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THERMOMECHANIC BEHAVIOR OF A POLYMER UPON ITS FORMATION IN A CRYSTALLIZATION PROCESS: THEORETICAL PRINCIPLES, HYPOTHESES, AND MATHEMATICAL MODEL

V. N. Aptukov and S. A. Bolgov

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A model of thermomechanic behavior of a polymer upon its formation in a crystallization process is proposed. Based on methods of nonequilibrium thermodynamics governing relationships are obtained which make it possible to establish the dependence of the final degree of crystallicity of the material on the "history" of the crystallization process and to explain the mechanism of formation of the remanent stresses in a polymer article.

1. The distinctive features of the physical properties of polymer materials are determined by the presence of complex polymer structures. In a number of cases formation of the material proceeds upon the transition of the polymer system from the liquid to the solid state. In this case the properties of the polymer are determined not only by the chemical structure of its molecules but by the formation conditions as well. The most characteristic in this regard is nonisothermic crystallization of a polymer from the melt. Formation of the dispersed system proceeeds as a result of the phase transition of the amorphous polymer from the viscous-flow state to the crystalline state.

The classical theory of phase transformations deals with the equilibrium between the initial and the newly created phases at the temperature which corresponds, in fact, to the completion of the process. However, at finite cooling rates formation of the new phase is possible solely upon a certain deviation from the equilibrium conditions. Such a thermodynamically nonequilibrated state can persist for a sufficiently long time since the characteristic formation time of the newly created phase upon polymer crystallization is as long as 10^1-10^5 sec.

Presently, the greatest amount of information on the thermodynamics, kinetics, and strucure of crystallized polymers has been gathered, which makes it possible to reveal the distinctive features of the phase transition of the 1st kind in polymers on the basis of a detailed investigation of the structure of macromolecules. These approaches explain many of the qualitative regularities in polymer crystallization; however, they prove to be rather cumbersome when applied to the solution of particular technological problems. Therefore, in actual practice one is forced to use rather simplified models of the process, taking the processes of formation of physicochemical parameters of the material and the strained-deformed polymer state to be, as a whole, independent of kinetic regularities and heat transfer upon crystallization of melts.

This means, in fact, that the traditional methods describe the crystallization process in the vicinity of the equilibrium state, and various artificial methods should be applied to account for the actual nonequilibrium conditions. In a series of cases such simplified schemes are justified since they make it possible to model the technological process within some narrow range of variation of parameters. Nonetheless, a more adequate description of what actually takes place requires taking into account the "history" of the crystallization process and the relationship between the structural transformations and macroscopic properties of the material obtained. The present work is devoted to the study of this problem.

2. Let us consider the process of nonisothermic bulk crystallization of a polymer material. Using the continuality hypothesis and the principle of the equivalent homogeneity [1, 2], we substitute the polymer system

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Institute of Mechanics of Continuous Media of the Ural Branch of the Russian Academy of Sciences, Perm', Russia. Institute of Technical Chemistry of the Ural Branch of the Russian Academy of Sciences, Perm', Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 68, No. 3, pp. 479-485, May-June, 1995. Original article submitted December 29, 1992.

being crystallized by an effective continuous medium. This will make it possible to apply conventional laws of continual mechanics as well as methods of thermodynamics of continuous media with intrinsic parameters of state [3].

Let us select some small elementary volume ΔV of the effective continuous medium. The state of the matter within this volume is determined by kinematic (u, v, and $\dot{\mathrm{v}}$) and internal (θ, ρ, $\hat{\varepsilon}$, $\hat{\sigma}$, and η) parameters, by the parameter of the energy state U^* or z, and, finally, by the internal parameters of state χ_i that reflect evolution of the structure of the system upon its transition from liquid to the solid state.

Variation of the parameter χ_i is given by the corresponding evolution equation:

$$\dot{\chi}_i = \Psi_i(\hat{\sigma}, \theta, \chi_i). \tag{1}$$

The dot denotes the time derivative. The functions Ψ_i are formed based on theoretical or experimental studies. These functions relate microstructural phenomena and macroscale effects.

