FORMATION OF THE MODEL OF THE POLYMER MATERIAL STRUCTURE DURING ORIENTATIONAL DRAWIG

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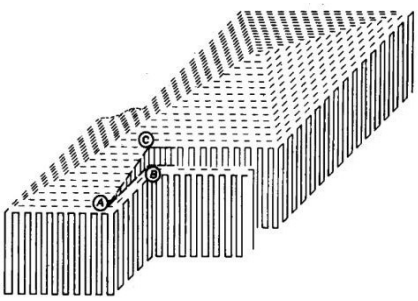
Introduction

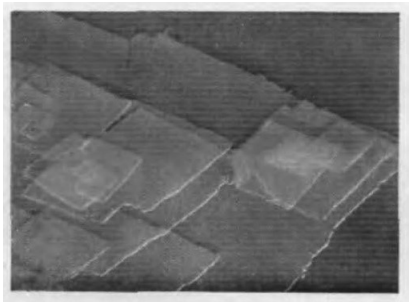
As a result of the structural analysis conducted by various physical methods [1..9], it was established that there are two main levels of SMS in the non-oriented state of amorphous crystalline polymers of the spheruline structure – spherulites of geometric shape close to the distorted sphere, possessing a microheterogeneous crystalline structure, and a homogeneous amorphous part of a medium with a disordered structure. In [10], a model of an non-oriented structure of amorphous-crystalline polymers was proposed, which satisfactorily linked the indices of their elastic properties with the parameters of the structure and the experimental data of the author and other researchers.

Taking the characteristics of structural elements – spherulite and amorphous phase [5, 7] as initial data, and neglecting the dissipative phenomena in the isolated elements, in the first approximation we break the entire drawing process of the polymer into a finite number of states with a fixed degree of deformation of the spherulites. It was established earlier [3...5] that up to the values of the degree of drawing equal to the natural $1 \le \lambda \le 9$, a direct genetic connection is maintained between the initial spherulitic order and the orientation one, and also that with An increase in the degree of drawing of λ also increases the degree of anisotropy of the material. These facts are the basis for the hypothesis of the existence of a quantitative relationship between the parameters of the drawing of spherulites and the indices of the mechanical characteristics of the medium in each of these states.

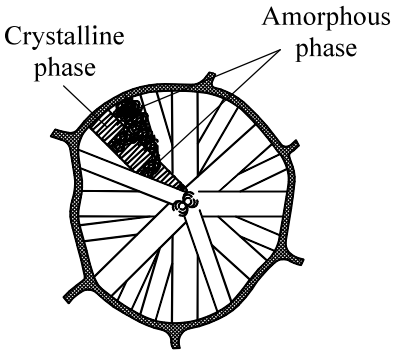
Many different supramolecular structures, occurring depending on the conditions of obtaining and processing of polymers, cannot now be described in one model of the mechanical properties of amorphous-crystalline polymers. The main idea of this work is model fixation of a polymer of supramolecular structure that changes with deformation.

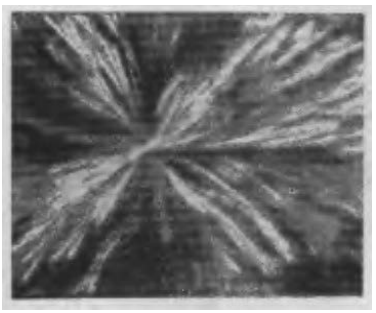
Undoubtedly the most convenient object for studying the structural changes taking place in polymers during deformation is monocrystals (Fig. 1a). However, the main and the most common structural form is spherulite structure (Fig. 1 b), which is formed during crystallization of amorphous crystalline polymers.





a





b

a – the monocrystal; b – spherulite.

