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CONSTITUTIVE RELATIONS FOR A VISCOELASTIC BODY UNDER CRYSTALLIZATION CONDITIONS

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The problem of describing the thermomechanical behavior of viscoelastic polymer materials under conditions of their post-production cooling accompanied by crystallization is considered. A variant for constructing phenomenological constitutive relations, which continuously reflect the relation between the stress and strain tensors in a wide range of temperature variation, is suggested. The relations are based on representation of the medium in the form of a composition of a melted material and a completely crystallized material with allowance for the history of permanent incipience and deformation of the new phase in the interval of phase-transformation temperatures. To determine the material functions and constants, experiments are planned on specimens at temperatures corresponding to particular phase states. Results of experiments and numerical analysis of the fields of displacements generated by solidification of a circular polyethylene plate are given.

Key words: *polymers, viscoelasticity, phase transition.*

The development of mathematical models of the mechanical behavior of viscoelastic bodies under phase-transition conditions is of significant interest [1–3] for describing the evolution of the stress–strain state of articles made of polymeric materials with a tendency to crystallization during their manufacturing. It is known that some polymeric materials (polyethylene, Caprolon, etc.), being in an amorphous state when melted, can form crystalline structures during their cooling, the relative fraction of these structures in the material volume (relative degree of crystallization) depending on the nature of the material and on the cooling mode [4]. The crystallization process in polymers normally proceeds without an explicit crystallization front and, by virtue of low thermal conductivity, is accompanied by substantial temperature and, as a consequence, strain inhomogeneity. As a result, technological and residual stresses are formed in the material, which can lead to origination of microdefects, deterioration of exploitation properties of articles, and even to failure of the latter already at the stage of manufacturing. Models of the behavior of such media should include constitutive relations that offer a unified description for the relation of stress and strain tensors in a wide range of temperatures, including the range of phase transitions.

1. Let us consider derivation of the constitutive relation for a crystallizing viscoelastic medium in the case of a uniaxial stress state with low strains within the framework of the following hypotheses and postulates:

— the crystallizing polymer system at each time and at each point of the system is considered as a mixture of the polymer melt and a completely crystallized product, whose relative fraction in the total volume is characterized by the degree of crystallization $\alpha(t)$;

— the material remains macroisotropic in the course of its transformation;

— the behavior of the polymer melt is described by a relation of linear viscoelasticity; with allowance for the small characteristic relaxation time of the polymer melt, as compared to the relaxation time of the crystalline phase and the time of the crystallization process, the relaxation function for the amorphous phase is assumed to be a constant equal to the long-term modulus of the elastic amorphous phase;

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— the elementary particle of the incipient crystalline phase is characterized by a certain initial stress equal to the stress in the polymer melt at the moment of crystallization;

— the stresses in the crystallizing polymer are determined in accordance with the principle of superposition of stresses in the linear viscoelasticity theory.

Let a fraction of the polymer characterized by the increment of the degree of crystallization $\Delta\alpha_1 = \Delta\alpha(t_1)$ be crystallized at the time t_1 and the strain increment be $\Delta\varepsilon(t_1)$. Respective strain increments $\Delta\varepsilon(t_2), \Delta\varepsilon(t_3), \ldots, \Delta\varepsilon(t_k)$ occur at subsequent times $t_2, t_3, \ldots, t_k$. In accordance with Boltzmann's superposition principle [5], the stresses arising in the considered part of the viscoelastic polymer at the time $t_k > t_1$ are a sum of stresses arising in this area at the times $t_1, t_2, \ldots, t_k$ owing to the corresponding strain increments:

$$\sigma_1(t_k) = \Delta\alpha_1[R(t_k - t_1, t_1 - t_1)\,\Delta\varepsilon(t_1) + R(t_k - t_1, t_2 - t_1)\,\Delta\varepsilon(t_2) + \ldots + R(t_k - t_1, t_k - t_1)\,\Delta\varepsilon(t_k)] + \sigma_{01}.$$

Here $R(t, \tau)$ is a function of material relaxation characterizing its mechanical properties, $\sigma_{01} = \Delta\alpha_1 E_{\mathrm{a},\infty}\varepsilon(t_0)$ is the initial stress for the crystalline phase of the polymer crystallized at the time t_1, and $E_{\mathrm{a},\infty}$ is the long-term modulus of elasticity of the polymer in the amorphous state.

