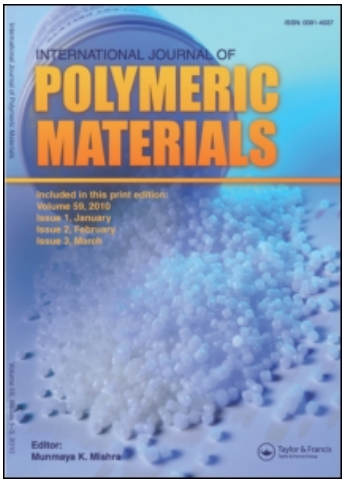

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Numerical Solution Problems of Highly Concentrated Rod-Like Macromolecules

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The structural phenomenological approach is used to describe the rheological behavior of materials exhibiting super-abnormal viscosity, that may be attributed to the orientational anisotropy of the material properties. It is assumed that the external fields and boundary conditions prevent the uniform orientation of all macromolecules in an arbitrary direction in the bulk of material, even though the concentration is above the critical one. A uniform orientation takes place only within the limits of local regions (domains) having unique directors. The domains are defined as super molecular formations rotating and elongating in the shear flow. The domain rotation is described using the Hinch and Leal models. Upon reaching the critical shear intensity the domains are deformed turning into a thin layer of unbound macromolecules aligned with flux. This is found to be the reason for orientational anisotropy and super-abnormal viscosity. The rheological equations developed are used to calculate numerically the flow of polymeric materials in the screw channels of the extruder.

KEY WORDS Rod-like molecules, rheology, extrusion, orientation, anisotropy.

1. INTRODUCTION

Examination of viscometric curves constructed for highly concentrated polymer solutions suggests that the orientational effects play an important role in polymer processing. The flow curves obtained with a capillary viscometer at the prescribed flow rate involve the shear stress maximum, the region of unstable flow and the region of transition from the internal friction to the external one. Furthermore, these curves are variable with respect to capillary sizes. When using rotational viscometers with constant angular velocity, the time evolution of shear stresses involves passing through a maximum and subsequent smooth falling to the stationary level. Once the instrument has been turned off and restarted, the material in it retains in memory the previous strain history, and shear stresses assume values corresponding to the extension of the evolution curve. Under conditions of constant torque moment, the initially slow growth of the angular velocity with the moment is followed by an abrupt increase as the torque reaches some limiting value. It is obvious that all these effects are due to the orientational effects and the related anisotropy of macroproperties.

Phenomenological and structural approaches to constructing equation of state

have not yet been found completely satisfactory for describing most technologically important operations involving polymer processing. Attempts to use purely phenomenological equations of state (obtained by approximating the viscometer test data) in describing complicated rheological polymer properties frequently lead to unpredictable results in proceeding from simple viscometer flow to real boundary problems. A more rigorous statistical approach provides an adequate rheology description solely for dilute polymer solutions and liquid suspensions. Highly concentrated suspensions and polymer solutions are commonly treated as liquid crystals and investigated in the framework of statistical or continuum theory. In this paper, an attempt has been made to describe the behavior of rigid chain polymers at different stages of polymer processing using the results of Hinch and Leal studies.

2. THEORETICAL PREMISES

The Doi theory[1] suggests that, at the concentration beyond the critical value, the rod-like macromolecules in the local regions are oriented arbitrary in one direction going to nematic phase. Let us assume that the bulk of material consists of domains in which all macromolecules are oriented in the direction of the unit vector $\mathbf{p}$. The domain dimensions and shape are defined by the size of macromolecules and the energy of their interaction. However, in most cases one may assume that the domain shape in equilibrium is nearly spherical and characteristic volume is small compared to the general volume of the material, yet contain a sufficiently large number of particles.

At rest, regardless of the limiting macromolecule orientation inside the domain, the material macroproperties are isotropic, since the domains are oriented arbitrarily. Under the influence of the shear flow, the domain may rotate and extend changing the shape from the spherical to the ellipsoidal one. This process is governed both by the elastic forces of macromolecular interaction and internal macromolecular friction. At low strain rates, the elastic forces prevail and every domain rotates without straining under the shear flow. The domains maintain the chaotic orientation and macroproperties remain isotropic. A more rapid increase of frictional forces causes the domain to extend and align with the flux, which results in material structure ordering and transversally isotropic macroproperties. Suppose initially that the domains are invariable in shape and have the form of ellipsoid with the axes ratio

