PRESSURE CRYSTALLIZATION OF A POLYMERIC SPHERE

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A calculation scheme is proposed to determine external pressure during frontal crystallization of a polymeric sphere in an effort to compensate internal stresses. An analytical dependence which relates an external pressure with the crystallization front coordinate specified by temperature conditions is obtained.

1. In order to develop new and improve existing manufacturing technologies items from flexible crystallizing polymers, it is necessary to find the mechanism of influence of the process parameters (with temperature T and pressure p being the main ones) on the stressed–strained state of items under crystallization.

For polymer systems [1], a marked rate of phase transition is observed when a melt is supercooled by 10-50 degrees relative to an equilibrium melting temperature T_m and the characteristic time of this transition is 10^1-10^5 sec. The characteristic time of heat transfer $\tau = R^2/a$ with the determining dimension of the field crystallization $R = 10^{-3}$-10^{-1} m is of the same order. Consequently, the crystallization rate may be controlled by a rate of the phase transition (kinetic region) or a heat transfer rate (thermal region) when a movable boundary of the phase transition — a crystallization front — is formed. Lastly a combined region may exist when the above rates are commensurable.

It is worth noting that during the crystallization of polymers intensive heat release occurs thus causing a temperature rise by tens of degrees.

In dependence on temperature conditions the polymer crystallization may be realized in two opposite modes: frontal and adiabatic.

At present a great bulk of data is accumulated on thermodynamics, kinetics and structure of crystallizing polymers which allow, the unified consideration of a phase transition in all the indicated regions on the basis of a comprehensive study of a structure of macromolecules and their interaction. Such approaches explain many qualitative and quantitative regularities in the crystallization of polymers, however they turn to be rather tedious when being applied to specific technological problems. Therefore in practice the simplified models of the process are used which reflect, however, the most important aspects of this or that phenomenon.

As a rule, the technological process of manufacturing a polymer item is accomplished in such a way that crystallization proceeds in a thermal region. In this case, surface layers of an item, being in contact with mold walls, are cooled and crystallized first. During further cooling, crystallization begins in internal layers, however the appropriate shrinkage cannot proceed uniformly throughout the volume because of the solidified external surface. Intensive heat release during crystallization and heat transfer to a surrounding medium lead to essential inhomogeneous temperature fields and degree of crystallinity and, as a consequence, strain nonuniformity with respect to an item thickness, being ultimately the cause of internal residual stresses. On the whole, essential tensile radial stresses develop at the center of an item (as an example, consider a sphere) which near the surface are converted to compression stresses. These stresses are responsible for occurrence of craters and cracks and sometimes cause the complete failure of an item.

To compensate tensile stresses σ_r, sometimes during the crystallization process a pressure is applied to an item surface which is sufficient to convert a polymer, crystallized to the given moment of time t, into a pseudoplastic state. To compensate for a change in a volume (shrinkage), a pressure technique is employed [2]. Pressure is related with volume shrinkage, item geometry and its overall dimensions. In this case, volume compensation takes place at any stage of the process, however a required pressure is chosen experimentally and recommended within the limits from 0.5 to 20 MPa.

The present work is aimed at development of the simplified calculation scheme reflecting the frontal crystallization effect and establishing the relationship between temperature conditions and applied pressure.

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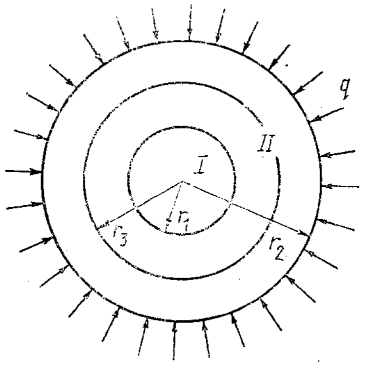

Fig. 1. Calculation scheme.