The following expression for the stress at the time t_k is valid for the polymer fraction crystallized at the time t_2:

$$\sigma_2(t_k) = \Delta\alpha_2[R(t_k - t_2, t_2 - t_2)\,\Delta\varepsilon(t_2) + R(t_k - t_2, t_3 - t_2)\,\Delta\varepsilon(t_3) + \ldots + R(t_k - t_2, t_k - t_2)\,\Delta\varepsilon(t_k)] + \sigma_{02}.$$

Here σ_{02} is the initial stress for the crystalline phase of the polymer crystallized at the time t_2, $\sigma_{02} = \Delta\alpha_2 E_{\mathrm{a},\infty}(\varepsilon(t_0) + \Delta\varepsilon(t_1))$.

We consider the kth discrete step in terms of the transformation $\Delta\alpha_k$, corresponding to the time t_k. By virtue of similar considerations, we write

$$\sigma_k(t_k) = \Delta\alpha_k[R(t_k - t_k, t_k - t_k)\,\Delta\varepsilon(t_k)] + \sigma_{0k},$$

where $\sigma_{0k} = \Delta\alpha_k E_{\mathrm{a},\infty}[\varepsilon(t_0) + \Delta\varepsilon(t_1) + \ldots + \Delta\varepsilon(t_{k-1})]$.

The stresses in the crystalline phase at the time $t > t_k$ can be obtained as a sum of stresses arising there at the times $t_1, t_2, \ldots, t_k$. Passing to the limit in terms of strains and degree of crystallization in the resultant expression, we obtain the expression for the stress of the crystalline phase:

$$\sigma_{\mathrm{cr}}(t) = \int\limits_0^{\alpha(t)} \Big(\int\limits_\omega^t R(t - \omega, \tau - \omega)\, d\varepsilon(\tau) \Big)\, d\alpha(\omega) + \sigma_{01} + \sigma_{02} + \ldots + \sigma_{0k}.$$

Assuming that the strains of the crystalline phase and melt are identical, we obtain the stresses in the system as the sum of stresses arising in the crystalline phase and in the melt. Taking into account that $\sigma_{01} + \sigma_{02} + \ldots + \sigma_{0k} = E_{\mathrm{a},\infty} \int\limits_0^{\alpha(t)} \varepsilon(\tau)\, d\alpha(\tau)$, we can write the following relation for the uniaxial stress state:

$$\sigma(t) = E_{\mathrm{a},\infty}(1 - \alpha(t))\varepsilon(t) + \int\limits_0^{\alpha(t)} \Big(\int\limits_\omega^t R(t - \omega, \tau - \omega)\, d\varepsilon(\tau) \Big) d\alpha(\omega) + E_{\mathrm{a},\infty} \int\limits_0^{\alpha(t)} \varepsilon(\tau)\, d\alpha(\tau).$$

With allowance for temperature strains and structural shrinkage, which accompanies the phase transition, the stress in the system has the form

$$\sigma(t) = E_{\mathrm{a},\infty}[\varepsilon(t) - \varepsilon_{T,\mathrm{a}}(t)](1 - \alpha(t))$$

$$+ \int\limits_0^{\alpha(t)} \Big[\int\limits_\omega^t R(t - \omega, \tau - \omega)\, d(\varepsilon(\tau) - \varepsilon_{T,\mathrm{cr}}(\tau) + kh(\tau - \omega)) \Big]\, d\alpha(\omega) + E_{\mathrm{a},\infty} \int\limits_0^{\alpha(t)} (\varepsilon(\tau) - \varepsilon_{T,\mathrm{a}}(\tau))\, d\alpha(\tau), \tag{1}$$

where $\varepsilon_{T,\mathrm{a}}$ and $\varepsilon_{T,\mathrm{cr}}$ are the temperature strains for the amorphous and crystalline phases, respectively, k is the coefficient of structural shrinkage, and h is the Heaviside function, which reflects the fact that the strain of structural shrinkage of a polymer particle crystallized at the time ω starts to contribute to the total strain only after the moment of particle origination.

If we assume that there is no relaxation in the crystalline phase and ignore the initial stresses in the crystalline phase of the crystallizing system, Eq. (1) is reduced to a particular case, which is the constitutive relation suggested earlier in [6]:

$$\sigma(t) = E_{\mathrm{a},\infty}(1-\alpha(t))\bar{\varepsilon}_{\mathrm{a}}(t) + E_{\mathrm{cr}} \int\limits_0^{\alpha(t)} [(\bar{\varepsilon}_{\mathrm{cr}}(t) - \bar{\varepsilon}_{\mathrm{cr}}(\omega)) + k]\, d\alpha(\omega),$$

$$\bar{\varepsilon}_{\mathrm{a}}(t) = \varepsilon(t) - \varepsilon_{T,\mathrm{a}}(t), \qquad \bar{\varepsilon}_{\mathrm{cr}}(t) = \varepsilon(t) - \varepsilon_{T,\mathrm{cr}}(t).$$

This relation can be conventionally called the model of a crystallizing medium in the "elastic approximation." Here, E_{cr} is the elasticity modulus of the crystalline phase.