$$G = \frac{a^2 - b^2}{a^2 + b^2} \tag{1}$$

The rotation of ellipsoid in viscous fluid will be described in the framework of Hinch and Leal structural-phenomenological model,[2] which in good approximation

is found to be valid both for weak and strong flows. In view of the Lipscomb and Den analysis[3] the approximated rheological model is reduced to the form

$$\frac{D\langle \mathbf{vv}\rangle}{Dt} = \boldsymbol{\Omega}\circ\langle \mathbf{vv}\rangle + \langle \mathbf{vv}\rangle\circ\boldsymbol{\Omega}^T + \mathbf{G}[\mathbf{E}\circ\langle \mathbf{vv}\rangle + \langle \mathbf{vv}\rangle\circ\mathbf{E} - \frac{2}{5}(6\langle \mathbf{vv}\rangle\circ\mathbf{E}\circ\langle \mathbf{vv}\rangle - \langle \mathbf{vv}\rangle\langle \mathbf{vv}\rangle\circ\circ\mathbf{E})] - 6D(\langle \mathbf{vv}\rangle - \frac{1}{3}\mathbf{I}), \quad (2)$$

$$\boldsymbol{\sigma} = -p\mathbf{I} + 2\mu_0\mathbf{E} + 2\mu_1(\langle \mathbf{vv}\rangle\circ\mathbf{E} + \mathbf{E}\circ\langle \mathbf{vv}\rangle) + \tfrac{2}{5}\mu_2(6\langle \mathbf{vv}\rangle\circ\mathbf{E}\circ\langle \mathbf{vv}\rangle - \langle \mathbf{vv}\rangle\langle \mathbf{vv}\rangle\circ\circ\mathbf{E}) + FD\langle \mathbf{vv}\rangle. \quad (3)$$

Here, $\mathbf{E}$, Ω are the symmetrical and antisymmetrical parts of the velocity gradient tensor, σ is the stress tensor, μ_0, μ_1, μ_2 are the phenomenological coefficients of viscosity, D is the coefficient of rotational diffusion.

Let us now rewrite these equations for the particular case of the plane Cuette flow.

The basis tensors are introduced by the formulae

$$T^{ij}_{+} = \sqrt{2}(e^x_i e^y_j - \tfrac{1}{3}e^x_i e^y_j \delta_{ij}), \quad (4)$$

$$T^{ij}_{-} = \frac{\sqrt{2}}{2}(e^x_i e^x_j - e^y_i e^y_j), \quad (5)$$

$$T^{ij}_{0} = \frac{\sqrt{3}}{2}(e^z_i e^z_j - e^z_i e^z_j \delta_{ij}), \quad (6)$$

$$T^{ij}_{a} = \frac{\sqrt{2}}{2}(e^x_i e^y_j - e^x_j e^y_i). \quad (7)$$

such, that $\mathbf{T}_m\circ\circ\mathbf{T}_n = \delta_{mn}$. Then, decomposition of the required tensors in the basis tensors is given by

$$\langle \mathbf{vv}\rangle = \tfrac{1}{3}\mathbf{I} + Q_+\mathbf{T}_+ + Q_-\mathbf{T}_- + R\mathbf{T}_0, \quad (8)$$

$$\boldsymbol{\sigma} = \sigma_+\mathbf{T}_+ + \sigma_-\mathbf{T}_- + \theta\mathbf{T}_0. \quad (9)$$

Suppose that at initial time the medium is in isotropic state, i.e. $Q_+ = Q_- = R = 0$. At time $t = 0$ there exists an instantaneously established Cuette flow with the strain rate $\dot{\gamma} = \frac{1}{2}(\partial v_x/\partial y)$. In this case the strain rate and vortex tensors are given by

$$\mathbf{E} = \frac{1}{\sqrt{2}}\dot{\gamma}\mathbf{T}_+, \qquad \boldsymbol{\Omega} = -\frac{1}{\sqrt{2}}\dot{\gamma}\mathbf{T}_a. \quad (10)$$

