behavior of a polymer system is characterized by the dynamic shear modulus, which is determined as

$$G(\omega) = i\omega \frac{\sigma_{12}(\omega, t)}{\nu_{12}(\omega, t)} .$$

Equations (8) lead to the following expression for $G(\omega)$ [2]:

$$G(\omega) = nT \sum_{\alpha=1}^{N} \left(\frac{\tau_\alpha^{\mathrm{R}}}{\tau_\alpha} \right)^2 \left(B \frac{-i\omega\tau_\alpha}{1 - i\omega\tau_\alpha} + E \frac{\tau_\alpha}{\tau} \frac{-i\omega\tau_\alpha^*}{1 - i\omega\tau_\alpha^*} \right). \tag{9}$$

The expressions for the relaxation times have the form

$$\tau_\alpha = \frac{\tau}{2} + \tau_\alpha^{\mathrm{R}} (B + E) , \quad \tau_\alpha^* = \frac{2\tau\tau_\alpha}{2\tau_\alpha + \tau} .$$

Next, it is convenient to separate in $G(\omega)$ involved in (9) the real and imaginary parts

$$G(\omega) = G'(\omega) - iG''(\omega) .$$

Thus, the behavior of the polymer system is characterized by the following four parameters: two dimensionless parameters, i.e., χ and $\psi = \frac{E}{B}$, and two dimensional parameters, i.e., $B\tau^*$ and nT. The parameter nT is determined from the values of the molecular weight and the weight concentration of the polymer, the value of the initial shear viscosity is found from the dependence $G''(\omega) = \eta_0\omega$ at small ω, and the values of the parameter $B\tau^*$ and the dimensionless parameters χ and ψ are determined from the relations [2]

$$B\tau^* = \frac{6\eta_0}{\pi^2 nT} , \quad \chi = \frac{\pi^2}{12} \frac{M_{\mathrm{e}}}{M} , \quad \psi = \frac{4\pi^2}{9\chi} .$$

The results of numerical modeling were compared to the experimental data [10] obtained for polystyrenes with molecular masses of M_1 = 166,000 and M_2 = 568,000 and their mixtures at the temperature T = 180°C. We found the following values of the parameters of the model:

$$\text{sample 1:} \quad nT = 22\,678 \text{ Pa} , \quad \eta_0 = 25\,000 \text{ Pa} , \quad B\tau^* = 0.8 \text{ sec} , \quad \chi = 0.09 , \quad \psi = 49 ;$$

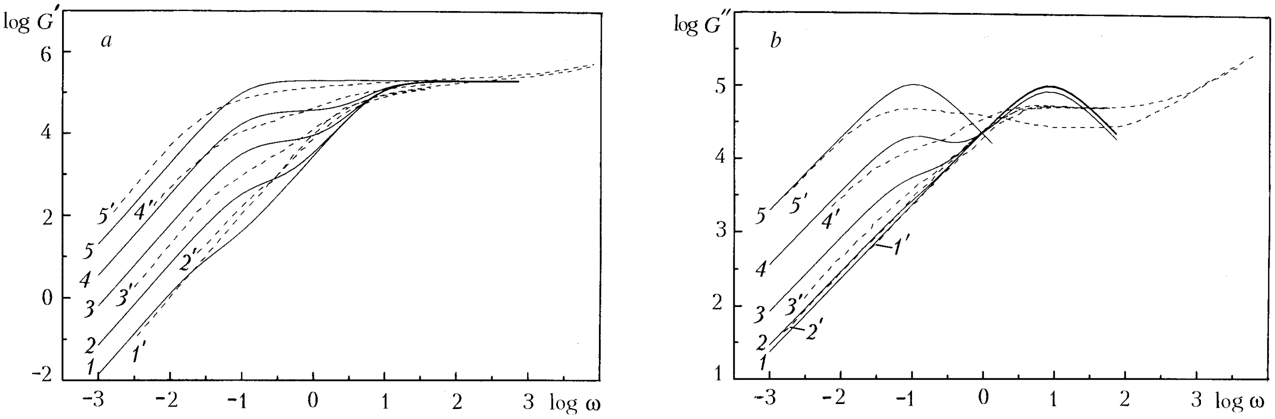

Fig. 1. Comparison of the experimental [10] and theoretical (10) dependences of the elastic modulus (a) and the loss modulus (b) on the vibrational frequency for variously composed mixtures of polystyrene: 1) M_1 = 166 kg/mole; 2) 99/1 mixture; 3) 90/10 mixture; 4) 58/42 mixture; 5) M_2 = 568 kg/mole (1–5, theoretical curves; 1′–5′, experimental data). G' and G'', Pa; ω, $\sec^{-1}$.

sample 2: $nT = 6629$ Pa , $\eta_0 = 2\,000\,000$ Pa , $B\tau^* = 184$ sec , $\chi = 0.03$, $\psi = 167$.