The above variables are dependent quantities as a result of the fundamental principle of the mechanics of continuous medium, namely, the principle of macroscopic determinability [4] (or the principle of determinism [1]), which states that any thermodynamic macroscopic quantity in the material particle under consideration is determined at the instant t by the process: $\hat{\varepsilon}(\tau)$; $\theta(\tau)$, $\chi_i(\tau)$, $\tau \in [t_0, t]$, and by the corresponding initial values at $t = t_0$.

Let us make use of the basic laws of thermodynamics in the form of the entropy balance [4]:

$$\rho\,\theta\,\dot{\eta} = -\operatorname{div}\mathrm{q} + W^* \tag{2}$$

and the dissipation inequality

$$W^* = \hat{\sigma}\cdot\cdot\dot{\hat{\varepsilon}} - \rho\,(\dot{U}^* - \theta\,\dot{\eta}) \geq 0. \tag{3}$$

Here $\cdot\cdot$ denotes the double scalar product of tensors. The heat flux vector q is connected with the temperature gradient by the Fourier law:

$$\mathrm{q} = -\hat{\kappa}\cdot\nabla\theta. \tag{4}$$

We use the specific free enthalpy (the Gibbs thermodynamic function) as a measure of the energy state:

$$z(\hat{\sigma}, \theta, \chi_i) = U^* - \theta\,\eta - \frac{1}{\rho}\hat{\sigma}\cdot\cdot\hat{\varepsilon}. \tag{5}$$

The inequality (3) can be transformed as follows in terms of (5):

$$W^* = -\dot{\hat{\sigma}}\cdot\cdot\hat{\varepsilon} - \rho\,(\dot{z} + \eta\,\dot{\theta}) \geq 0.$$

Substituting the complete time derivative of z, namely, $\dot{z} = \partial z/\partial\hat{\sigma}\cdot\cdot\dot{\hat{\sigma}} + (\partial z/\partial\eta)\dot{\eta} + (\partial z/\partial\chi_i)\dot{\chi}_i$, into this inequality we obtain:

$$W^* = -\dot{\hat{\sigma}}\cdot\cdot\left(\hat{\varepsilon} + \rho\frac{\partial z}{\partial\hat{\sigma}}\right) - \rho\,\dot{\theta}\left(\eta + \frac{\partial z}{\partial\theta}\right) - \rho\frac{\partial z}{\partial\chi_i}\dot{\chi}_i \geq 0.$$

Here and in what follows summation is performed over the repeated indices. The relationships that hold for both reversible and irreversible processes stem from this expression:

$$\hat{\varepsilon} = -\rho\frac{\partial z}{\partial\hat{\sigma}}, \quad \eta = -\frac{\partial z}{\partial\theta}. \tag{6}$$

We should recall that a reversible process, by definition, does not lead to energy dissipation: $W^* \equiv 0$. Irreversible energy dissipation is connected in the case under consideration with the change in the degree of crystallicity of the substance:

$$W^* = -\rho \frac{\partial z}{\partial \chi_i} \dot{\chi}_i \geq 0 . \tag{7}$$

In addition, variation of state within the particle obeys the conservation laws for mass and momentum:

$$\frac{I}{\rho} \dot{\rho} + \operatorname{div} \mathrm{v} = 0 , \quad \operatorname{div} \hat{\sigma} + \rho \mathrm{F} = \rho \dot{\mathrm{v}} . \tag{8}$$

In the case of the crystallization process inertial forces $\rho \dot{\mathrm{v}}$ can be neglected.

Defining the total time derivative of the first of the expressions of (6) we obtain an evolution equation for the tensor of the total deformation:

$$\dot{\hat{\varepsilon}} = \hat{\hat{H}} \cdot\cdot \dot{\hat{\sigma}} + \hat{\alpha} \dot{\theta} + \hat{X}_i \dot{\chi}_i , \tag{9}$$

$$\hat{\hat{H}} = -\rho \frac{\partial^2 z}{\partial \hat{\sigma} \otimes \partial \hat{\sigma}} , \quad \hat{\alpha} = -\rho \frac{\partial^2 z}{\partial \hat{\sigma} \partial \theta} , \quad \hat{X}_i = -\rho \frac{\partial^2 z}{\partial \hat{\sigma} \partial \chi_i} ,$$

where $\otimes$ denotes the tensor product.

