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Abstract

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Rheology of Polymers. Theory of Thixotropy

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Until recently the phenomenon of thixotropic transformations in condensed polymer systems remained unstudied. However, [1] thixotropy may be strongly pronounced in such widely known polymers as polyisobutylene. The point is that reversible thixotropic transformations in polymers in the condensed state are most readily detected by recording the dependence of the shear stress τ on the deformation γ at a constant rate of deformation $\dot{\gamma}$, which for polymer melts and amorphous condensed polymer systems in the visco-flow state have recently been described [2]. The theory of thixotropy has recently been developed by Eyring and co-workers [3,4]. In the present work a substantially different approach is set forth to the phenomenon of thixotropy, which represents a reversible time-dependent change in the structure and properties of systems under the influence of external, for example mechanical, actions.

Beginning with the works of V. A. Kargin and G. L. Slonimskii [5], mechanostatistical models have been widely used to describe the behavior of polymers under deformation. In the theory proposed below, the viscoelastic properties of thixotropic systems are described by a model consisting of N Maxwell elements connected in parallel, with relaxation times θ_n and shear moduli G_n, these elements being arranged in order of increasing θ_n. The model as a whole is described by the relaxation function $\psi(t)$, which determines the relaxation spectrum and its change with time. The Maxwell elements model structural elements that contain the development of deformations in the substance. These structural elements are, above all, reversibly destructible supramolecular formations in polymers or bonds between particles of the dispersed phase in disperse systems. A feature of the modeling method set forth here for the viscoelastic behavior of thixotropic systems is the representation of the successive rupture (destruction) and restoration of parallel-connected Maxwell elements, which corresponds to a change in the function ψ under the influence of deformation and with time. It is assumed that rupture of the n-th element occurs when its elastic energy reaches the value E_n^{p}. The process of rupture of Maxwell elements proceeds in the direction from element $n+1$ to n. It is accompanied by compression of the relaxation spectrum. During restoration of the structure, expansion of the relaxation spectrum occurs in the direction from n to $n+1$. In steady flow there is a dynamic equilibrium between the processes of destruction and restoration of the structure. Below we consider the case in which the energies

of elastic rupture and restoration of the structural elements are equal.

The theory is constructed on the basis that, for many systems, it is possible to determine experimentally, first, the relaxation characteristic under such conditions that their structure is not changed by deformation; second, the dependence of the rate of deformation in steady flow $\dot{\gamma}_\infty$ on τ_∞ under conditions of one-dimensional shear deformation. For steady flow regimes the following expressions are valid:

$$\tau_\infty = \eta_{\rm e}(\dot{\gamma}_\infty)\dot{\gamma}_\infty, \qquad \eta_{\rm nb} = \lim_{\dot{\gamma}_\infty \to 0} \eta_{\rm e}, \tag{1}$$

where $\eta_{\rm e}$ is the effective viscosity, and $\eta_{\rm nb}$ is the greatest Newtonian viscosity. In the case of one-dimensional shear deformation occurring with low intensity ($\tau \to 0,\ \gamma \to 0$), the relation between τ and $\dot{\gamma}$ for an elastic-viscous mate-

of the material described by the N-element model adopted here has the form [6]

$$\tau(t) = \int_{-\infty}^{t} \dot{\gamma}(\xi)\psi(t-\xi)\,d\xi, \qquad \psi(t) = \sum_{n=1}^{N} G_n e^{-t/\theta_n}. \tag{2}$$

Equation (1) corresponds to deformation of a medium with a nondestructing structure. Let us now consider deformation of the material at sufficiently large τ and $\dot{\gamma}$, when destruction of the structure occurs. Let $k(t)$ be the number of undestroyed structural elements at time t. Obviously, $k(t)$ is a step function of time. Then, on the basis of relations (2) and the hypothesis of destruction–restoration of the structure, we obtain the following equations for one-dimensional deformation of the medium under consideration:

$$\tau(t) = \sum_{n=1}^{k(t)} G_n \int_{-\infty}^{t} \dot{\gamma}(\xi) e^{-(t-\xi)/\theta_n}\,d\xi, \tag{3}$$

$$\frac{1}{2}G_k \left(\int_{-\infty}^{t} \dot{\gamma}(\xi) e^{-(t-\xi)/\theta_k}\,d\xi \right)^2 < E_k, \qquad \frac{1}{2}G_{k+1} \left(\int_{-\infty}^{t} \dot{\gamma}(\xi) e^{-(t-\xi)/\theta_{k+1}}\,d\xi \right)^2 \geq E_{k+1} \tag{4}$$

$$(k = N,\ N-1,\ N-2, \ldots, 1).$$

Relation (3) is a generalized Boltzmann–Volterra principle, and relations (4) are the strength condition for the k-th element. The expressions on the left-hand sides of inequalities (4) are the elastic energy accumulated by the k-th and $(k+1)$-th elements. Destruction and restoration of structural elements

occur at the instants t_k for which the first inequality (4) becomes an equality. Let us now determine the destruction energy of the k-elements E_k through the known dependence $\tau_\infty(\dot\gamma_\infty)$, or, equivalently, through the non-Newtonian viscosity $\eta_{\text{e}}(\dot\gamma_\infty)$. We note that, since the model adopted is discrete, in the process of steady flow the non-Newtonian viscosity η_{e} and the instantaneous modulus of elasticity of the material G_{e} will be step functions of $\dot\gamma_\infty$, because if k structural elements have remained undestroyed in steady flow, then

$$\eta_{\text{e}} = \sum_{n=1}^{k} G_n\theta_n, \qquad G_{\text{e}} = \sum_{n=1}^{k} G_n. \tag{5}$$

