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STRUCTURALLY INHOMOGENEOUS REGIMES OF SPREADING OF FILM-FORMING POLYMER SOLUTIONS

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Results of mathematical modeling of the process of spreading of polymer materials are discussed. Viscosimetric data obtained in the experiments have been analyzed and processed with the aim of determining the rheological properties of the polymer compositions used.

Introduction. One is well aware of the method of formation of lamellar polymer coatings through implementation of the process of spreading of film-forming polymer solutions under the conditions of centrifugal actions. The difference in the molecular organization of a polymer solution both in the volume and at the phase boundary brings about certain structures capable of influencing the process of spreading of the polymer material. Therefore, one of the most important problems of polymer materials science is the development of models of the process of spreading of polymer materials which make it possible to evaluate the interaction of hydrodynamic, rheological, and structural factors.

Experimental investigations of the thickness of thin-film coatings in spreading of solutions of latent polyisocyanates under the action of centrifugal forces have revealed an interesting feature of the spreading: under certain conditions, the dependence of the coating thickness on the value of the force action is nonmonotone. This phenomenon can be described using the basic theoretical propositions of the rheodynamics of complex media. It is known that under the conditions of shear flow of structurized systems, there can be qualitatively different stationary regimes of flows (uniform and spatially nonuniform) for the same values of temperature, pressure, and stress [1]. Which of them is implemented in actual practice depends on the structure-formation conditions. The possibility for the structurally inhomogeneous regimes of flow to form in the process of formation of polymer fibers has been shown in [2]. The reasons for morphological changes in the liquid in shear flow under the conditions of viscosity superanomaly are discussed in [3] in detail. The spatially nonuniform regime of flow manifests itself in the parametric range of the rheological curve that corresponds to a decrease in the resistance to deformation with increase in the rate of this process. In this case, the rheological curve has a drooping branch, and the phenomenon itself has been called viscosity superanomaly.

In the present work, we have investigated rheodynamic processes in spreading of polymer materials on the basis of mathematical modeling of flow and the kinetics of structural transformations with allowance for the actual rheological behavior of these materials. The mathematical modeling of the spreading was carried out in two steps: (1) analysis and processing of viscosimetric data obtained in the experiment with the aim of determining the rheological properties of the polymer compositions used; (2) numerical investigation of the process on the basis of an analysis of the kinetic curves stress–time ($\sigma(t)$), fractional conversion–time ($a(t)$), and radius (thickness of the coating)–time ($R(t)$) depending on the parameters of the model.

Foundation of the Problem. We consider the simplest model of flow of a two-component liquid with allowance for the kinetics of mutual transformation of structural units [4]. Let the rheological system consist of A- and B-type structures with a concentration of them in the volume of a and $b = 1 - a$. The gross diagram of the process of structural transformations has the simplest form: $A \rightleftarrows B$. This diagram corresponds to the kinetic equation

$$da/dt = -k_1 \varphi(a) + k_2 \psi(a) .$$

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Assuming that the processes of restoration and destruction of the structure are activating, we can write the rate constants of these processes in the form

$$k_1 = k_{10} \exp\left(-\frac{E-U}{RT}\right), \quad k_2 = k_{20}\left(-\frac{E+U}{RT}\right).$$

As is well known, the action of the mechanical field results in the deformation of bonds in the destroyed structure, which is dependent on the value of the stress, and the orientation of randomly directed molecular-kinetic units, which is dependent on the velocity gradient. Assuming the independence of these two processes, we write

$$U = p_1\sigma + q_1\gamma^2 .$$

According to the ideas of Eyring, the relationship between the deformation rate and the shear stress has the form

$$\gamma = (aF_1 + (1-a)\,F_2)\,\sigma .$$

The viscosity of the material is represented as

$$\mu = (aF_1 + (1-a)\,F_2)^{-1} .$$

The process of spreading on a smooth horizontal surface relative to a thick cylindrical layer will be described on the basis of a simplified Navier–Stokes equation. We assume the regime of viscous spreading under the action of gravitational forces where the inertial effects can be disregarded. In this case the kinetics of spreading will be written as follows:

$$r^7\,\frac{dr}{dt} = \frac{D}{\mu\,(a)} .$$

The system of equations has been reduced to dimensionless form with the following dimensionless variables and parameters:

$$\bar{\mu} = \mu F_2\,, \quad \bar{\sigma} = \sigma F_2\,, \quad \bar{\gamma} = \gamma/\gamma_0\,, \quad \bar{r} = \frac{r}{r_0}\,, \quad \tau = \frac{t}{t_*}\,, \quad t_*^{\mathrm{spr}} = \frac{r_0^8}{DF_2}\,, \quad t_*^{\mathrm{r}} = \frac{1}{k_{20}}\,, \quad t_1 = \frac{t_*^{\mathrm{spr}}}{t_*^{\mathrm{r}}}\,, \quad t_2 = \frac{t_*^{\mathrm{r}}}{t_*^{\mathrm{spr}}}\,,$$

$$\kappa = k_{10}/k_{20}\,, \quad \lambda = F_1/F_2\,, \quad p = 2p_1/RT\,, \quad q = 2q_1/RT\,, \quad k = \kappa \exp\,(p\sigma + q\gamma^2) .$$