2. Let us illustrate the constitutive relation (1) by the example of solving a model problem on stress evolution of a clamped rod made of a polymeric material within the framework of the uniaxial stress state. Because of changes in temperature with time, the material consecutively passes the stages of melting, solidification, completely solidified product, and melting again. During a closed temperature cycle, the rod is first cooled with a constant rate uniformly over its entire length from a certain initial temperature, which is higher than the melting point of the material. When the temperature decreases below the melting point, the process of crystallization begins. The rod continues to be cooled to a temperature at which the crystallization process is completed, and the rod is retained at this temperature for a certain time. After that, the rod is uniformly heated with a constant rate to the initial temperature; during this process, the rod material is completely transformed from the crystalline to the amorphous phase.

For this example, the dependences of the relaxation time and transformation degree on time were chosen in the form

$$R(t) = E_{\mathrm{cr}}[1 - (1-\exp{(-t/B)})(1 - E_{\mathrm{cr},\infty}/E_{\mathrm{cr}})]; \tag{2}$$

$$\alpha(t) = (1 + \sin{(t/A - \pi/2)})/2, \qquad t \in [0, t_{\mathrm{cr}}], \tag{3}$$

where $E_{\mathrm{cr},\infty}$ is the long-term modulus of elasticity in the crystalline state, the time $t = 0$ in Eq. (3) corresponds to the beginning of the crystallization process, $A = t_{\mathrm{cr}}/\pi$, where t_{cr} is the time of the crystallization process and the parameter A allows variation of the crystallization rate (to take into account the influence of the rate of variation of the material temperature on the rate of crystallization), and $B = 5$ sec. The initial temperature of the rod is $T_0 = 450$ K, the melting point is $T_{\mathrm{m}} = 415$ K, and the temperature to which the polymer is cooled is $T^* = 340$ K. The form of dependences (2) and (3) and the parameters in Eqs. (1)–(3) correspond to low-pressure polyethylene (LPPE). Their particular values are given below.

Figure 1 shows the time evolution of stresses arising in the rod for two cases with different rates of temperature variation in the rod and different times of crystallization and melting. In addition, the stresses were calculated with the use of two types of constitutive relations: with and without allowance for viscoelastic properties of the crystalline phase. The segment AB of the curves corresponds to the stage of material melting ($\alpha = 0$ and $\Delta T < 0$), and the segment BC_i ($i = 1, 2$) reflects the process of stress formation at the stage of crystallization ($\Delta\alpha > 0$ and $\Delta T < 0$). When the crystallization process is completed, the rod temperature is fixed, and the segments C_iD_i of the curves correspond to retaining of the completely crystallized rod at a constant temperature ($T = 340$ K and $\alpha = 1$). At the segment D_iE_i, the rod is heated to the melting point ($\alpha = 1$ and $\Delta T > 0$); after that, being further heated with a constant rate, the rod melts, which is described by the segment E_iG_i ($\Delta\alpha < 0$ and $\Delta T > 0$). At the last stage, the rod in the completely melted state reaches the initial temperature again, which is shown by the segment G_iK ($T = T_0$ and $\alpha = 0$).

It is seen from Fig. 1 that the level of stresses calculated with allowance for viscoelastic properties of the crystalline phase is substantially lower already at the stage of crystalline-phase formation than the level of stresses obtained under the assumption of the elastic behavior of the polymer in the crystalline state. At a constant temperature, clearly expressed relaxation of stresses occurs in a completely crystallized material. In addition, in the case of a twofold decrease in the crystallization rate and temperature-variation rate in the rod, the difference between the maximum values of stresses calculated in both models becomes significantly greater; at lower rates, the crystalline phase of the polymer has enough time to reach a state corresponding to the long-term modulus of elasticity.