The elastic modulus and the loss modulus for the mixtures were computed from the formulas yielded by the expressions for the stress tensor of a polymer system with allowance for polydispersity [11]:

$$G' = \frac{c_1 n_1}{c_1 n_1 + c_2 n_2} G_1' + \frac{c_2 n_2}{c_1 n_1 + c_2 n_2} G_2' ; \quad G'' = \frac{c_1 n_1}{c_1 n_1 + c_2 n_2} G_1'' + \frac{c_2 n_2}{c_1 n_1 + c_2 n_2} G_2'' . \tag{10}$$

The experimental data [10] for the dependence of the shear modulus and the loss modulus and the results of numerical modeling are presented in Fig. 1. Curves 1 and 1′ are constructed for the melt of polystyrene with a molecular mass of M_1 = 166,000, curves 5 and 5′ are plotted for the sample with a molecular mass of M_2 = 568,000, and curves 2, 2′, 3, 3′, 4, and 4′ are constructed for the mixtures of these two polymers in ratios indicated in the caption to the figure, where the percentage of the first sample is given in the numerator while the percentage of the second sample is given in the denominator.

We emphasize that if one employs for calculations the expressions of the elastic modulus and the loss modulus for the mixtures [12]

$$G' = \left(c_1 \sqrt{G_1'} + c_2 \sqrt{G_2'}\right)^2 , \quad G'' = \left(c_1 \sqrt{G_1''} + c_2 \sqrt{G_2''}\right)^2 , \tag{11}$$

the results obtained insignificantly differ from those given in the figure. However, as we believe, the method of obtaining relations (9) is more simple and consistent than the method employed in derivation of relations (11).

Thus, within the framework of a consistent theory of microviscoelasticity, one can satisfactorily describe the dynamic characteristics of polymer mixtures, which is the basis for taking account of the influence of the polydispersity of polymer samples on their rheological properties.

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NOTATION

$\rho(\mathbf{x}, t)$, density; $\rho\mathbf{v}(\mathbf{x}, t)$, momentum density; t, time; $\mathbf{x}$, radius vector of the selected point of space; m, mass of a Brownian particle; $\mathbf{r}^{\alpha\nu}(t)$ and $\mathbf{u}^{\alpha\nu}(t)$, radius vector and vector of the velocity of the αth bead of the νth macromolecule; δ, delta function; $r_i^{\alpha\nu}$, ith component of the radius vector of the αth particle of the νth macromolecule;

$u_i^{\alpha\nu}$, *i*th component of the velocity of the αth particle of the νth macromolecule; $P_i^{\alpha\nu}$, frictional force; $Q_i^{\alpha\nu}$, force of internal friction; $\Phi_i^{\alpha\nu}$, random force; $2T\mu$, coefficient of elasticity of the small model spring; $A_{\alpha\gamma}$, force matrix; x_i, *i*th component of the radius vector; v_i, *i*th component of the velocity; σ_k, average force acting on particles from the carrier medium; q^ν, center of mass of the νth macromolecule; q_i^ν, *i*th component of the center of mass of the νth macromolecule; ρ_i^α, *i*th generalized coordinate of the αth particle; T_i^α, *i*th component of the force of internal viscosity acting on the αth particle; n, density of the number of molecules; T, temperature in energy units; δ_{ik}, Kronecker delta symbol; λ_α, eigenvalue of the force matrix; v_{ik}, velocity-gradient tensor; γ_{ik}, symmetrized velocity-gradient tensor; τ_α^{R}, Routh set of relaxation times; τ, relaxation time; τ^*, characteristic time of relaxation of the undiluted system; ψ, measure of internal viscosity; B, measure of amplification of the coefficient of friction due to the involvement of the surrounding macromolecules in motion; E, coefficient of "internal" friction of a macromolecule in the undiluted system; b_{ik}^α, c_{ik}^α, f_{ik}^α, and d_{ik}^α, tensor coefficients of friction; α_{ik}, anisotropy tensor; I, first invariant of the additional-stress tensor; η_0 and τ_0, initial values of the sheer viscosity and the relaxation time; κ and β, phenomenological parameters of the model, which take account of the size and shape of a coiled molecule in the equations of macromolecular dynamics; ω, vibrational frequency; $G(\omega)$, dynamic shear modulus; τ_α^* and τ_α, sets of relaxation times; χ, parameters of environmental aftereffect; N, number of subchains in the model of a macromolecule; $G'(\omega)$, elastic modulus; $G''(\omega)$, loss modulus; M_e, length of the chain between the "linkages" in the undiluted system [2]; M, molecular mass; G_1', G_1'', G_2', and G_2'', values of the elastic modulus and the loss modulus of polymers with molecular masses M_1 and M_2; c_1 and c_2, weight concentration of the polymer in the mixture; n_1 and n_2, number of macromolecules per unit volume. Subscripts and superscripts: i, j, k, l, m, and n, numbers of Cartesian coordinates (they take on values of 1, 2, and 3); ν, No. of the macromolecule; α, No. of the bead in the macromolecule (it takes on values of 1 to N); e, linkage.

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