Figure 1 – The structural model of the structure of the polymer material

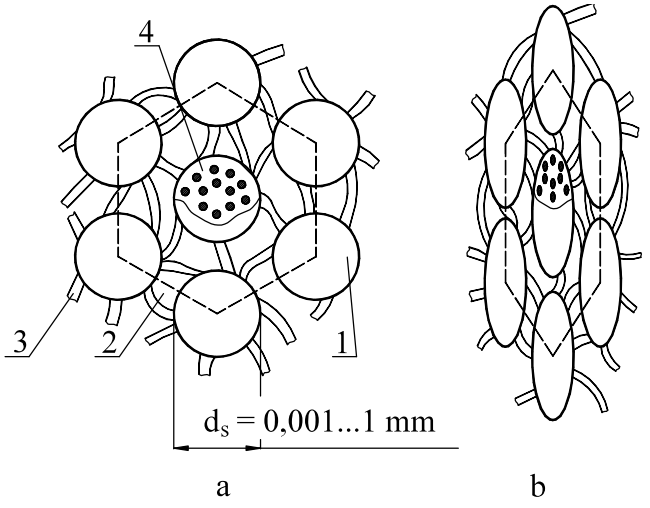
The structural model of spheruline structure of a polymer (see. Figure 1 b) consists of two interconnected models that describe two states of supramolecular structure of polymers: before deformation – a model of spherulite structure of polymers in non-oriented state; after deformation – a model of spheruline structure of polymers in oriented state.

Research & Results

A model of spheruline structure of a polymer can be represented as infinite elastic isotropic medium [11], consisting of spheruline structure placed in a homogeneous amorphous matrix. Following assumptions were adopted during the construction of the model: spherulites have the same shape (spherical) and dimensions; spherulites are located in the corners of the spatial lattice [11]; the crystalline polymer medium is concentrated in spherulites (Fig. 2).

As a result of the orientation drawing, occurs uniform [6] in the direction of the x_1 axis and with an unchanged volume of spherulites [7, 8] ($\rho_s = const$), we will model the orientational drawing as a uniform compression (stretching) of the space with a coefficient η numerically equal to the stretching degree λ of the polymer: $\eta = \lambda$. In this case, a uniform compression (stretching) of the spherulite actually

occurs in the direction from the plane $x_2 0 x_3$, taken as the main one (Fig. 2). The formulas for transforming the coordinates taking into account the invariance of the volume of the spherulite will have the form $x_1^* = x_1 \lambda$, $x_2^* = x_3^* = x_2 \lambda^{-1/2}$.



1 – an amorphous phase; 2 – spherulites (a crystalline phase); 3 – penetrating microfibrills; 4 – a model of internal structure of the spherulite
Figure 2 – A model of supermolecular spheruline structure of amorphous crystalline polymers in non-oriented (a) and oriented (b) state

Two cases can occur: for $\lambda > 1$, uniaxial stretching of the space takes place (obtaining fibers and films by drawing); when $\lambda < 1$, uniaxial compression of the space takes place (obtaining fibers and films by rolling or calendering).

The equation of spherulites with a radius r ($x_1^2 + x_2^2 + x_3^2 = r^2$), undergoing uniform stretching with the drawing coefficient λ, as a result of substituting the formulas for the transformation of coordinates and bringing it to the canonical form has the form

$$\frac{(x_1^*)^2}{\lambda^2 r^2} + \lambda \frac{(x_2^*)^2 + (x_3^*)^2}{r^2} = 1. \quad (1)$$

The determining of relative volumetric medium filling with spherulites ξ, sizes of spherulites in the shape of a sphere with a diameter d_s; type of packaging μ and cyclic symmetry in its structure have paramount value in building of a theory of effective modules of spheruline structure in the first approximation

As characteristic that determines probable spatial lattice type, shape and type of spherulites, we will use the exponent of bulk crystalline polymer material [12].

$$\chi = \frac{\rho - \rho_a}{\rho_s - \rho_a}, \quad (2)$$

where ρ – density of a sample; ρ_a, ρ_s – density of amorphous and crystalline phase of a polymer, found by X-ray diffraction data.