The substitution of (8), (9) into (2)–(3) and convolutions in basis tensors yield the system of equations for scalar functions Q_+, Q_-, R

$$\frac{DQ_+}{Dt} + \dot{\gamma}Q_- = G\frac{\dot{\gamma}}{\sqrt{2}}\frac{2}{5}\left(1 - \frac{R}{\sqrt{6}} - 2Q_+^2 + 3Q_-^2 - R^2\right) - 6DQ_+, \quad (11)$$

$$\frac{DQ_-}{Dt} - \dot{\gamma}Q_+ = G\frac{\dot{\gamma}}{\sqrt{2}}Q_+Q_- - 6DQ_-, \quad (12)$$

$$\frac{DR}{Dt} = -G\frac{\dot{\gamma}}{\sqrt{2}}\frac{2}{5}\left(RQ_+ + \frac{Q_+}{\sqrt{6}}\right) - 6DR. \quad (13)$$

The analysis of the system (11)–(13) shows that at $G < 1$ and $D > 0$ its solution takes the form of damping periodic oscillations representing the ability of rigid particles to rotate in the flow plane. The longer the particles, the closer the value of G to unit and the longer the oscillation period, i.e. in the range of $G \to 1$ this period is equal to infinity and the solution is of monotonic character. The coefficient of rotational diffusion specifies the time of reverse transition of the oriented material into isotropic state. If $G = 1$, $D \ll 1$, $\dot{\gamma}$ is linearly involved in every term of the system Equations (11)–(13) and their solution for nondimensional time $t^* = \dot{\gamma}t$ is independent of $\dot{\gamma}$. The stationary solution is also independent of $\dot{\gamma}$. The shear stresses are expressed by the following equation

$$\tau_{xy} = \dot{\gamma}\left[\mu_0 + \frac{1}{5}\mu_2\left(\frac{2}{3} + 2Q_+^2 - 3Q_-^2 + R^2 - \frac{4}{\sqrt{6}}R\right)\right] + F_D Q_+, \quad (14)$$

and the first difference of the normal stresses is given by

$$\sigma_x - \sigma_y = \mu_2\dot{\gamma}Q_+Q_-. \quad (15)$$

In the stationary state the solution to the Equations (11)–(13) takes the form

$$Q_+ = 0, \qquad Q_- = -\frac{1}{\sqrt{2}}, \qquad R = -\frac{1}{\sqrt{6}} \quad (16)$$

and corresponds to the orientation of all macromolecules along the velocity vector.

The solution of the non-stationary Equations (11)–(13) may be obtained only numerically, for example, using the Runge-Kutt's method. Figure 1 demonstrates the development of the orientation from the initial isotropic state without heat motion. The angle φ between the direction of the oriented macromolecules and velocity vector is calculated from the formula

$$\varphi = \tfrac{1}{2}\,\mathrm{arctg}(Q_+/Q_-). \quad (17)$$

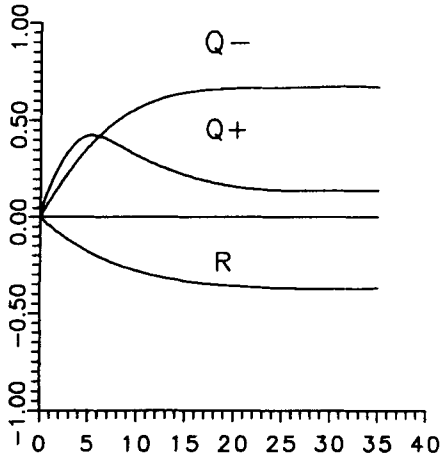

FIGURE 1 Solution of nonstationary Equations (11)–(13).

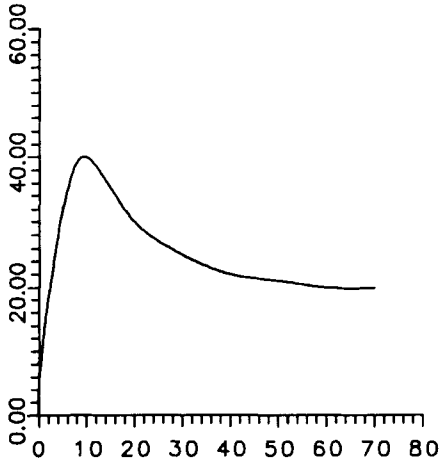

FIGURE 2 Development of shear stress in nondimensional time.

The corresponding development of the shear stress in nondimensional time is given in Figure 2.