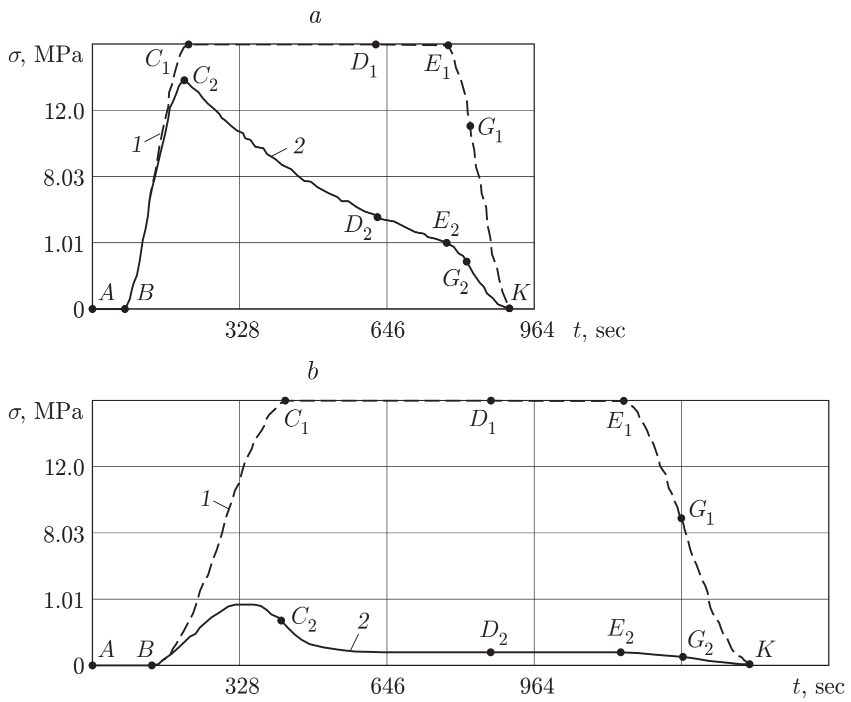

Fig. 1. Time evolution of stresses in the rod: (a) the rate of temperature variation is 0.5 K/sec and the crystallization time is 150 sec; (b) the rate of temperature variation is 0.25 K/sec and the crystallization time is 300 sec; curves 1 and 2 refer to the calculations without and with allowance for viscoelastic properties of the crystalline phase, respectively.

Thus, the example considered shows that allowance for viscoelastic properties of the crystalline phase of the polymer under certain rates of the processes in the polymer material can lead to significant quantitative and qualitative differences in the evolution of the stress state from the features obtained with the use of elastic models.

3. It should be noted that, physically, relation (1) at each time instant describes the stresses in the crystallizing system in the form of a superposition of stresses in an infinite number of elements connected in series, which obey the laws of the behavior of elasticity and viscoelasticity. Hence, as in the theory of linear elasticity and viscoelasticity [5, 7], we can write physical relations for a complicated stress state, which results from the transfer of the form of the stress–strain relation in the uniaxial case to the form of the relation of spherical and deviatoric components of the stress and strain tensors. Such a generalization of relations (1) for an isotropic polymer yields the expressions

$$\hat{\sigma}(t) - \sigma(t)\hat{E} = \int_0^{\alpha(t)} \Big[\int_\omega^t R_1(t-\omega, \tau-\omega)\, d(\hat{\varepsilon}(\tau) - \theta(\tau)\hat{E}/3)\Big]\, d\alpha(\omega); \tag{4}$$

$$\sigma(t) = B_{\mathrm{a},\infty}(\theta(t) - \theta_{T,\mathrm{a}}(t))(1 - \alpha(t))$$

$$+ \int_0^{\alpha(t)} \Big[\int_\omega^t R_2(t-\omega, \tau-\omega)\, d(\theta(\tau) - \theta_{T,\mathrm{cr}}(\tau)) + 3kR_2(t-\omega, 0)\Big]\, d\alpha(\omega) + B_{\mathrm{a},\infty} \int_0^{\alpha(t)} (\theta(\tau) - \theta_{T,\mathrm{a}}(\tau))\, d\alpha(\tau), \tag{5}$$

where $\hat{\sigma}$ and $\hat{\varepsilon}$ are the stress and strain tensors, respectively, $R_1(t,\tau)$ and $R_2(t,\tau)$ are independent functions of shear and volume relaxation of the crystalline phase, $\theta = \varepsilon_{kk}$ is the volume strain, $\hat{E}$ is a unit tensor, $\sigma = \sigma_{kk}/3$ is the mean normal stress, $B_{\mathrm{a},\infty}$ is the long-term volume modulus of the amorphous phase, and $\theta_{T,\mathrm{a}}$ and $\theta_{T,\mathrm{cr}}$ are the temperature volume strains of the polymer in the amorphous and crystalline states, respectively.