Considering the assumption that all crystalline part of the polymer is concentrated in spherulites that consist of alternating lamellar crystalline regions and interlamellar amorphous layers [13], we can say that the degree of crystallinity χ is associated with the relative volume of spherulite in a spatial lattice, filling the medium with spherulites ξ and compactness coefficient of a spatial lattice μ [11].

$$\xi = \chi^2 = k^2 \cdot \mu, \tag{3}$$

where $k = d_s / L_s$ – a density coefficient of spherulites packing ($0 \le k \le 1$); L_s – the distance between the centers of spherulites.

Coefficient of compactness of the spatial lattice, in the corners of which spherulites are located, is determined by its type. The expression $\mu = \pi/6$ – corresponds the simplest cubic lattice; $\mu = \pi/3$ – body-centered cubic lattice; $\mu = 2\pi/3$ – face-centered cubic lattice; $\mu = \sqrt{2}\pi/6$ – hexagonal structure of cubic lattice.

Clearly, the most densely packed spheres with a radius $d_s/2$, and boundary filling of the spatial lattice, accord to this structure, when the spheres touch one another, i.e. in $d_s = L_s$. In this case $k = 1$, and $\xi = \chi^2 = \mu$.

The task of this modeling of the spheruline supramolecular structure of a polymer material is to determine the degree of influence of the polymer elastic properties and its stress-strain state on the form of the spatial lattice, the shape and the size of spherulites that will help to predict the change in the form of spatial lattice in the corners of which spherulites are located, and the shape and size of the spherulites themselves under any deformation of spheruline polymer structure. The models of regularities of elastic constants influence on the shape and size of spherulites and on kind of their mutual arrangement can be used in the modeling of spheruline structures formed during the drawing of polymers.

In connection with the foregoing, we consider the mode of deformation of the spherical crystalline phase, which is located in unlimited amorphous isotropic environment that is exposed to stretching along the axis x_3 (Fig. 3).

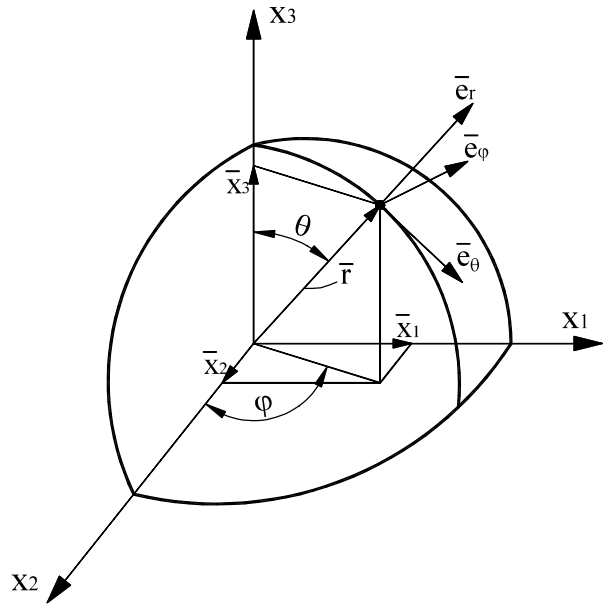


Figure 3 – Scheme of the stress-strain state of spherulites in the polymer structure

Assuming that the structure of amorphous and crystalline phase of the polymer is isotropic medium, as well as that spherulites are packed in a hexagonal lattice and between them there are homogeneous strain interaction, we will solve the problem in a curvilinear coordinate system (q^1, q^2, q^3), which is associated with the interface environment and the origin is at the center of a spherulite.

As known from [14], the main local basis vectors of curvilinear coordinate system are defined by the formula:

$$\vec{e}_i = \partial\vec{r}/\partial q^i, \quad i = 1, 2, 3 \qquad (4)$$

and is tangent to coordinate lines q^i, that pass through the point $\vec{r} = \vec{r}\left(q^1, q^2, q^3\right)$.