A set of the values of these parameters provides information on the course of the process of structural transformations. We can say that the parameter κ characterizes the strength of the structure. Since κ is the ratio of the rate constants of destruction and restoration of the structure, we have $\kappa < 1$. The viscosity conventionally decreases in the course of structural transformations; therefore, $\lambda < 1$ $(F_1 < F_2)$. The quantity λ characterizes the range of variation of the viscosity in the course of deformation. The parameters p and q characterize the bond strength and the probability of orientational rotation. For the sake of convenience in what follows we will write r, γ, σ, and μ instead of $\bar{r}$, $\bar{\gamma}$, $\bar{\sigma}$, and $\bar{\mu}$.

The problem in dimensionless form is given below:

$$\frac{da}{d\tau} = \sqrt{\frac{\kappa}{k}}\,(1 - a\,(1+k))\,, \quad \frac{dr}{d\tau} = t_2\left(\frac{1 - a\,(1-\lambda)}{r^7}\right), \quad \mu = \frac{1}{1 - a\,(1-\lambda)}\,, \quad \sigma = \frac{\gamma}{1 - a\,(1-\lambda)} .$$

It has been solved numerically according to the implicit difference scheme [5], as a result of which the concentrations, the stresses, and the radius as functions of the time have been found for different values of technological parameters.

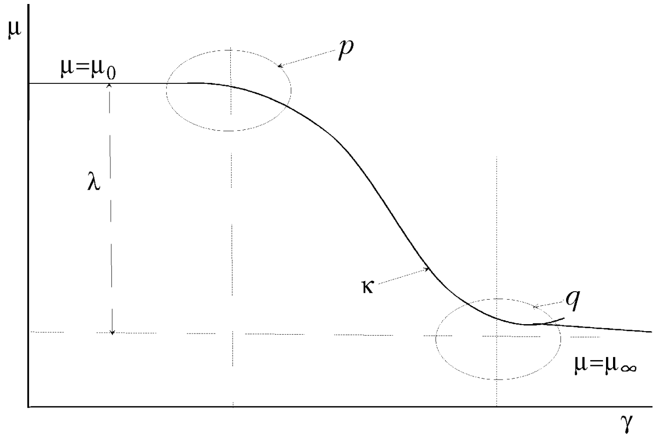

Fig. 1. Determination of the parameters of the model: $\kappa = k_1/k_2$, $\lambda = F_1/F_2$, q (probability of orientational rotation), and p (probability of breaking of bonds).

TABLE 1. Model Parameters Calculated for Different Polyisocyanates

Material	Model parameters					Content of the oligomer fractions, mole %, with a degree of polymerization n			
	κ	λ	p	q	$f = \kappa/\lambda$	2–7	8	10	12
BPI1	0.01	0.0023	0.00069	$3.1 \cdot 10^{-7}$	4.3	3.9	–	–	96.1
BPI1 + butyl alcohol	0.002	0.0006	0.00042	$8.1 \cdot 10^{-8}$	3.3	–	–	–	–
BPI2	0.17	0.0037	0.001	$3.8 \cdot 10^{-7}$	45.9	12.5	2.0	84.4	–

Analysis and Processing of Viscosimetric Data under the Conditions of Viscosity Superanomaly. A fundamental feature of the method proposed below for processing viscosimetric data is allowance for the process of structural transformations. In this case, the concept of inverse rheology problems, which are aimed at obtaining information on the kinetics of structural transformations now and not only at determining the viscosity characteristics of materials, changes.

