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Model of the Behavior of Viscoelastic Media at High Strain Rates

Corresponding Member of the RAS **V. G. Kulichikhin, A. V. Semakov, and A. Ya. Malkin**

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Abstract—A new model was proposed to describe the behavior of melts and concentrated solutions of polymers at high strain rates. This model is a lattice of elastic elements, which, under deformation, transform into ellipsoids, are oriented, and elastically interact with each other. The calculation results give a qualitatively correct insight into the onset of structural instability and self-organization, as it is really observed in experiments in rotational flows and extrusion of polymer melts from capillaries.

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In our previous work [1], we showed that there is a fundamental difference in behavior of a network of intermolecular entanglements in melts and concentrated solutions of polymers at low and high strain rates. At low strain rates, in the linear region of mechanical behavior, there is affine deformation of the network, whereas at high strain rates, accumulations of entanglement nodes form, the role of which is similar to the role of nodes of chemical bonds in rubbers. The position of the boundary between the ranges of low and high strain rates is determined by the Weissenberg number $\mathrm{Wi} = \tau_d\dot{\gamma} < 1$, where τ_d is the characteristic time of tube renewal (the main parameter of the reptation model [2]) and $\dot{\gamma}$ is the strain rate. This quantity can also be related to the lifetime of entanglements, the sliding in which is due to the Brownian motion.

Thus, the following fundamental facts are responsible for the behavior of melts and concentrated solutions of polymers in the range of high strain rates. First, this is the transition from the fluid state to the forced high-elastic state; this transition is determined by the fact that the flow (caused by slip at nodes of the entanglement network) becomes impossible and the strains become completely reversible, more specifically, rubber-like. Second, this is the heterogeneity of the structure of the medium, which is caused by local and inhomogeneous accumulations of entanglement nodes. Such local inhomogeneities allow one to consider the state of the melt as an analogue of a high-concentration suspension, the high strain rate in which also leads to local hindrances and fluidity loss [3, 4].

Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninskii pr. 29, Moscow, 119991 Russia
e-mail: alex_malkin@mig.phys.msu.ru

The above concepts formed the basis for a new model of the behavior of melts and concentrated solutions of polymers at high strain rates. According to this model, the behavior of spherical particles constituting a regular lattice is considered (Fig. 1).

Under an external action, first, the initially spherical elastic particles (model elements) are deformed taking the shape of ellipsoids, and second, they interact with each other by elastic collisions.

Then, in a simplified two-dimensional case (which does not limit the generality of the model), the evolu-

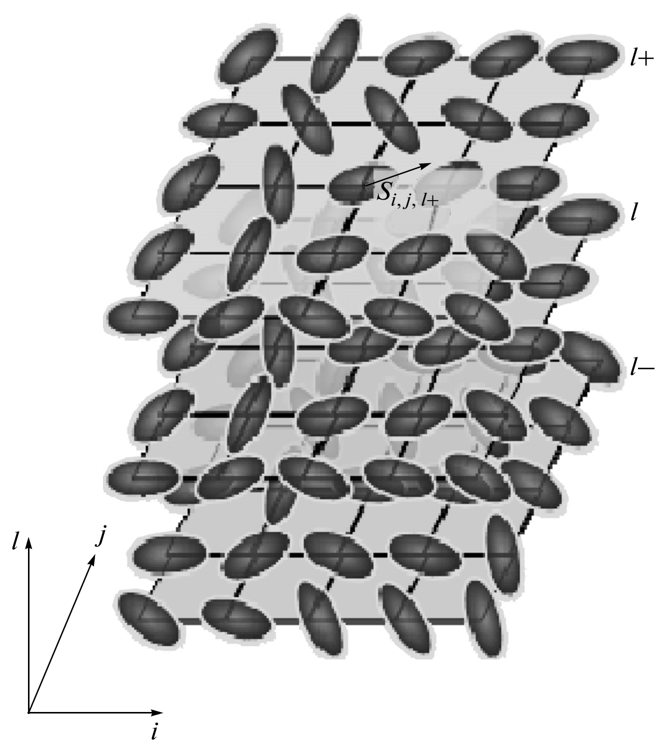

Fig. 1. Multilayer model of interacting elastic elements.

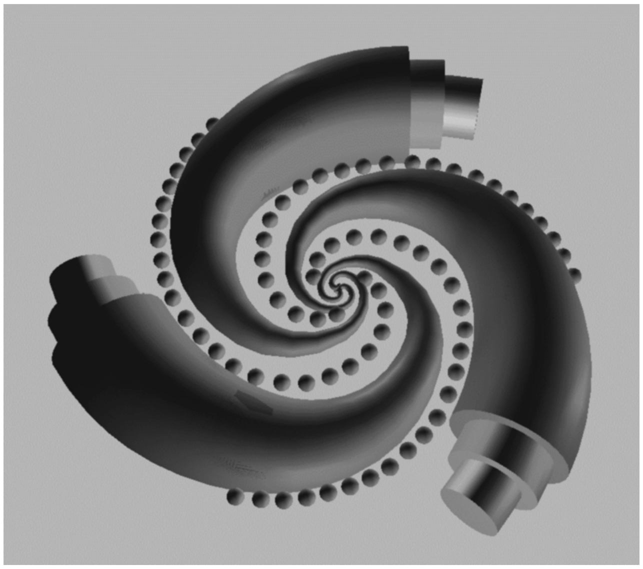

Fig. 2. Computer modeling results demonstrating the formation of a regular structure comprising three arms (for illustration purposes, the boundaries of these arms are set off by markers—particles of a filler in the melt).