Coordinates q^1, q^2, q^3 uniquely determine the vector $\vec{r}$ in a curvilinear coordinate system, and coordinates x_1, x_2, x_3 uniquely determine this vector in the Cartesian coordinate system (Fig. 2). Cartesian coordinates x_i and curvilinear coordinates q^i can have different dimensions, ie curvilinear base components and Cartesian coordinate systems can be different.

To take account of this, we need to determine the appropriate length of the main vectors of the local coordinate system curvilinear basis:

$$H_\nu = \sqrt{\left(\frac{\partial x_1}{\partial q^\nu}\right)^2 + \left(\frac{\partial x_2}{\partial q^\nu}\right)^2 + \left(\frac{\partial x_3}{\partial q^\nu}\right)^2}, \qquad \nu = 1, 2, 3 \qquad (5)$$

and divide them by these vectors, ie:

$$\vec{e}_{(\nu)} = \frac{\vec{e}_\nu}{H_\nu}. \qquad (6)$$

Local basis of the unit vectors $\vec{e}_{(\nu)}$ is called physical basis in the scientific literature, and its use is very convenient for solving physical problems.

Since the spherulite has the shape of a sphere, we will use a spherical coordinate system, which is a particular case of curvilinear coordinate system. Then, the position of the vector $\vec{r}$ will be determined by spherical coordinates r, θ, φ. From Fig. 2, we define the Cartesian coordinates x_1, x_2, x_3 through spherical coordinates r, θ, φ.

$$x_1 = r \cdot \sin\theta \cdot \sin\varphi, \quad x_2 = r \cdot \sin\theta \cdot \cos\varphi, \quad x_3 = r \cdot \cos\theta, \tag{7}$$

here with $0 \le r < \infty$, $0 \le \theta \le \pi$, $0 \le \varphi \le 2\pi$.

Using equation (4) and expressions (7), we decompose unit vectors of the spherical coordinate system by unit vectors of the Cartesian coordinate system.

$$\begin{aligned}
\vec{e}_r &= \sin\theta \sin\varphi \cdot \vec{e}_1 + \sin\theta \cos\varphi \cdot \vec{e}_2 + \cos\theta \cdot \vec{e}_3, \\
\vec{e}_\theta &= r \cdot \cos\theta \sin\varphi \cdot \vec{e}_1 + r \cdot \cos\theta \cos\varphi \cdot \vec{e}_2 - r \sin\theta \cdot \vec{e}_3, \\
\vec{e}_\varphi &= r \cdot \sin\theta \cos\varphi \cdot \vec{e}_1 - r \cdot \sin\theta \sin\varphi \cdot \vec{e}_2 + 0 \cdot \vec{e}_3.
\end{aligned} \tag{8}$$

We put component dimensions of the basis of a curvilinear coordinate system to the dimension of the vector $\vec{r}$ (or basis dimensions of Cartesian coordinates), ie the unit. To do this, we divide the unit vectors of the spherical coordinate system by their lengths (Lame parameters $H_\nu (\nu = 1,2,3)$) that are determined from equation (5). As a result, the system (8) can be rewritten as follows:

$$\begin{aligned}
\vec{e}_{(r)} &= \sin\theta \sin\varphi \cdot \vec{e}_1 + \sin\theta \cos\varphi \cdot \vec{e}_2 + \cos\theta \cdot \vec{e}_3, \\
\vec{e}_{(\theta)} &= \cos\theta \sin\varphi \cdot \vec{e}_1 + \cos\theta \cos\varphi \cdot \vec{e}_2 - \sin\theta \cdot \vec{e}_3, \\
\vec{e}_{(\varphi)} &= \cos\varphi \cdot \vec{e}_1 - \sin\varphi \cdot \vec{e}_2 + 0 \cdot \vec{e}_3,
\end{aligned} \tag{9}$$

where $e_{(\nu)} (\nu = 1,2,3)$ – adjusted or physical basis. Later braces, standing at the index, will be dropped.