The calculated evolution of shear stresses in time displays specific features. First, when the material is close to the isotropic state the shear stress slightly increases approaching its maximum and then decreases to the stationary value with the development of the orientation effects. Thus, at small axes ratios the ellipsoids experience rotation whereas at $G = 1$ they are oriented in the direction of the velocity vector. Suppose further that the ellipsoid is modeled by a dumbbell oriented in the flow direction. If there is enough time for establishing the stationary state we may write for sufficiently large elongation the stationary distribution function in uniaxial approximation as

$$\Psi(x) = \text{const} \exp\left(-\frac{U(x)}{kT}\right), \tag{18}$$

where x is the domain size in ν-direction.

The free energy in linear approximation is defined by the relation

$$U(x) = -\int_0^x (F_{el} + F_{fr})\, dx, \tag{19}$$

Here $F_{el} = -kx$, $F_{fr} = \varsigma\nu = \varsigma\dot{\gamma}x$ are elastic and friction forces, x is the end-to-end distance, ν is the velocity difference of dumbbell ends, k is the coefficient of elasticity, ς is the friction coefficient, $\dot{\gamma}$ is the velocity gradient.

In terms of nondimensional parameter $l = x/Nx_0$ the mean square of the domain extension is written as

$$S = \langle l^2 \rangle = Z^{-1} \int_0^1 l^2 \exp\left(-\frac{U(l, \dot{\gamma})}{kT}\right) d\beta \tag{20}$$

where $Z = \int_0^1 \exp(-U(l, \dot{\gamma})/kT)\, dl$, $U(l, \dot{\gamma}) = 3N(1 - \tau_c)l^2$, and τ_c is the relaxation time.

The average value $\langle l^2 \rangle$ is defined by l^* in the minimum U. If $\dot{\gamma}$ is small, the free energy has only one minimum at $l = 0$, i.e. in this region of $\dot{\gamma}$ variation the elastic forces predominate, the shape of the domains remains spherical and macroproperties are still isotropic. The critical value of γ^* is determined from the condition

$$\frac{\partial^2 U}{\partial l^2}(l, \dot{\gamma})_{l=0} = 0, \qquad \text{and equal } \dot{\gamma}^* = \frac{1}{\tau_c}. \tag{21}$$

At the strain rate beyond the critical value, the frictional forces become prevailing, the free energy decreases and the domain extension occurs as the phase transition of the second kind.

A more comprehensive and rigorous investigation into behavior of the dumbbell model is made by Fuller and Leal.[4] In this paper, an analysis is made of the influence of the elastic and hydrodynamic forces on the dumbbell elongation using Fokker–Plank equation. It has been demonstrated that dumbbell elongation involves the hysteresis phenomenon, which becomes more drastic when allowance is made for nonlinear elasticity and effects of conformation-dependent friction. This leads to transformation of the second-order transition into the first-order one.

In view of the above, it is assumed that the parameter of orientational order is proportional to the mean square of the domain extension.

$$\langle \mathbf{vv} \rangle = \langle l^2 \rangle \mathbf{nn} = S\mathbf{nn}. \tag{22}$$

Then the rheological equations in the stationary state take the form

$$\boldsymbol{\sigma} = -p\mathbf{I} + \hat{\mathbf{M}} \circ\circ \mathbf{E}, \tag{23}$$

where $m_{iklm} = \mu_0 \delta_{il} \delta_{km} + \mu_1 S(n_i n_l \delta_{km} + \delta_{im} n_k n_l) + (\frac{1}{5})\mu_2 S^2 (6 n_i n_m n_k n_l - n_i n_k n_l n_m)$.

In the flow regions, in which $\dot{\gamma} < \dot{\gamma}^*$, the domains may rotate with the surrounding effect medium without changing their shape. Here the medium is linear isotropic fluid. In the range of $\dot{\gamma} > \dot{\gamma}^*$ the domains are oriented in the velocity direction and abruptly stretched to the limiting size, which results in transversely isotropic behavior of material.

$$S = 0, \qquad \mathbf{nn} = \tfrac{1}{3}\mathbf{I}, \qquad \text{when } \dot{\gamma} < \dot{\gamma}^* \tag{24}$$

$$S = 1, \qquad \mathbf{nn} = \frac{\boldsymbol{\nu}\boldsymbol{\nu}}{(\boldsymbol{\nu} \cdot \boldsymbol{\nu})}, \qquad \text{when } \dot{\gamma} \geq \dot{\gamma}^*. \tag{25}$$

Such simplified calculation of flows with oriented structure provide some upper estimate.