Mechanical properties of polymers are temperature-dependent. If the material in the state corresponding to the equilibrium degree of crystallization displays a thermorheologically simple behavior [5, 7] in tests for shear and volume relaxation (or creep), it is possible to use the principle of the temperature–time analogy with two

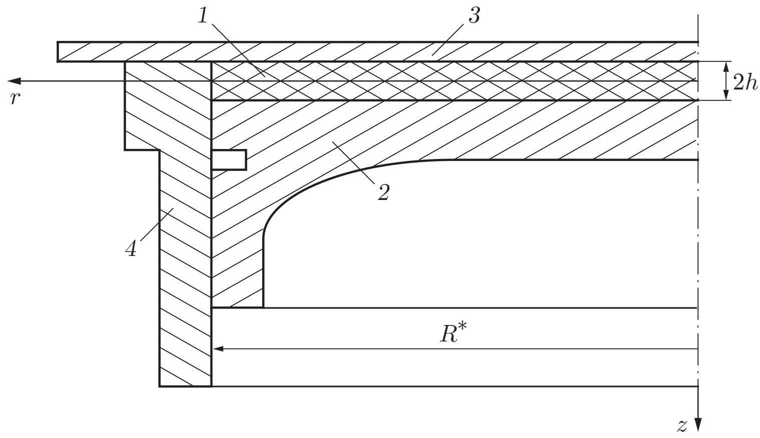

Fig. 2. Layout of the experimental setup: 1) LPPE plate; 2) bottom; 3) cover; 4) steel glass.

independent functions of the temperature–time shift (for the function of volume relaxation and for the function of shear relaxation).

An important advantage of this approach is the possibility of describing the material behavior under phase-transition conditions on the basis of physical equations containing material functions and constants determined from well-established experiments with specimens of the material in a stable state outside the phase and relaxation transitions: in a completely crystallized or a completely amorphous state. To use the physical relations obtained, one has to know the dependences $R_1(t,\tau)$, $R_2(t,\tau)$, $\alpha(t)$, and $T(t)$, constants $B_{\mathrm{a},\infty}$ and k, and coefficients of temperature expansion of the polymer in the viscous-flow and crystalline states (a_{a} and a_{cr}, respectively).

With the use of the approach described in [8], we performed a thermodynamic analysis of the physical relations derived. It was found that it is necessary to take into account the initial stresses for the crystalline phase of the polymer in physical relations; otherwise, the crystallizing system becomes dissipative even in the case of the elastic approximation of mechanical properties of the polymer.

4. To verify the reliability of the physical relations (4) and (5), we compared the results of the numerical solution and experimental data on determining the fields of displacements of a circular plate made of low-pressure polyethylene at the moment the crystallization process was completed.

Polyethylene plates 6.14 and 5.65 mm thick and 90 mm in diameter were manufactured under laboratory conditions. In the course of the experiment, the plate was located into a setup (Fig. 2), which was then heated to a temperature $T \approx 170$–180°C. The process of polymer melting was completed. After that, the setup was removed from the furnace, and the plate was cooled, which was accompanied by polyethylene crystallization. Two cooling modes were used.

1. The initial temperature was $T_0 = 170^\circ$C. When the setup was removed from the furnace, the plate 6.14 mm thick together with cover was placed for 5 sec into water whose temperature was 16°C, then into air for 5 sec, and then the setup was cooled without the cover under a water stream with a temperature of 16°C.

2. The initial temperature was $T_0 = 180^\circ$C. The initial stage of cooling of the plate 5.65 mm thick included cooling of the setup with the cover in water whose temperature was 20°C during 10 sec, then by spraying during 5 sec (temperature of water 20°C), and then the setup was cooled without the cover under a water shower (temperature of water 16°C).

The nonuniformity of the temperature and conversion fields over the plate thickness, formed in the course of cooling, is responsible for generation of technological and residual stresses and for plate deformation. By the moment the crystallization process is completed, the plate becomes convex toward the cooling surface. Plate bending was determined by a thickness meter.

The numerical analysis of evolution of the stress–strain state (SSS) of the plate was based on the boundary-value problem of thermomechanics for a crystallizing polymer divided into two independent problems: thermokinetic and boundary-value problems, which were solved consecutively (the effect of the SSS on the crystallization process was ignored). The solution was performed in a cylindrical coordinate system.