Using the first of the expressions of (6), the energy conservation law (2), and the Fourier law (4), we can write an evolution equation for the temperature (the generalized heat conduction equation)

$$\rho c \dot{\theta} = \nabla (\hat{\kappa} \cdot \nabla \theta) - \theta \hat{\alpha} \cdot\cdot \dot{\hat{\sigma}} - \rho \frac{\partial}{\partial \chi_i} \left(z - \theta \frac{\partial z}{\partial \theta} \right) \dot{\chi}_i , \quad c = -\theta \frac{\partial^2 z}{\partial \theta^2} . \tag{10}$$

It is evident that in addition to heat conduction, additional heat sources do exist, such as the effect of stress and energy dissipation upon variation of structure (the generalized heat conduction equation). In order to use the physical Eq. (9) and the heat conduction Eq. (10) one should specify the functions Ψ_i and z related by the thermodynamic inequality (7).

The equations obtained are highly general and make it possible to describe diversified processes of deformation and structural variations of polymer systems. Nevertheless, they should be specified in more detail based on additional hypotheses.

First of all, in the present work we restrict ourselves to a single intrinsic parameter of state χ that will have the meaning of the volume fraction of the crystalline phase of the substance within the elementary volume ΔV of the polymer system. It is clear that this integral parameter bears minimum information on the polymer structure.

Various approaches exist for determination of the form of the dependence $z = z(\hat{\sigma}, \theta, \chi)$ (see, e.g., [5]). Following Coleman and Gurtin [3], we consider the locus $\chi^* = \chi(\hat{\sigma}, \theta)$ in the state space $(\hat{\sigma}, \theta, \chi)$ which is obtained in an infinitely slow (equilibrium) crystallization process. This locus is a surface of the equilibrium behavior in the state space on which the condition $\dot{\chi} = \Psi(\hat{\sigma}, \eta, \chi^*(\hat{\sigma}, \eta)) \equiv 0$ is satisfied. If now we are in the vicinity of this equilibrium curve at fixed $\hat{\sigma}$ and θ then it follows from the dissipation inequality that $-\rho \dot{z} \geq 0$ or $z(\hat{\sigma}, \eta, \chi^*) \leq z(\hat{\sigma}, \eta, \chi)$ for all χ in the vicinity of χ^*. This means that the maximum value of the free enthalpy z is attained on the equilibrium curve and, consequently:

$$\frac{\partial z}{\partial \chi} (\hat{\sigma} , \theta , \chi) \Big|_{\chi=\chi^*} = 0 , \quad \frac{\partial^2 z}{\partial \chi^2} (\hat{\sigma} , \theta , \chi) \Big|_{\chi=\chi^*} > 0 . \tag{11}$$

For the states in the vicinity of the equilibrium curve the function z can be represented in the form of an expansion:

$$-\rho z (\hat{\sigma} , \theta , \chi) = z_1 (\hat{\sigma} , \theta , \chi^*) + f (\hat{\sigma} , \theta , \chi^*) - \chi^* (\theta))^2 . \tag{12}$$

The function z characterizes the energy state of the system in the equilibrium state and therefore can be specified in the conventional form, for example [6]:

$$z_1 = \frac{1}{2}\hat{\sigma}\cdot\cdot\hat{\hat{H}}^*\cdot\cdot\hat{\sigma} + \theta\hat{\alpha}^*\cdot\cdot\hat{\sigma} + \rho c^*\theta(\ln\theta - 1)\,. \tag{13}$$

The physical meaning of the second term in the right-hand part of expansion (12) consists in the energy dissipation conditioned by the nonequilibrium crystallization process.