So orthogonal matrix of transition from Cartesian to spherical basis is written as follows:

$$\begin{aligned}
\vec{e}_r &= a_{11} \cdot \vec{e}_1 + a_{12} \cdot \vec{e}_2 + a_{13} \cdot \vec{e}_3, \\
\vec{e}_\theta &= a_{21} \cdot \vec{e}_1 + a_{22} \cdot \vec{e}_2 + a_{23} \cdot \vec{e}_3, \\
\vec{e}_\varphi &= a_{31} \cdot \vec{e}_1 + a_{32} \cdot \vec{e}_2 + a_{33} \cdot \vec{e}_3,
\end{aligned} \tag{10}$$

where a_{ij} – components of orthogonal matrix of transition from Cartesian to spherical basis:

$$\begin{aligned} a_{11} &= \sin\theta\sin\varphi, & a_{12} &= \sin\theta\cos\varphi, & a_{13} &= \cos\theta, \\ a_{21} &= \cos\theta\sin\varphi, & a_{22} &= \cos\theta\cos\varphi, & a_{23} &= -\sin\theta, \\ a_{31} &= \cos\varphi, & a_{32} &= -\sin\varphi, & a_{33} &= 0. \end{aligned} \tag{11}$$

The reverse transformation implemented by the following equations:

$$\begin{aligned} \vec{e}_1 &= a_{11}\cdot\vec{e}_r + a_{21}\cdot\vec{e}_\theta + a_{31}\cdot\vec{e}_\varphi, \\ \vec{e}_2 &= a_{12}\cdot\vec{e}_r + a_{22}\cdot\vec{e}_\theta + a_{32}\cdot\vec{e}_\varphi, \\ \vec{e}_3 &= a_{13}\cdot\vec{e}_r + a_{23}\cdot\vec{e}_\theta + a_{33}\cdot\vec{e}_\varphi. \end{aligned} \tag{12}$$

To determine the elastic properties (elastic modulus and Poisson coefficient) in the direction of the axis of polymer stretching (axis x_3) we consider the case of longitudinal tensile of non-oriented spheruline structure.

During the stretching, a stress state occurs in spherulites, that, according to the diadic presentation [11, 15], can be written as follows:

$$\mathbf{T} = \vec{e}_x\vec{e}_x\sigma_{xx} + \vec{e}_y\vec{e}_y\sigma_{yy} + \vec{e}_z\vec{e}_z\sigma_{zz} + \left(\vec{e}_x\vec{e}_y + \vec{e}_y\vec{e}_x\right)\cdot\sigma_{xy} + \left(\vec{e}_y\vec{e}_z + \vec{e}_z\vec{e}_y\right)\cdot\sigma_{yz} + \left(\vec{e}_z\vec{e}_x + \vec{e}_x\vec{e}_z\right)\cdot\sigma_{zx}, \tag{13}$$

where $\vec{e}_x$, $\vec{e}_y$, $\vec{e}_z$ – single orts of Cartesian coordinate system; σ_{xx}, σ_{yy}, σ_{zz} – normal stresses occurring on the perpendicular to the corresponding axes of the coordinate system; σ_{xy}, σ_{yz}, σ_{zx} – tangential tension occurring on the same fields.

If we orient the axes in a way that on platforms of elementary volume, bounded by spherical surface, tangential tensions are not present. Then equation (13) can be rewritten as follows:

$$\mathbf{T} = \vec{e}_1\vec{e}_1\sigma_1 + \vec{e}_2\vec{e}_2\sigma_2 + \vec{e}_3\vec{e}_3\sigma_3, \tag{14}$$

where $\vec{e}_1$, $\vec{e}_2$, $\vec{e}_3$ – unit orts of the Cartesian coordinate system, x_1, x_2, x_3; σ_1, σ_2, σ_3 – tensions in major fields, perpendicular to the corresponding axes of the coordinate system x_1, x_2, x_3.