tion of the orientation S'_{ij} of particles is described [5] by the vector equation

$$\frac{\partial}{\partial t}S_{i,j} = \frac{\alpha\tau}{1 + h_{i,j}\cdot S_{i,j}}h_{i,j}\cdot S_{i,j} + \frac{\beta E}{1 + S_{i,j}\cdot S_{i\pm1,j\pm1}}S_{i,j}\cdot S_{i\pm1,j\pm1}, \quad (1)$$

where the product $\alpha\tau$ characterizes the contribution of external tangential stresses τ, the product βE is the elastic potential of sterically interacting particles, the parameters α and β are numerical coefficients on the order of unity, and h are unit vectors of direction.

The first term reflects the effect of external stresses on the transformation of spherical particles into ellipsoids. The second term describes the elastic interaction between ellipsoids.

This equation can be represented in the form of the nonlinear Schrodinger finite-difference differential equation

$$i\frac{\partial}{\partial t}q_{i,j} = \sum q_{i\pm1,j\pm1} - 4q_{i,j} + |q_{i,j}|^2\sum q_{i\pm1,j\pm1}, \quad (2)$$

in which the variables q and S are related as follows

$$1 + |q_{i,j}|^2 = \frac{2}{1 + S_{i,j}\cdot S_{i+1,j+1}}, \quad (3)$$

$$i\left(q_{i,j}\tilde{q}_{i-1,j-1} - \tilde{q}_{i,j}q_{i-1,j-1}\right) = \frac{2S_{i,j}\cdot\left(S_{i+1,j+1} + S_{i-1,j-1}\right)}{\left(1 + S_{i,j}\cdot S_{i+1,j+1}\right)\left(1 + S_{i,j}\cdot S_{i-1,j-1}\right)}. \quad (4)$$

The nonlinear Schrodinger equation

$$i\,q_t + q_{xx} + |q|^2 q = 0 \quad (5)$$

is an integrable equation, the solutions of which describe the propagation of solitons or their superposition (multisoliton solutions) in a medium. In hydrodynamics problems, these solutions may characterize vortex-like structures.

Interestingly, the considered model of elastically interacting molecular coils and the model of the spin system in the classical approximation are described by identical equations, so that the results obtained for the spin system are fully applicable to the mechanical model.

Omitting mathematical details, let us dwell on the fundamental results of numerically solving the obtained equation and their comparison with the experimental data.

The most important result is achieved by analyzing the behavior of the system in a shear field. Analysis of the obtained solutions showed that, under shear deformation in axially symmetric geometries, instability emerges, which finally gives rise to ordered structures.

Figure 2 presents the results of computer modeling of structuring under deformation of a polymer melt between a plane surface and a spherical surface of large radius.

Such a pattern was really observed in the experiment in a rotational flow [5], and ordering of dispersed particles was also repeatedly detected in the shear planar flow of a viscoelastic liquid (see, e.g. [6]). Similar regular ring structures emerge in filled polymers: the initially randomly dispersed filler under high-rate deformation form regular rings.

It is significant that the transition from the random motion caused by elastic instability to the formation of a large-scale regular structure is related to the transition from the molecular motion to the motion of large structural units [7, 8], which is consistent with the basic concepts of the considered model. Note also that, in this work, we consider only the mechanism of elastic instability, i.e., instability caused by elastic deformations with ignoring inertial phenomena (Reynolds instability). In polymer systems, the elasticity can be varied over very wide range; therefore, in principle, a transition from inertial to elastic instability is also possible.

Thus, as the calculations showed, under considerable elastic deformations at $\mathrm{Wi} \gg 1$, the medium at the macroscopic scale becomes essentially inhomogeneous, forming a system of elastic twisted tubes. Meanwhile, the total topological charge is conserved; the tubes are born in pair with different twisting directions so that the sum of clockwise twists is equal to the sum of counterclockwise twists. This means that such formations, being independent structural units to a certain extent, at the same time interact with each