Formulation of the thermokinetic problems includes [4]:

— unsteady heat-conduction equation with variable coefficients

$$c(T)\rho(T)\,\frac{\partial T}{\partial t}=\frac{1}{r}\,\frac{\partial}{\partial r}\Big(r\lambda(T)\,\frac{\partial T}{\partial r}\Big)+\frac{\partial}{\partial z}\Big(\lambda(T)\,\frac{\partial T}{\partial z}\Big)+\rho(T)\dot{Q}; \tag{6}$$

— equation of kinetics of nonisothermal crystallization

$$\frac{d\alpha}{dt}=K_1\exp\Big(-\frac{U_1}{RT}-\frac{\psi}{T_p-T}\Big)(1+A_0\alpha)(\alpha_p(T)-\alpha), \tag{7}$$

where c is the specific heat, ρ is the density, λ is the thermal conductivity of the material, $\dot{Q}=Q_k\dot{\alpha}$ is the heat-release rate in the course of the crystallization reaction, Q_k is the thermal effect of the crystallization reaction, α is the degree of material crystallization varying in the course of the reaction from zero to a certain time-dependent limiting value $\alpha_{\rm eq}$ (equilibrium degree of crystallization), R is the universal gas constant, T_p is the melting point, K_1, U_1, ψ, and A_0 are macrokinetic constants determined experimentally, and r and z are the radial and axial coordinates, respectively;

— boundary and initial conditions

$$t=0\colon\quad T=T_0,\quad \alpha=0,\qquad z=-h^*\colon\quad \lambda\,\frac{\partial T}{\partial z}=H(T_s-T),$$

$$r=R^*\colon\quad \frac{\partial T}{\partial r}=0,\qquad z=h^*\colon\quad \frac{\partial T}{\partial z}=0,$$

where T_0 is the initial temperature, H is the heat-transfer coefficient, T_s is the temperature of the cooling medium, and R^* and $2h^*$ are the plate radius and thickness.

The results of solving the thermokinetic problem are the space–time fields of distributions of temperature and degree of crystallization, which are used to solve the problem of determining the SSS of the article. Formulation of the boundary-value quasi-static problem of finding the SSS of a solidifying system includes:

— the physical relations (4) and (5) in the form

$$\sigma_{rr}=\int\limits_0^{\alpha(t)}\Big[\int\limits_\omega^t R_1(t-\omega,\tau-\omega)\,d(\varepsilon_{rr}(\tau)-\theta(\tau)/3)\Big]d\alpha(\omega)+B_{\rm a,\infty}(\theta(t)-3a_{\rm a}(T(t)-T_0))(1-\alpha(t))$$

$$+B_{\rm cr}\int\limits_0^{\alpha(t)}[\theta(t)-\theta(\omega)-3a_{\rm cr}(T(t)-T(\omega))+3k]\,d\alpha(\omega)+B_{\rm a,\infty}\int\limits_0^{\alpha(t)}(\theta(\tau)-3a_{\rm a}(T(\tau)-T_0))\,d\alpha(\tau),$$

$$\sigma_{\varphi\varphi}=\int\limits_0^{\alpha(t)}\Big[\int\limits_\omega^t R_1(t-\omega,\tau-\omega)\,d(\varepsilon_{\varphi\varphi}(\tau)-\theta(\tau)/3)\Big]d\alpha(\omega)+B_{\rm a,\infty}(\theta(t)-3a_{\rm a}(T(t)-T_0))(1-\alpha(t))$$

$$+B_{\rm cr}\int\limits_0^{\alpha(t)}[\theta(t)-\theta(\omega)-3a_{\rm cr}(T(t)-T(\omega))+3k]\,d\alpha(\omega)+B_{\rm a,\infty}\int\limits_0^{\alpha(t)}(\theta(\tau)-3a_{\rm a}(T(\tau)-T_0))\,d\alpha(\tau),$$

$$\sigma_{zz}=\int\limits_0^{\alpha(t)}\Big[\int\limits_\omega^t R_1(t-\omega,\tau-\omega)\,d(\varepsilon_{zz}(\tau)-\theta(\tau)/3)\Big]d\alpha(\omega)+B_{\rm a,\infty}(\theta(t)-3a_{\rm a}(T(t)-T_0))(1-\alpha(t))$$

$$+B_{\rm cr}\int\limits_0^{\alpha(t)}[\theta(t)-\theta(\omega)-3a_{\rm cr}(T(t)-T(\omega))+3k]\,d\alpha(\omega)+B_{\rm a,\infty}\int\limits_0^{\alpha(t)}(\theta(\tau)-3a_{\rm a}(T(\tau)-T_0))\,d\alpha(\tau),$$