Submitting each of main tensions as the product of the average tension $\overline{\sigma}_1$ that influences spherulites along the axis x_3, and unknown constants σ° characterizing the tension level of homogeneous interaction and the level of tension on the main fields, we get the following:

$$\mathbf{T^c} = \left(\vec{e}_1\vec{e}_1\sigma_1^{\circ} + \vec{e}_2\vec{e}_2\sigma_2^{\circ} + \vec{e}_3\vec{e}_3\sigma_3^{\circ}\right)\overline{\sigma}_1, \qquad (15)$$

Tension of homogeneous interaction between the spherulites result from changes in stress-strain state of spherulites.

Tension tensor (15) in spherical coordinates (7) can be expressed as follows [11]:

$$\mathbf{T^c} = \left(\vec{e}_r\vec{e}_r\sigma_r^{\circ} + \vec{e}_\theta\vec{e}_\theta\sigma_\theta^{\circ} + \vec{e}_\varphi\vec{e}_\varphi\sigma_\varphi^{\circ} + \left(\vec{e}_r\vec{e}_\theta + \vec{e}_\theta\vec{e}_r\right)\cdot\sigma_{r\theta}^{\circ}\right)\overline{\sigma}_1, \qquad (16)$$

The unknown constants σ° in spherical coordinates are expressed through Cartesian by substitution of expressions (12) in equation (15)

$$\begin{aligned}\mathbf{T^c} = &\left[\vec{e}_r\vec{e}_r\left(a_{11}^2\sigma_1^{\circ} + a_{12}^2\sigma_2^{\circ} + a_{13}^2\sigma_3^{\circ}\right) + \vec{e}_\theta\vec{e}_\theta\left(a_{21}^2\sigma_1^{\circ} + a_{22}^2\sigma_2^{\circ} + a_{23}^2\sigma_3^{\circ}\right) + \vec{e}_\varphi\vec{e}_\varphi\left(a_{31}^2\sigma_1^{\circ} + a_{32}^2\sigma_2^{\circ} + a_{33}^2\sigma_3^{\circ}\right) + \right.\\ &+ \left(\vec{e}_r\vec{e}_\theta + \vec{e}_\theta\vec{e}_r\right)\cdot\left(a_{11}a_{21}\sigma_1^{\circ} + a_{12}a_{22}\sigma_2^{\circ} + a_{13}a_{23}\sigma_3^{\circ}\right) + \left(\vec{e}_r\vec{e}_\varphi + \vec{e}_\varphi\vec{e}_r\right)\cdot\left(a_{11}a_{31}\sigma_1^{\circ} + a_{12}a_{32}\sigma_2^{\circ} + a_{13}a_{33}\sigma_3^{\circ}\right) + \\ &\left. + \left(\vec{e}_\theta\vec{e}_\varphi + \vec{e}_\varphi\vec{e}_\theta\right)\cdot\left(a_{21}a_{31}\sigma_1^{\circ} + a_{22}a_{32}\sigma_2^{\circ} + a_{23}a_{33}\sigma_3^{\circ}\right)\right]\cdot\overline{\sigma}_1\end{aligned} \qquad (17)$$

It was assumed above that the spherulites form a hexagonal lattice. In the microstructure corresponding to hexagonal packing, elastic properties do not depend on the chosen direction (is isotropic), that is why in the adopted approach we will direct axis x_3 so that the stress state of spherulites is independent of the angle φ. In this case, we assume that angle $\varphi = 0$, and taking into account the expressions (11) we get:

$$\mathbf{T^c} = \left[\vec{e}_r\vec{e}_r\left(a_{23}^2\sigma_2^{\circ} + a_{22}^2\sigma_3^{\circ}\right) + \vec{e}_\theta\vec{e}_\theta\left(a_{22}^2\sigma_2^{\circ} + a_{23}^2\sigma_3^{\circ}\right) + \vec{e}_\varphi\vec{e}_\varphi\sigma_1^{\circ} + \left(\vec{e}_r\vec{e}_\theta + \vec{e}_\theta\vec{e}_r\right)\cdot\left(\sigma_3^{\circ} - \sigma_2^{\circ}\right)\cdot a_{22}a_{23}\right]\cdot\overline{\sigma}_1. \qquad (18)$$