2. Consider a polymeric sphere in a mold at the melting temperature T_m. At some moment of time, assumed as the onset of measurements $t = 0$, we place the mold into a medium with a given temperature $T_c < T_0 < T_m$ where the crystallization process begins. The conditions of heat transfer with the surrounding medium ensure a frontal mode of crystallization.

As mentioned earlier, for partial compensation of shrinkage and stresses developing on the sphere surface $r = r_2$ during crystallization (Fig. 1), pressure $-q = \sigma_r$ is to be applied whose value is unknown (and is to be investigated in the present work) but determined from the condition of conversion of a crystalline polymer, formed behind the crystallization front with a coordinate r_1, into a plastic state. The uncrystallized fraction of the material (region I: $0 \leq r \leq r_1$) is considered to be an ideal compressible fluid and characterized by a bulk modulus K_1.

A layer of the crystalline polymer (region II: $r_1 \leq r \leq r_2$) will be represented as an elastoviscous substance with material constants E_2; ν_2; G_2; σ_s^{II}; $\sigma_\theta - \sigma_r = \kappa\sigma^{II}$ is the yield condition of the material; $\kappa = \pm 1$, a sign of κ is chosen from the condition $\kappa = \operatorname{sign}(p - q)$ where $-p = \sigma_r$ is some unknown stress on the crystallization front.

A solution for σ_r, σ_θ, and u in the elastic region is written in the form [3]:

$$\sigma_r = \frac{\sigma_s^{II}}{\sqrt{3}}\left(C_1 - C_2\frac{r_2^3}{r^3}\right); \quad \sigma_\theta = \frac{\sigma_s^{II}}{\sqrt{3}}\left(C_1 + C_2\frac{r_2^3}{2r^3}\right);$$
$$u = \frac{\sigma_s^{II} r}{\sqrt{3}E_2}\left[(1-2\nu_2)C_1 + C_2(1+\nu_2)\frac{r_2^3}{2r^3}\right]. \tag{1}$$

For determination of an arbitrary constant C_1, at an external boundary we have the condition $\sigma_r \mid_{r=r_2} = -q$.

At the boundary of elastic and plastic zones at $r = r_3$ all the stresses and displacements are continuous and, therefore, the yield condition is valid which allows determination of C_2 in terms of the radius of this boundary.

Then we may write for σ_r, σ_θ, and u the following expressions

$$\sigma_r = -q + \varkappa\frac{2}{3}\sigma_s^{II}\frac{r_3^3}{r_2^3}\left(1 - \frac{r_2^3}{r^3}\right); \quad \sigma_\theta = -q + \varkappa\frac{2}{3}\frac{r_3^3}{r_2^3}\left(1 + \frac{r_2^3}{2r^3}\right);$$
$$u = -\frac{qr}{E_2}(1-2\nu_2) + \varkappa\frac{2}{3}\frac{\sigma_s^{II}}{E_2}r\frac{r_3^3}{r_2^3}\left[(1-2\nu_2) + (1+\nu_2)\frac{r_2^3}{2r^3}\right]. \tag{2}$$

The solutions for σ_r, σ_θ, and u in the plastic region are of the form [3]:

$$\sigma_r = -p + \varkappa 2\sigma_s^{II}\ln\frac{r}{r_1}; \quad \sigma_\theta = -p + \varkappa\sigma_s^{II}\left(1 + 2\ln\frac{r}{r_1}\right);$$
$$u = -\frac{pr}{E_2}(1-2\nu_2) + \varkappa\frac{\sigma_s^{II}}{E_2}r\left[(1-\nu_2)\frac{r_3^3}{r^3} + 2(1-2\nu_2)\ln\frac{r}{r_1}\right]. \tag{3}$$