Assuming the dependence $\eta_{\text{e}}(\dot\gamma_\infty)$ to be known, on the basis of (5) it is easy to find values $\dot\gamma_k$ such that

$$\eta_{\text{e}}(\dot\gamma_\infty) = \eta_{ek} \qquad (\dot\gamma_{k+1} \le \dot\gamma_\infty < \dot\gamma_k), \qquad \eta_{eN} = \eta_{\text{nb}}. \tag{6}$$

In doing so we assume that $\dot\gamma_{N+1} = 0$. The quantity $\dot\gamma_1$ in (6) may be chosen arbitrarily (here we set $\dot\gamma_1 = \dot\gamma_2 + l(\dot\gamma_2 - \dot\gamma_3)$, where $l > 1$ is arbitrary). If we also denote the smallest viscosity by $\eta_{\text{nm}} = \lim_{\dot\gamma\to\infty}\eta_{\text{e}}$, then the case $\eta_{\text{nm}} \neq 0$ corresponds to the presence in the material of an ultimately nondestructing structure. In our case, owing to the discreteness of the model adopted, we have, in addition to (6),

$$\eta_{ek}\big|_{k=a} = \eta_{\text{nm}} \qquad (\dot\gamma_a \le \dot\gamma_\infty), \tag{6a}$$

where a is the number of nondestructing elements as $\dot\gamma_\infty \to \infty$.

Introduce the numbers f_n, related to E_n by the relation

$$f_n = \frac{1}{\theta_n}\sqrt{\frac{2E_n}{G_n}},$$

then formulas (4) take the form:

$$\frac{1}{\theta_k}\left|\int_{-\infty}^{t} \dot\gamma(\xi)e^{-(t-\xi)/\theta_k}\,d\xi\right| < f_k, \qquad \frac{1}{\theta_{k+1}}\left|\int_{-\infty}^{t} \dot\gamma(\xi)e^{-(t-\xi)/\theta_{k+1}}\,d\xi\right| \ge f_{k+1}. \tag{4a}$$

Let there exist $\lim\limits_{t\to\infty}\dot\gamma(t) = \dot\gamma_\infty > 0$; then it is easy to show that expressions (3), (4a) for $t \to \infty$ may be written as

$$\tau_\infty = \dot\gamma_\infty \sum_{n=1}^{k} G_n\theta_n, \qquad f_{k+1} \leqslant \dot\gamma_\infty < f_k. \tag{7}$$

Comparing (7) with (6), taking into account that $\tau_\infty/\dot{\gamma}_\infty = \eta_e(\dot{\gamma}_\infty)$, we have:

$$f_k = \dot{\gamma}_k. \tag{8}$$

Thus, the specified values f_k are limiting shear rates in the viscous component of the k-elements. From (8) and (6) it follows that f_k is a decreasing sequence in k such that $f_{N+1} = 0$, $f|_{k \leqslant a} = 0$. The energy expended in the destruction of the structure at time t is determined by the formula

$$\mathcal{E} = \frac{1}{2} \sum_{k(t)}^{N} G_n \theta_n^2 f_n^2. \tag{9}$$

Thus, from the equilibrium flow curve and the relaxation characteristic of the material with undisturbed structure, a closed system of relations has been constructed that describes the behavior of elastic-viscous thixotropic media. The case of an infinite number of k-elements differs in no way from the case considered, except for the natural requirement of convergence of the series

$$\sum_{n=1}^{\infty} G_n, \qquad \sum_{n=1}^{\infty} G_n \theta_n,$$

associated with the existence of G and η .

To illustrate the theory presented, let us assume that the relaxation function of a material with undisturbed structure has the form ([5], [7]):

$$\psi(t) = A \sum_{n=1}^{N} e^{-t/\theta_n}, \qquad \theta_n = a \sin^{-2}[\pi(N - n + 1)/2(N + 1)], \tag{10}$$

and $\eta_e(\dot{\gamma}_\infty)$ is determined by the Bueche formula ([8])

$$\eta_e = \eta \ \frac{1}{1 + (\theta_0 \dot{\gamma}_\infty)^{3/4}}, \tag{11}$$

where A, a, θ_0 are material constants. According to (10), we have:

$$G \ = AN, \qquad \eta \ = A \sum_{n=1}^{N} \theta_n. \tag{12}$$

Approximating the quantity η_e by a step function

$$\eta_{ek} = \eta \frac{1}{1 + (\theta_0 \dot{\gamma}_{k+1})^{3/4}} = A \sum_{n=1}^{k} \theta_n \qquad (\dot{\gamma}_{k+1} \leqslant \dot{\gamma}_\infty < \dot{\gamma}_k), \tag{13}$$

we find from (10), (11), (13) the values $f_k = \dot{\gamma}_k$:

$$f_k = \frac{1}{\theta_0} \left\{ \frac{\sum_{n=k}^{N} \sin^{-2}[\pi(N-n+1)/2(N+1)]}{\sum_{n=1}^{k-1} \sin^{-2}[\pi(N-n+1)/2(N+1)]} \right\}^{4/3} \qquad (k = 1, \ldots, N); \qquad f_{N+1} = 0. \tag{14}$$