3. NUMERICAL APPLICATIONS

As an example, let us consider the calculation of the flow in the channel of the screw extruder. Assume that processing of the disperse material with anisometric particles is performed using the cylindrical screw extruder with constant pitch and screw channel depth. The screw length is such that the inlet effects are exhibited only in the initial relatively small part. With the exception of this part, the flow picture is the same through the full length of the screw channel and the pressure gradient is constant.

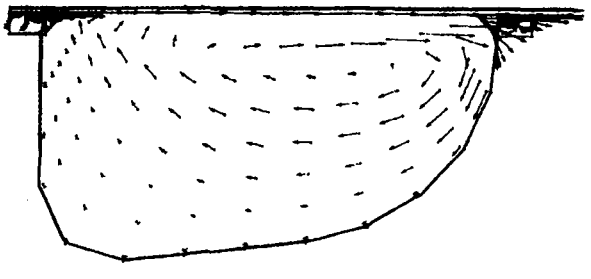

FIGURE 3 Computational region.

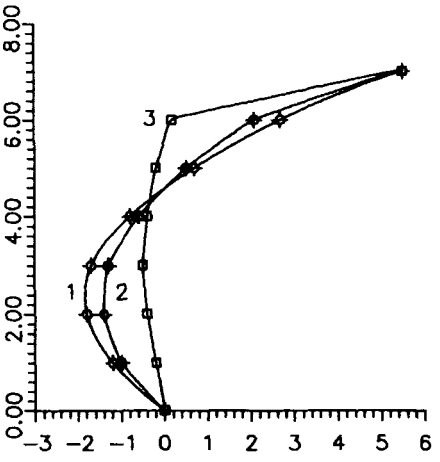

FIGURE 4 Velocity profile of circulatory flow.

Therefore, we may consider one section of the channel perpendicular to the helical generating line and state two-dimensional problem in cylindrical coordinates.

The fluid flow is described by the following:

(a) Momentum equations

$$\rho(\mathbf{v}\circ\nabla)\mathbf{v} = -\nabla p + \nabla\circ(\hat{\mathbf{M}}\circ\circ(\nabla\mathbf{v} + \mathbf{v}\nabla)), \tag{26}$$

(b) Continuity equation

$$\nabla\circ\mathbf{v} = 0, \tag{27}$$

In order to discretize Equations (26)–(27) we consider their weak formulation

$$\int_V \{\rho(\mathbf{v}\circ\nabla)\mathbf{v}\circ\mathbf{u} - p(\nabla\circ\mathbf{u}) + \hat{\mathbf{M}}\circ\circ(\nabla\mathbf{v} + \mathbf{v}\nabla)\circ\circ\nabla\mathbf{u}\}\, dV = \int_S \mathbf{g}\circ\mathbf{u}\, dS,$$

$$\int_V (\nabla\circ\mathbf{v})w\, dV = 0. \tag{28}$$

which must hold for all virtual fields $\mathbf{u}$, w.

The computational region is divided into triangular elements on which p and w is approximated by a constant and the fields $\boldsymbol{\nu}$, $\mathbf{u}$ are approximated by piecewise linear functions. Substituting the approximative functions into Equations (28) and integrating over the triangular area yield the system of nonlinear algebraical equations, which is solved by iteration method. The shear rate and its direction determined at each k-th iteration are then used on the $(k + 1)$ step. The iteration process continues until the condition of convergence

$$J_2^{(k)}/J_2^{(k+1)} < \varepsilon \tag{29}$$

is satisfied for all elements.

Figure 4 shows the value and direction of the circulatory flow velocity calculated numerically for the computational region as presented in Figure 3. In accordance with the adopted requirements (21) the direction of the main axis of the orientational tensor coincides with the velocity direction. Following the obtained results the domain orientation occurs near the barrel walls. The velocity profile of the main flow is seen to involve localization of the shear strains. In extrusion such localization causes part of material in the screw channels to adhere to the stationary barrel walls, while the rest of the material rotates with a screw without moving toward the discharge end.

Thus, the orientation of particles and the resulting anisotropy of material properties (decreasing effective viscosity in the regions of highly intensive shear flow) are found to be responsible for changes in the velocity profiles and the reduction of the pumping effect of the extruder.

4. CONCLUSIONS

The proposed modified Hinch and Leal model allows us to take into account the reduced pumping effect during extruder processing of highly concentrated polymer solutions and is easily applied to numerical modeling of engineering processes.

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