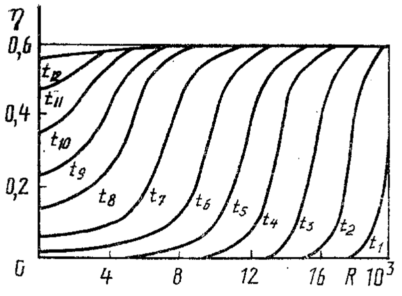

Fig. 2

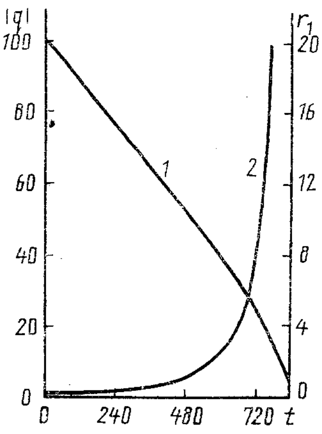

Fig. 3

Fig. 2. Distribution of a degree of crysallinity with respect to a sphere radius at different moments of time: $t_1 = 20$ sec; $t_2 = 120$; $t_3 = 220$; $t_4 = 320$; $t_5 = 420$; $t_6 = 520$; $t_7 = 620$; $t_8 = 720$; $t_9 = 790$; $t_{10} = 860$; $t_{11} = 920$; $t_{12} = 980$ R, m.

Fig. 3. The calculated external pressure and front coordinate as a function of time: 1) front coordinate; 2) external pressure. $|q|$, MPa; r_1, m; t, sec.

Note that we preset the external pressure p while q is specified by interaction with region I.

The solutions for σ_r, σ_θ, and u in region I are taken in the form of (1). In this case, we have the condition $u|_{r=0} = 0$ for determination of the constant C_2, while for determination of C_1 the continuity conditions

$$\sigma_r^{\mathrm{I}} = \sigma_r; \; u^{\mathrm{I}} = u$$

are to be fulfilled on the crystallization front at $r = r_1$.

After simple transformations, using the relation $1/3K = (1 - 2\nu)/E$ we obtain the expression for p

$$-p = 3\varkappa \frac{\sigma_s^{\mathrm{II}}(1-\nu_2)}{E_2\left(\frac{1}{K_1}-\frac{1}{K_2}\right)} \frac{r_3^3}{r_1^3}. \tag{4}$$

The expression (4) contains only one unknown parameter r_3. To determine this parameter, we use the following relation [3]

$$p - q = \varkappa \frac{2}{3} \sigma_s^{\mathrm{II}} \left(1 - \frac{r_3^3}{r_2^3} + 3 \ln \frac{r_3}{r_1}\right). \tag{5}$$

Since such external pressure q is of interest to us at $r_3 \equiv r_2$, then $p - q = \kappa 2\sigma_s^{\mathrm{II}} \ln(r_2/r_1)$. Taking p from the latter expression and substituting it into (4), we arrive at the expression for the desired pressure q:

$$|q| = \sigma_s^{\mathrm{II}} \left[3 \frac{(1-\nu_2) K_1}{2G_2(1+\nu_2) - 3K_1(1-2\nu_2)} \frac{r_2^3}{r_1^3} + 2 \ln \frac{r_2}{r_1}\right]. \tag{6}$$

Thus, $|q|$ is the current pressure required to convert the entire crystallized part of the sphere at an arbitrary moment of time t into a plastic state.

It is seen that besides the material constants, determined experimentally, the expression (6) contains the ratio r_2/r_1 characterizing dimensions of the crystallized region.

The position of the crystallization front as a function of time $r_1 = r_1(t)$ may be determined, for instance, within the framework of the quasistatistical model [4] based on simultaneous solution of the equations of heat conduction and kinetics of nonisothermal crystallization.

For axisymmetric items, the heat conduction equation, allowing for a source of heat release due to a crystallization process, may be written in the form

$$\frac{\partial T}{\partial t} = a\left(\frac{\partial^2 T}{\partial r^2} + \frac{n}{r}\frac{\partial T}{\partial r}\right) + \frac{\Delta H}{c}\frac{d\eta}{dt}. \tag{7}$$

Write the kinetic equation of crystallization:

$$\frac{d\eta}{dt} = K\exp\left[-\frac{E}{T - T_c} - \frac{\psi}{T_m - T}\right](1 + C_0\eta)(\eta_p - \eta); \tag{8}$$

$\eta_p = \eta_p(T) = 0.69\,[1 - 0.11\sqrt{T/(T_m - T)}]$; $n = 0, 1, 2$ for flat, cylindrical and spherical reactors, respectively.