The following assumptions are connected immediately with the distinctive features of the crystallization process at low pressures. First, let us come in the unknown function f of the stress tensor $\hat{\sigma}$ to the mean pressure p, i.e., we neglect the effect of the shear component of the stress tensor on deformations resulting from the crystallization process, compared to the effect of pressure. Second, we will consider the surface of the equilibrium behavior to be pressure-independent at relatively low pressures: $\chi^* = \chi(\theta)$. Third, we consider in what follows the special isotropic version of the model:

$$H^*_{ijkl} = \frac{1}{2G^*}\delta_{ik}\delta_{lk} - \frac{1}{3}\left(\frac{1}{2G^*} - \frac{1}{3K^*}\right)\delta_{ij}\delta_{kl}\,, \quad \alpha^*_{ij} = \alpha^*\delta_{ij}\,, \quad \kappa^*_{ij} = \kappa^*\delta_{ij}\,. \tag{14}$$

Based on the assumptions made and relationships (14), the function of the specific free enthalpy takes the form:

$$-\rho z(\hat{\sigma}, \theta, \chi) = \frac{1}{2}\left(\frac{p^2}{K^*} + \frac{\hat{S}\cdot\cdot\hat{S}}{2G^*}\right) + 3\theta\alpha^* p + \rho c^*\theta(\ln\theta - 1) + f(p, \theta)(\chi - \chi^*)^2\,. \tag{15}$$

Using Eq. (15) and keeping terms of up to the 2nd order, we obtain governing relationships of the type of Eq. (9), which we write for the spherical and deviator parts ($\hat{\varepsilon} = \hat{e} + \varepsilon I$, $\hat{\sigma} = \hat{S} + pI$):

$$\dot{\varepsilon} = \frac{1}{3K}\dot{p} + \alpha\dot{\theta} + k\dot{\chi}\,, \quad \dot{\hat{e}} = \frac{1}{2G}\dot{\hat{S}}\,, \quad k = \frac{2}{3}\frac{\partial f}{\partial p}(\chi - \chi^*)\,. \tag{16}$$

The expressions for the nonequilibrium parameters K, G, and α possess the following form which is determined by the equilibrium values and the current degree of crystallicity:

$$\frac{1}{K} \approx \frac{1}{K^*} + \frac{\partial^2 f}{\partial p^2}(\chi - \chi^*)^2\,, \quad \frac{1}{G} \approx \frac{1}{G^*}\,,$$

$$\alpha \approx \alpha^* + \frac{1}{3}\frac{\partial^2 f}{\partial p\partial\theta}(\chi - \chi^*) - \frac{2}{3}\frac{\partial f}{\partial p}(\chi - \chi^*)\frac{\partial\chi^*}{\partial\theta}\,. \tag{17}$$

The generalized heat conduction equation also retains its form, but with the last term transformed:

$$\rho c\dot{\theta} = \nabla(\kappa\cdot\nabla\theta) - 3\alpha\theta\dot{p} + Q\dot{\chi}\,, \quad Q = 2\left[\left(f - \theta\frac{\partial f}{\partial\theta}\right)(\chi - \chi^*) + f\theta\frac{\partial\chi^*}{\partial\theta}\right]. \tag{18}$$

The theory provides the expression for the heat source conditioned by crystallization. It is sufficient that the quantity Q be a variable, the first term in Q being the nonequilibrium contribution, the second term being the heat release in the equilibrium process.

3. The next step towards specifying the governing equations is connected with the unknown function f. A structural approach based on physical concepts of the polymer structure and the crystallization process can be used to determine this function. In the present work we restrict ourselves to the phenomenological approach.

Let us formulate the basic principles of the theory.

A. For infinitely slow (equilibrium) crystallization processes the rate of heat release $\dot{q}$ is proportional to the growth rate of the crystalline phase $\dot{\chi}$ with the proportionality coefficient Q_{eq}:

$$\dot{q} = Q_{\text{eq}}\dot{\chi}\,. \tag{19}$$

The given concept is widely used in models, e.g., in [7], where it is extended to arbitrary processes.