Comparing the obtained expression (18) to the equation (16), we determine the unknown components of the stress tensor of spherulites:

$$\sigma_r^s = \left(a_{23}^2\sigma_2^{\circ} + a_{22}^2\sigma_3^{\circ}\right)\cdot\overline{\sigma}_1, \quad \sigma_\theta^s = \left(a_{22}^2\sigma_2^{\circ} + a_{23}^2\sigma_3^{\circ}\right)\cdot\overline{\sigma}_1, \quad \sigma_\varphi^s = \sigma_1^{\circ}\cdot\overline{\sigma}_1, \quad \sigma_{r\theta}^s = \left(\sigma_3^{\circ} - \sigma_2^{\circ}\right)\cdot a_{22}a_{23}\cdot\overline{\sigma}_1. \qquad (19)$$

According to solving the problem of elasticity of the axially symmetric mode of deformation field [11, 15], we define unknown components of the stress tensor of spherulites as follows:

$$\sigma_r^s = -2\cdot E_s\cdot A_0 - \frac{2\cdot E_s}{1+\nu_s}\cdot\left(3\cdot A_2\cdot\nu_s\cdot r^2 - B_2\right)\cdot P_2(\cos\theta),$$

$$\sigma_{r\theta}^s = \left(\frac{E_s}{1+\nu_s}\cdot\left(A_2\cdot(2\nu_s+7)\cdot r^2 + B_2\right)\right)\cdot\frac{dP_2(\cos\theta)}{d\theta},$$

$$\sigma_\theta^s = -2E_s\cdot A_0 - \frac{2E_s}{1+\nu_s}\left(3A_2\cdot r^2(7+\nu_s) + 2B_2\right)\cdot P_2(\cos\theta) - \frac{E_s}{1+\nu_s}\left(A_2\cdot r^2(7-4\nu_s) + B_2\right)\cdot\frac{dP_2(\cos\theta)}{d\theta}ctg\theta,$$

$$\sigma_\varphi^s = -2E_s\cdot A_0 - \frac{E_s}{1+\nu_s}\left(30\cdot A_2\cdot\nu_s\cdot r^2 - 2B_2\right)\cdot P_2(\cos\theta) + \frac{E_s}{1+\nu_s}\left(A_2\cdot r^2(7-4\nu_s) + B_2\right)\cdot\frac{dP_2(\cos\theta)}{d\theta}ctg\theta. \tag{20}$$

where E_s – elasticity modulus of a spherulite; ν_s – Poisson coefficient of spherulites; $P_0(\cos\theta)$, $P_1(\cos\theta)$, $P_2(\cos\theta)$ – Legendre polynomials of the first kind of zero, first and second order; A_0, A_1, A_2, B_2 – unknown constants that are of marginal conditions; r – the radius vector of volume of the spherulites.

We will express the components of the displacement vector in the spherulite in a spherical coordinate system:

$$\mathbf{u}^s = \vec{\mathbf{e}}_r u_r^s + \vec{\mathbf{e}}_\theta u_\theta^s + \vec{\mathbf{e}}_\varphi u_\varphi^s. \tag{21}$$