Initial and boundary conditions for simultaneous solution of Eqs. (7), (8) may be written as

$$\text{at } t = 0: T(r) = T_{\text{н}},\ \eta = 0;$$

$$\text{at } r = 0: \partial T/\partial r = 0;$$

$$\text{at } r = r_2: \partial T/\partial r = -\mathrm{Bi}\,(T - T_0)/r_2.$$

3. Concrete experimental data and results of calculations are reported for polyamide-6 crystallization to proceed in a spherical mold with a 2 cm radius.

The crystallization constants have been obtained by solving the inverse problem of nonisothermal kinetics with the use of experimental data on temperature variation during a crystallization process to give: $\psi = 210.4$ K; $K = 3.3\ \mathrm{sec}^{-1}$; $E = 213$ K; $\Delta H = 164$ kJ/kg; $C_0 = 42.6$; $T_c = 318$ K; $T_m = 501$ K.

Figure 2 represents the calculated degrees of crystallinity with respect to a sphere radius at different moments of time. It is seen that at the chosen heat removal conditions ($\mathrm{Bi} = 5.12$; $T_0 = 393$ K) a distinct boundary of the crystallization front is observed. A position of the crystallization front in time $r_1 = r_1(t)$ is shown in Fig. 3 (curve 1). A characteristic degree of crystallinity, by which the front position has been traced, is assumed equal to 0.3, which corresponds to the degree of crystallinity of those specimens, during the tests of which the temperature dependences of material constants G_2 and σ_s^{II} have been obtained [5]. Note that the temperature over the crystallization front varies from point to point insignificantly ($T\,|_{r=r_i} = 452 - 461$K). Therefore the constants G_2 and σ_s^{II} have been evaluated at $T = 457$ K ($G_2 = 80$ MPa; $\sigma_s^{\mathrm{II}} = 1.3$ MPa). The remaining constants in the temperature range T_m-T_0 change insignificantly and are assumed equal to $K_i = 63$ MPa; $v_2 = 0.36$; $c = 2.87$ kJ/(kg·deg); $a = 10^{-7}\ \mathrm{m}^2\cdot\mathrm{sec}$.

Note that the velocity of the crystallization front $v = dr_1/dt$ during the whole process remains practically constant $v \approx 4.8\times10^{-3}$ m/min (Fig. 3). Small deviations are observed only at $r_1/r_2 < 0.3$.

Characteristically, at t = 660 sec, the pressure begins abruptly to decrease tending to infinity at $r_1/r_2 \to 0$ (see Fig. 3, curve 2). A portion of the uncrystallized material at t = 660 sec makes up less than 3% of the total volume of the sphere $V_{sp}/V = r_1^3/r_2^3 = 0.027$. Consequently, in practice a pressure level may be limited by values of about 30 MPa.

Thus, the suggested calculation scheme allows one not only to relate temperature conditions of fabricating the polymer items with the external pressure of the crystallization process but also to evaluate its level.

NOTATION

E_2, elasticity modulus; v_2, Poisson coefficient; G_2, shear modulus; σ_s^{II}, yield strength; K_1, volumetric modulus; σ_r, radial stresses; σ_θ, circumferential stresses; u, displacements; p, q, pressure; T_m, melting point; T_c, glass transition temperature; T_0, initial temperature; η, degree of crystallinity; η_p, equilibrium degree of crystallinity; c, heat capacity; a, thermal diffusivity; ΔH, enthalpy of the process; n, form-factor; Bi, Biot number; E, ψ, K, C_0, constants characterizing the crystallization process; t, time; r, current radius of a sphere; r_2, sphere radius; r_1, radius of region I; r_3, radius of the boundary of elastic and plastic zones.

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