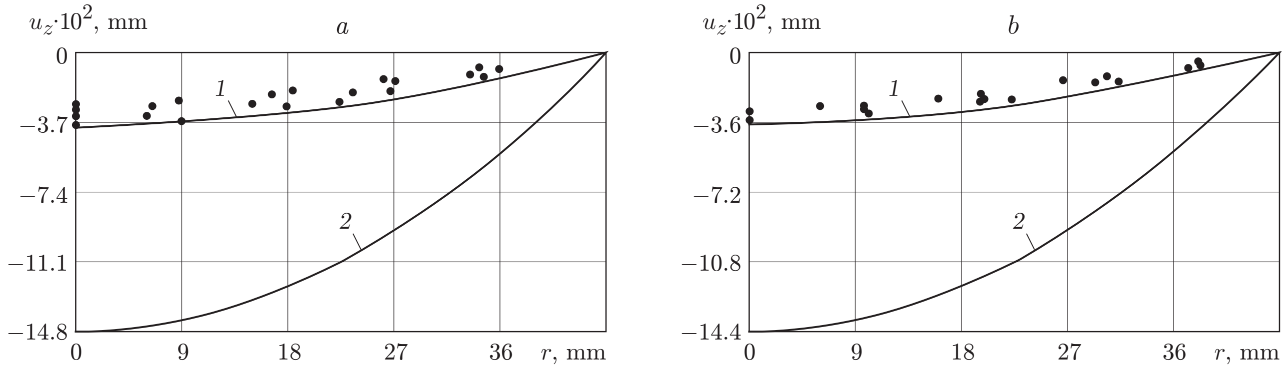

Fig. 3. Axial displacements of the plate points on the cooling surface versus the radius by the moment the crystallization process is completed: curves 1 and 2 refer to the calculations with and without allowance for viscoelastic properties of the crystalline phase of polyethylene; the points show the experimental data.

$$\tau_{rz} = \int\limits_0^{\alpha(t)} \Big[\int\limits_\omega^t R_1(t-\omega, \tau-\omega)\, d\varepsilon_{rz}(\tau) \Big]\, d\alpha(\omega),$$

where we used $R_2(t,\tau) = B_{\rm cr}$ (because we failed to find information about the function of volume relaxation for LPPE), $B_{\rm cr}$ is the volume modulus of the crystalline phase;

— equilibrium equations

$$\frac{\partial \sigma_{rr}}{\partial r} + \frac{\partial \tau_{rz}}{\partial z} + \frac{\sigma_{rr} - \sigma_{\varphi\varphi}}{r} = 0, \qquad \frac{\partial \tau_{rz}}{\partial r} + \frac{\partial \sigma_{zz}}{\partial z} + \frac{\tau_{rz}}{r} = 0; \tag{8}$$

— Cauchy relations

$$\varepsilon_{rr} = \frac{\partial u_r}{\partial r}, \qquad \varepsilon_{\varphi\varphi} = \frac{u_r}{r}, \qquad \varepsilon_{zz} = \frac{\partial u_z}{\partial z}, \qquad \varepsilon_{rz} = \frac{1}{2}\Big(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\Big); \tag{9}$$

— boundary conditions depending on the stage of the process considered

$$r = R^*\colon \quad u_r = u_z = 0, \qquad r = 0\colon \quad u_r = 0; \tag{10}$$

$$r = R^*\colon \quad u_r = u_z = 0, \qquad r = 0\colon \quad u_r = 0, \qquad z = h^*\colon \quad u_z = 0, \tag{11}$$

where u_r and u_z are the components of the displacement vector in a cylindrical coordinate system. The constraints on displacements (11) correspond to the initial stage of crystallization, when the plate tends to become convex toward the bottom, which prevents its deformation.