The state of dynamic equilibrium between the processes of destruction and restoration of the structure is reached under the conditions of steady-state flow. The values of the concentrations of structure A (or B) and the flow curve are determined from the steady-state solution of the model:

$$a = \frac{1}{\kappa + 1}\,, \quad \sigma = \frac{1}{F_2}\frac{k+1}{k+\lambda}\gamma\,.$$

The values of the parameters of the model κ, λ, p, and q can be calculated from the total curves of flow $\sigma(\gamma)$. However, certain characteristic features (found experimentally) of the viscosity curve $\mu(\gamma)$ enable us to approximately estimate the values of these characteristics. We note first of all the limit relations

$$\lim_{\gamma\to\infty} \mu = 1/F_2\,, \quad \lim_{\gamma\to 0} \mu = (1/F_2)\,(1+k)/(k+\lambda)\,.$$

The first relation means that for large γ we have the regime of flow with the lowest Newtonian viscosity $\mu_\infty = F_2^{-1}$ coincident with the viscosity of structure B. For low values of σ (or γ) the highest Newtonian viscosity μ_0 is realized, which, as the second relation shows, generally does not coincide with the viscosity of structure A. We have $\mu_0 = F_1^{-1}$ only when $\kappa << \lambda$.

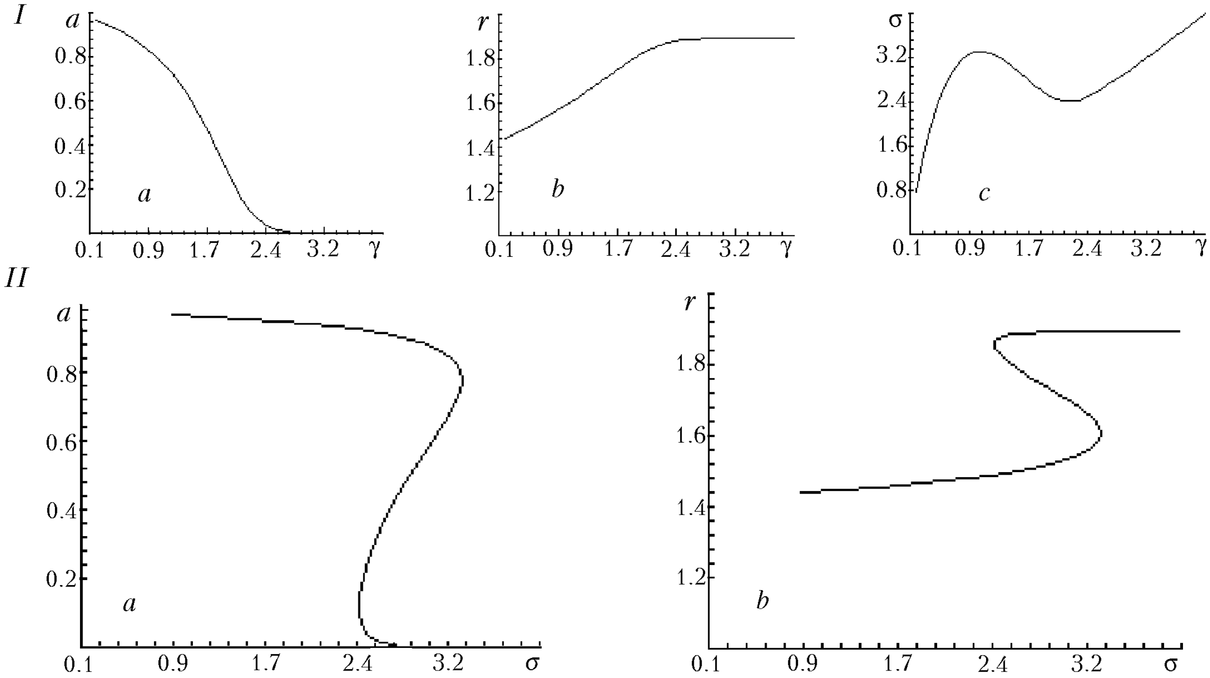

Fig. 2. Dependences, in the case of viscosity superanomaly, of the steady-state values of the concentrations (a), the radius (b), and the steady-state values of the stresses (c) on the deformation rates γ (*I*) and on the stresses σ (*II*).

On the basis of the dependence of the viscosity μ on the rate of shear γ (Fig. 1), we can determine all the parameters of the model and predict the basic features of the process of structure formation.

Table 1 gives as an example the values of the parameters of the model κ, λ, p, and q which have been calculated from the total curves of flow of 30% ethyl-cellosolve-acetate solutions of blocked polyisocyanates (BPIs [6, 7]) differing in molecular-weight distributions [BPI1 and BPI2] and with an addition of butyl alcohol.

We can infer that, since the additions of the solvent lead to a decrease in κ, p, and q, the resulting structure is stronger and has a lower probability of orientational rotation and a stronger bond, which is in agreement with the results of the experiment.