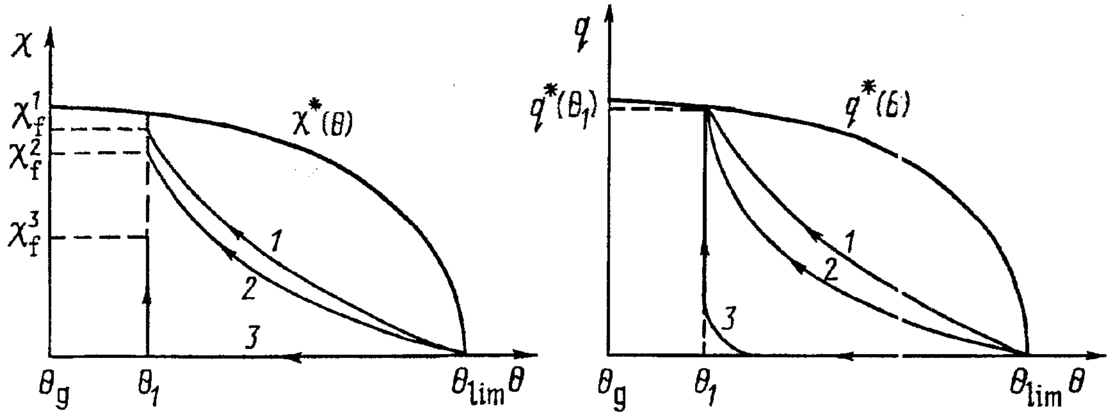

Fig. 1. Phase trajectories of nonequilibrium crystallization process in the space of variables χ, θ and q, θ.

Comparison of Eqs. (18) and Eq. (19) for equilibrium processes yields an expression for determination of the unknown function:

$$f = \frac{1}{2} Q_{eq} \left(Q \frac{\partial \chi^*}{\partial \theta} \right)^{-1} . \tag{20}$$

B. Upon cooling at an arbitrary rate to a certain temperature $\theta_1 > \theta_g$ the total heat release is a constant at $t \to \infty$ due to the phase transition; this constant depends only on temperature θ_1: $q_1 = q^*(\theta_1)$, i.e., in the space of variables q, θ the existence is postulated of a unique equilibrium curve $q = q^*(\theta)$ on which the process is completed irrespectively of its trajectory $q(\theta)$.

The given concept is also assumed inexplicitly in the known models, e.g., in [7], where the heat release is identified, in fact, with the change in the degree of crystallicity.

What consequences stem from these concepts?

First, using Eq. (20) we determine the relationship between the rate of the heat release and the rate of variation in the degree of crystallicity
$\dot{q} = Q\dot{\chi} \equiv Q_{eq} A(\chi, \theta) \dot{\chi}$,

$$A(\chi, \theta) = 1 + \left(Q \frac{\partial \chi^*}{\partial \theta} \right)^{-1} \left[2 + \theta \left(\frac{\partial \chi^*}{\partial \theta} \right)^{-1} \frac{\partial^2 \chi^*}{\partial \theta^2} \right] (\chi - \chi^*) . \tag{21}$$

According to the first postulate, the unique curve $q^*(\theta) = Q_{eq}\chi^*(\theta)$ corresponds to the curve $\chi^*(\theta)$ in the space q, θ. Deviations from the nonequilibrium state are included in the second term in the right-hand part of the expression for $A(\chi, \theta)$.

Second, integrating the equation $\dot{q} = Q\dot{\chi}$ over time from t_0 to $t \to \infty$ we obtain an equation for determination of the final degree of crystallicity χ_f:

$$q^*(\theta_1) = \int_{t_0}^{\infty} Q\dot{\chi} dt = \int_{0}^{\chi_f} Q d\chi . \tag{22}$$

Equation (22) is one of the basic results of the theory proposed: the final degree of crystallicity χ_f upon approaching the designated temperature $\theta_1 > \theta_g$ depends on the trajectory of the crystallization process in the space χ, θ. Indeed, since the left-hand part of the equation is a constant, whereas the expression Q under the integral depends on the difference $\chi - \chi^*$ (on the degree of deviation of the process from the equilibrium curve in the space χ, θ), the value of χ_f is process-dependent.