The development of the algorithm of numerical implementation of problem (4)–(11) was considered in [9]. Conditions of convective heat transfer with heat-transfer coefficients different for individual stages of cooling were set on the cooling surface in the numerical solution of the problem on determining the fields of temperature and degree of crystallization in the plate. The parameters were $H_1 = 450$ W/(m$^2\cdot$K), $H_2 = 100$ W/(m$^2\cdot$K), and $H_3 = 800$ W/(m$^2\cdot$K) for the first cooling mode, and $H_1 = 450$ W/(m$^2\cdot$K), $H_2 = 300$ W/(m$^2\cdot$K), and $H_3 = 550$ W/(m$^2\cdot$K) for the second cooling mode. The following values of thermophysical and mechanical parameters of LPPE were used: $K_1 = 2.33 \cdot 10^4$ sec^{-1}, $U_1 = 30,200$ J/mole, $\Psi = 182$ K, $T_{\rm m} = 415$ K, $A_0 = 82$, $Q_k = 164{,}000$ J/kg, and $k = 0.1$ [4, 10]; $E_{{\rm a},\infty} = 1.25 \cdot 10^7$ Pa, $\nu_{\rm a} = 0.49$, $a_{\rm a} = 2.8 \cdot 10^{-5}$ K^{-1}, $E_{\rm cr} = 1.6 \cdot 10^8$ Pa, $\nu_{\rm cr} = 0.35$, and $a_{\rm cr} = 0.9 \cdot 10^{-5}$ K^{-1} [11–15]. The dependence of mechanical properties of polyethylene on temperature was taken into account by using the principle of the temperature–time analogy with the data of [13]. The temperature dependences of the heat capacity, thermal conductivity, density, and equilibrium degree of LPPE crystallization were borrowed from [4, 10–12].

Figure 3 shows the axial displacements u_z of the plate points lying on the cooling surface versus the radius for two cooling modes, which were obtained experimentally (points), with the use of the physical relations (4) and (5) proposed in the present work (curves 1), and with the use of relations that imply the elastic behavior of the polymer in the crystallized state (curves 2).

As is seen from Fig. 3, the experimental data are in good agreement with the numerical results obtained with the use of the physical relations that take into account viscoelastic properties of the crystalline phase of the polymer: for points near the axis of symmetry, the difference in results is about 20%. The neglect of relaxation properties leads to significant differences with the experiment (curves 2).

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REFERENCES

1. N. Kh. Arutyunyan, A. D. Drozdov, and V.É. Naumov, *Mechanics of Growing Viscoelastoplastic Bodies* [in Russian], Nauka, Moscow (1987).
2. V. V. Bolotin and A. N. Vorontsov, "Formation of residual stresses in articles made of layer composites in the course of solidification," *Mekh. Polimer.*, No. 5, 790–795 (1976).
3. V. T. Tomashevskii and V. S. Yakovlev, "Constitutive equations of polymer systems with structural and rheological transitions," in: *Abstracts of the 7th Forum on Theoretical and Applied Mechanics* [in Russian], Moscow (1991), pp. 341–342.
4. A. Ya. Malkin and V. P. Begishev, *Chemical Formation of Polymers* [in Russian], Khimiya, Moscow (1991).
5. A. A. Il'yushin and B. E. Pobedrya, *Fundamentals of the Mathematical Theory of Thermoviscoelasticity* [in Russian], Nauka, Moscow (1970).
6. I. N. Shardakov, V. P. Matveyenko, N. V. Pistsov, and V. P. Beghishev, "Simulation of thermomechanical processes in crystallising polymer," *Polym. Eng. Sci.*, **37**, No. 8, 1270–1279 (1997).
7. Yu. N. Pabotnov, *Elements of the Heritage Solid-State Mechanics* [in Russian], Nauka, Moscow (1977).
8. V. V. Moskvitin, *Cyclic Loading of Structural Elements* [in Russian], Nauka, Moscow (1981).
9. N. A. Trufanov, O. Yu. Smetannikov, and T. G. Zav'yalova, "Numerical solution of boundary-value problems of polymer mechanics with allowance for phase and relaxation transitions," *Mat. Model.*, **12**, No. 7, 45–50 (2000).
10. A. A. Berlin, S. A. Volfson, and N. S. Enikolopyan, *Kinetics of Polymerization Processes* [in Russian], Khimiya, Moscow (1978).
11. Yu. S. Lipatov (ed.), *Thermophysical and Rheological Characteristics of Polymers* [in Russian], Naukova Dumka, Kiev (1977).
12. A. N. Piven', N. A. Grechanaya, and N. I. Chernobyl'skii, *Thermophysical Properties of Polymer Materials* [in Russian], Vishcha Shkola, Kiev (1976).
13. A. Ya. Goldman, *Prediction of Strain-Strength Properties of Polymers and Composites* [in Russian], Khimiya, Moscow (1988).
14. *Polymer Encyclopedia* [in Russian], Vols. 1–3, Sov. Éntsiklopediya, Moscow (1972).
15. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York (1974).