Distinctive Features of the Kinetics of Spreading under the Conditions of Viscosity Superanomaly. The calculations have shown that in a certain range of the parameters, as γ increases the steady-state values of the stress decrease in a limited range of γ (negative differential viscosity) and the $\sigma(\gamma)$ curve represents a multiple-valued function (Fig. 2, *I*, c). This corresponds to the phenomenon of viscosity superanomaly. We note that here the regularities of the processes of structural transformations and spreading in the regimes of deformation γ = const or σ = const are fundamentally different. In the first regime (γ = const), the steady-state values of the concentration monotonically decrease (Fig. 2, *I*, a) whereas the spreading radius monotonically increases with change in γ (Fig. 2, *I*, b). We emphasize that the limit value of the radius can be spoken of only by convention; in fact, the process of spreading is substantially unsteady and the spreading radius tends to infinity for each specific value. But in actual practice the process of spreading is observed over a limited period, and we took the value of the spreading radius at the instant when the velocity of spreading became equal to a small prescribed value as its limit value in numerical calculations.

A different situation arises with the regime σ = const. In the region of viscosity superanomaly, each value of σ corresponds to three values of the equilibrium concentration (a) (Fig. 2, *II*, a) and three values of the radius (r) (Fig. 2, *II*, b), but only the upper and lower values of these quantities determine stable equilibrium states, while the intermediate value corresponds to an unstable state.

These circumstances enable us to explain the fact observed in the experiments on deposition of polymer coatings on disks: the film thickness as a function of the centrifugal force behaves nonmonotonically, which is physically a consequence of the formation of a structurally inhomogeneous regime in the process of formation of a polymer coating. We note that under the conditions of a monotone change in $\sigma(\gamma)$ (in the absence of viscosity superanomaly), the

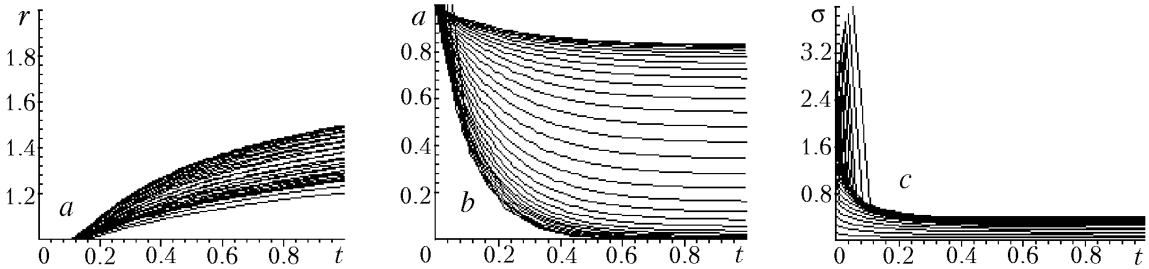

Fig. 3. Changes in the spreading radius (r) (a), the concentration (a) (b), and the stress (σ) (c) with time (t) for different values of γ.

dependence of the radius on σ is also monotone while for the case of a rheological simple liquid (Newton's model) the concentrations and the spreading radius are independent of the value of the velocity gradient or the stress.

Interesting features can be established on the basis of an analysis of the kinetic curves $\sigma(t)$ and $a(t)$ with change in γ. Figure 3 shows the dependences of the stress, the concentration, and the spreading radius on the time for different values of γ. Darkened portions corresponding to a nonmonotone change in the limit values of the stress as γ increases are a consequence of the viscosity superanomaly and the formation of a structurally inhomogeneous regime of flow. Detailed investigation of the distinctive features of the kinetics of spreading and the structure formation for different deformation regimes is of independent importance.

The process of spreading is limited not only by the time range but also by the factors influencing the viscosity. For example, for a polymerizing system such a factor could be the rise in the viscosity with time, while under nonisothermal conditions the process of spreading is influenced by the cooling of the material. These factors are disregarded in the given model, and it is of independent interest to consider them.

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NOTATION

a and b, concentrations in the volume of structures of the A and B type; $\varphi(a)$ and $\psi(a)$, kinetics laws of destruction and restoration of the structure respectively; k_{10} and k_{20}, rate constants of the processes of destruction and restoration of the structures; E, effective activation energy; U, mechanical-field energy; T, absolute temperature; R, universal gas constant; p_1 and q_1, constants expressing respectively the intensities of the processes of breaking of bonds and of orientational rotations; F_i (i = 1, 2), fluidity of the ith component; t, time, sec; r, spreading radius, m; $D = m^3g/(2\pi\rho^2)$; m, mass of the material, kg; ρ, density of the material, kg/m^3; g, acceleration of gravity; t_*, characteristic time of the process; t_*^{spr} and t_*^{r}, characteristic times of spreading and restoration respectively; r_0, initial value of the radius; γ_0, initial value of the deformation rate; μ, viscosity of the system, Pa·sec; σ, stress, Pa. Superscripts: spr, spreading; r, restoration.

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