Analysis of the expression for $A(\chi, \theta)$ shows that $A \geq 1$ in the crystallization process, whereas $A = 1$ corresponds to the equilibrium process. Therefore the following statement holds: among all trajectories of crystallization processes in the space χ, θ the maximum degree of crystallicity is achieved in the equilibrium process upon approaching the designated temperature $\theta_1 > \theta_g$: $\max\{\chi_f\} = \chi^*$. The physical meaning of this result lies in the fact that the "closest packing of macromolecules in the crystalline phase" is achieved, all other factors being the same, in the infinitely slow (equilibrium) process (see Fig. 1). Proceeding of the process along the differing trajectories 1 and 2 in the space χ, θ leads to different final degrees of crystallicity $\chi_f^1 > \chi_f^2$. As is clear from Fig. 1 (curve 3), the most nonequilibrium process is the crystallization process under isothermic conditions when temperature θ_1 is achieved by such fast cooling that the crystalline phase has no time to be created at intermediate temperatures $\theta_1 < \theta \leq \theta_{\lim}$. The minimum possible value $\min\{\chi_f\} = \chi^m$ corresponds to this regime.

In addition, trajectories can exist which differ in the space χ, θ but lead to one and the same value of χ_f. Most likely, there are infinitely many trajectories of the type for any specified value of $\chi^m < \chi_f < \chi^*$. All these trajectories are equivalent in the sense of the integral estimate of the degree of the deviation from the equilibrium state.

4. Particular experimental results and calculations based on the theory proposed will be presented in forthcoming communications. Here we dwell on one more fundamental question.

The theory predicts the effect of the history of the process on the final degree of crystallicity. This result explains easily the mechanism of formation of the remanent stresses in the process of crystallization of massive bodies. Cooling of internal points of the body proceeds as a result of heat conduction and heat transfer across the outer walls. In this case the cooling rate and, consequently, trajectories in the space χ, θ differ for internal and near-surface particles of the polymer system: the crystallization process for internal points is closer to the equilibrium one than that for the near-surface points. Therefore, the final degree of crystallicity and, consequently, shrinking of the internal layers are greater than that of the external ones. This leads to remanent stretching stresses and possible disruption of continuality (disintegration).

NOTATION

$\mathbf{u}$, translation vector; $\mathbf{v}$, velocity vector; $\dot{\mathbf{v}}$, acceleration vector; θ, absolute temperature; ρ, density; c, specific heat capacity; $\hat{\varepsilon}$, deformation tensor; $\hat{\sigma}$, strain tensor; η, specific enthropy; U^*, internal energy; z, specific free enthalpy; χ_i, internal parameters of state; t, time; $\mathbf{q}$, heat flux vector; $\hat{\kappa}$, matrix of heat conduction coefficients; W^*, energy dissipation; $\mathbf{F}$, vector of mass forces; $\hat{\hat{H}}$, the 4th rank tensor of elastic pliabilities; $\hat{\alpha}$, matrix of heat expansion coefficients; $\hat{X}_i$, tensor of contribution of structural variations to deformation; $\hat{\hat{H}}^*$, $\hat{\alpha}^*$, c^*, G^*, K^*, functions of equilibrium value χ^*; p, mean pressure; $\hat{e}$, deviator of the tensor of deformations; ε, spherical part of the deformation tensor; $\hat{S}$, deviator of the tensor of stresses; K, volume modulus; $\hat{I}$, unity tensor; Q, enthalpy of the crystallization process; Q_{eq}, enthalpy of the equilibrium crystallization process; θ_g, glass transition temperature; $\chi^*(\theta)$, the curve obtained in the equilibrium crystallization process; χ_f, final degree of crystallicity.

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