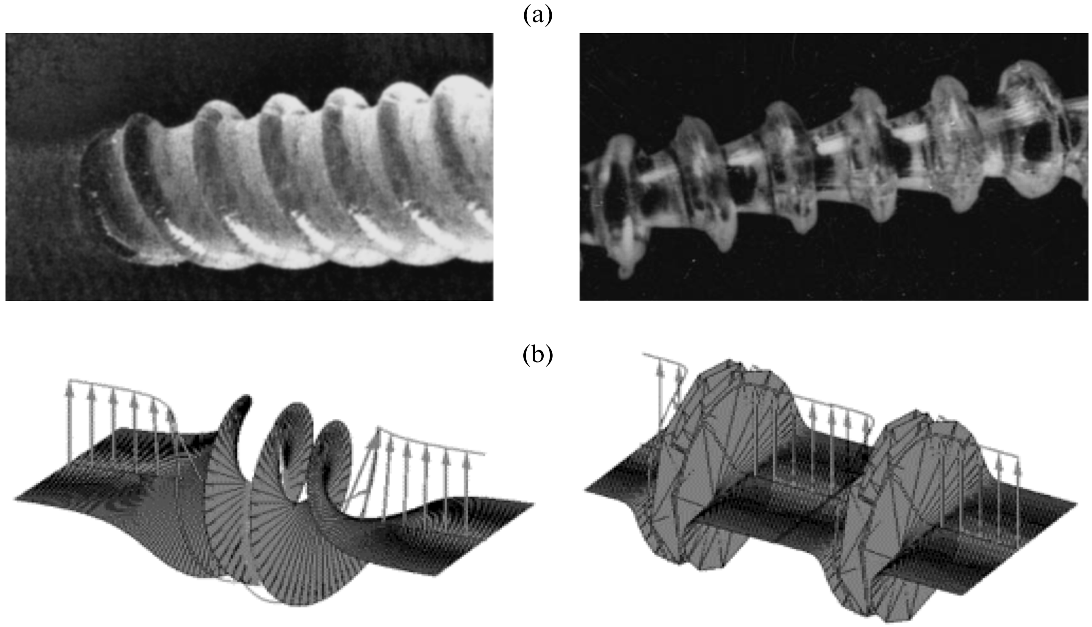

Fig. 3. Formation of regular periodic structures on the surface of extrudates in capillary extrusion (a) modeled by the results of calculations based on the considered model (b).

other because their behavior is self-consistent. It is best seen in considering high-rate deformation in the flow of a viscoelastic polymer medium through a capillary.

There can be quite a lot of such tubes, such that they can form a regular sequence. In the considered model, the chaos–order transition is related to the location of motion modes in the configurational and real spaces. If such a set of tubes has risen to the surface of, e.g., a round extrudate, they form distortions (surface defects) as a regular sequence of wavy helical lines. Such a structure can be small-scale, as a ripple on the flow surface, or large-scale, when defects constitute a helical surface.

Figure 3 shows how the type of irregularity depends on the model parameters that correspond to different experimental cases. Formally, an attractor forms at zero absolute temperature of the system because the formulation of the problem ignored thermal fluctuation noise, i.e., the thermal Brownian motion of particles. This is because, under high-rate deformation, the elastic energy considerably exceeds the energy of the Brownian motion [9], and the size of fluctuations caused by accumulation of entanglements is large enough for the Peclet number to take a required value, which was one of the concepts of the basis of the model.

The formation of a heterogeneous structure in an elastic medium in the shape of elastic tubes, as well as the kinetic energy of modes of motion of these structural elements, paves the way for disintegration of the medium. This is due to the generation of tensile stresses between tubes, which can reach the ultimate strength of the medium; in turn, this leads to the formation of new surfaces and, eventually, to decomposition of the medium.

Thus, the proposed model adequately describes the main features of the behavior and the mechanism of structuring under high-rate deformation of viscoelastic polymeric (and probably other) liquids. Such systems are characterized by the fact that, under certain conditions, there is a relaxation transition from the liquid to rubber-like state. This is accompanied by fluidity loss, and the medium can be regarded as elastic, and its behavior is determined by a set of discrete heterogeneous particles.

It bears repeating that the discussed model describes elastic liquids, and it is elasticity that plays a decisive role in features of the behavior of a medium under high-rate deformation.

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REFERENCES

1. Semakov, A.V., Malkin, A.Ya., and Kulichikhin, V.G., *Dokl. Chem.*, 2011, vol. 438, part 1, pp. 137–139.

2. Doi, M. and Edwards, S.F., *The Theory of Polymer Dynamics*, New York: Oxford Univ. Press, 1986.
3. Bonnecaze, R.T. and Cloitre, M., *Adv. Polym. Sci.*, 2010, vol. 236, pp. 117–161.
4. Faroughi, S.A. and Huber, Ch., *Rheol. Acta.*, 2015, vol. 54, pp. 85–108.
5. Semakov, A.V. and Kulichikhin, V.G., *Polym. Sci. Ser. A*, 2009, vol. 51, nos. 11–12, pp. 1313–1328.
6. Pasquino, R., Snijers, F., Grizzuti, N., and Vermant, J., *Rheol. Acta.*, 2010, vol. 49, pp. 993–1001.
7. Monsenti, A.A., Pena, A.A., and Pasquali, P., *Phys. Rev. Lett.*, 2004, vol. 92, p. 058303.
8. Malkin, A.Ya. and Kulichikhin, V.G., *Appl. Rheol.*, 2015, vol. 25, no. 3, p. R35358.
9. Malkin, A.Ya., Semakov, A.V., and Kulichikhin, V.G., *Rheol. Acta.*, 2011, vol. 50, pp. 485–489.

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