Consider the particular case of deformation $\dot{\gamma} = \text{const}$. Let

$$\dot{\gamma}(t) = \dot{\gamma}_0 \quad (t > 0); \qquad \dot{\gamma}(t) = 0 \quad (t \leqslant 0). \tag{15}$$

Substituting (15) into (3) and (4a), we obtain:

$$\tau(t) = \dot{\gamma}_0 \sum_{n=1}^{k} G_n (1 - e^{-t/\theta_n}), \qquad \dot{\gamma}_0 (1 - e^{-t/\theta_k}) < f_k, \qquad \dot{\gamma}_0 (1 - e^{-t/\theta_{k+1}}) \geqslant f_{k+1}. \tag{16}$$

From formulas (16) it follows that $k(t)$ is a nonincreasing step function of t; moreover, if $\dot{\gamma}_0 < f_N$, then $k = N$, i.e., destruction of the structure does not occur. The function $\tau(t)$ in (16) is piecewise smooth, with discontinuities at the points t_k,

for which equality is realized in the non-strict inequality (16). For the particular case of deformation under consideration, when f_k are defined by formulas (14) and $G_n = A$, the dependence $\tau(t)$ for various constant values $\dot{\gamma}_{0i}$, with $\dot{\gamma}_{01} < \dot{\gamma}_{02} < \dot{\gamma}_{03}$, has the form represented by the dashed curves in Fig. 1. It can be shown that, independently of the characteristic functions of the material $\eta_s(\dot{\gamma})$ and $\psi(t)$, in the case under consideration of the discrete model the dependence $\tau(t)$ at $\dot{\gamma} = \text{const}$ will have the form shown in Fig. 1 if the sequence f_k satisfies the condition of nonconvexity: $f_{k+1} - f_k \ll f_k - f_{k-1}$ (it is easy to carry out a proof of this for the f_k defined by formula (14)). The theory set forth above is easily generalized to the case of continuous relaxation spectra. In this case the dependences $\tau(t)$ are shown in Fig. 1 by solid lines.

According to the theory developed, at sufficiently low shear rates $\dot{\gamma}$, when the rate of the external action is small in comparison with the rate of the relaxation processes, destruction of the structure in polymer systems is practically absent. This corresponds to the monotonic curve in Fig. 1. When a certain region

Fig. 1. Dependence of $\tau(t)$ at $\dot{\gamma} = \dot{\gamma}_0 = \text{const}$ ($\dot{\gamma}_{01} < f_N$, $\dot{\gamma}_{03} > \dot{\gamma}_{02} > f_N$)

Figure 1: Fig. 1. Dependence of $\tau(t)$ at $\dot{\gamma} = \dot{\gamma}_0 = \text{const}$ ($\dot{\gamma}_{01} < f_N$, $\dot{\gamma}_{03} > \dot{\gamma}_{02} > f_N$)

of critical values of $\dot{\gamma}$, which in general may be sufficiently narrow, is reached, destruction of the structure begins; this, first, corresponds to the appearance of maxima on the $\tau(t)$ curves and, second, to a viscosity anomaly in steady flow regimes. On the $\tau(t)$ curves with maxima, destruction of the structure in polymer systems may begin before the maxima are reached. It becomes especially intense near the extremum. This justifies the notion of $\max \tau$ as the limit of shear strength ([2]). Upon passing through the maximum and moving along the descending branches of the $\tau(t)$ curves, the rates of structure recovery increase, so that in steady flow there exists a dynamic equilibrium between the processes of destruction and recovery of supramolecular structures. With increasing $\dot{\gamma}_{0i}$, the maxima on the $\tau(t)$ curves become more intense and shift to the left along the t-axis. According to the theory under consideration, the conditions can be determined for attaining the highest value $\max \tau$, at which the second Newtonian branch is realized on the flow curves, when $\eta = \eta_{\text{nm}} = \text{const} > 0$. On the basis of the theory, the dependence of the shear-strength limit on $\dot{\gamma}_{0i}$ can be obtained.

Fig. 1. Dependence of $\tau(t)$ at $\dot{\gamma} = \dot{\gamma}_0 = \text{const}$
($\dot{\gamma}_{01} < f_N$, $\dot{\gamma}_{03} > \dot{\gamma}_{02} > f_N$)

The qualitative illustration of the theory presented in Fig. 1 agrees well with experiment ([1,2]).

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Note: Figure translations are in progress. See original paper for figures.