The unknown components of displacement vector in the spherulite are defined as follows:

$$u_r^s = A_0\cdot r\cdot(-2)(1-2\nu_s)\cdot P_0(\cos\theta) + \left(A_1\cdot r^2\cdot 2\cdot(-1+4\nu_s) + B_1\right)\cdot P_1(\cos\theta) +$$
$$+\left(A_2\cdot r^3\cdot 3\cdot 4\nu_s + 2B_2\cdot r\right)\cdot P_2(\cos\theta) = -2\cdot(1-2\nu_s)\cdot A_0\cdot r + 2\cdot\left(A_2\cdot r^3\cdot 6\nu_s + B_2\cdot r\right)\cdot P_2(\cos\theta),$$

$$u_\theta^s = \left(A_0\cdot r\cdot(5-4\nu_s) + B_0\cdot r^{-1}\right)\cdot\frac{dP_0(\cos\theta)}{d\theta} + \left(A_1\cdot r^2\cdot(6-4\nu_s) + B_1\right)\cdot\frac{dP_1(\cos\theta)}{d\theta} + \tag{22}$$
$$+\left(A_2\cdot r^3\cdot(7-4\nu_s) + B_2\cdot r\right)\cdot\frac{dP_2(\cos\theta)}{d\theta} = \left(A_2\cdot r^3\cdot(7-4\nu_s) + B_2\cdot r\right)\cdot\frac{dP_2(\cos\theta)}{d\theta},$$

$$u_\varphi^s = 0.$$

According to [11, 15] tension components at each point of the amorphous phase of polymer material can be represented as follows:

$$\sigma_r^{м} = \frac{1}{3}\cdot Q + \frac{2\cdot E_{м}}{1+\nu_{м}}\cdot\frac{D_0}{r^3} + \left(\frac{2\cdot E_{м}}{1+\nu_{м}}\cdot\left(\frac{6\cdot D_2}{r^5} - \frac{C_2}{r^3}\cdot(10-2\nu_{м})\right) + \frac{2}{3}\cdot Q\right)\cdot P_2(\cos\theta),$$

$$\sigma_{r\theta}^{м} = \left(\frac{2\cdot E_{м}}{r^3}\cdot C_2 - \frac{4\cdot E_{м}}{1+\nu_{м}}\cdot\frac{D_2}{r^5} + \frac{1}{3}Q\right)\cdot\frac{dP_2(\cos\theta)}{d\theta},$$

$$\sigma_{\theta}^{м} = \frac{2}{3}Q - \frac{E_{м}}{1+\nu_{м}}\frac{D_0}{r^3} - \left(\frac{2E_{м}}{1+\nu_{м}}\frac{C_2}{r^3}(1-2\nu_{м}) - \frac{9E_{м}}{1+\nu_{м}}\frac{D_2}{r^5} - \frac{2}{3}Q\right)\cdot P_2(\cos\theta) -$$

$$-\left(2E_{м}\cdot\frac{C_2}{r^3}\cdot\frac{1-2\nu_{м}}{1+\nu_{м}} + \frac{E_{м}}{1+\nu_{м}}\cdot\frac{D_2}{r^5}\right)\cdot\frac{dP_2(\cos\theta)}{d\theta}\cdot ctg\theta,$$

$$\sigma_{\varphi}^{м} = -\frac{E_{м}}{1+\nu_{м}}\frac{D_0}{r^3} + \frac{E_{м}}{1+\nu_{м}}\left(\frac{C_2}{r^3}(10-20\nu_{м}) - \frac{3D_2}{r^5}\right)\cdot P_2(\cos\theta) +$$

$$+\frac{E_{м}}{1+\nu_{м}}\left(\frac{C_2}{r^3}\cdot(2-4\nu_{м}) + \frac{D_2}{r^5}\right)\cdot\frac{dP_2(\cos\theta)}{d\theta}\cdot ctg\theta. \qquad (23)$$

where $E_{м}$ – elasticity modulus of amorphous matrix; $\nu_{м}$ – Poisson coefficient of the amorphous matrix; Q – uniform tension of spherulites interaction; D_0, D_2, C_2 – unknown constants that are of marginal conditions.

Equations (23) show that the tension, arising at some point in the amorphous matrix, decrease with distance from the beginning of the coordinate system. This is because the deformed spherulite has some influence on the amorphous phase of polymer that consists of microfibrils that connect spherulites. And the greater is the distance from the spherulite to the point of amorphous phase of a polymer, the less impact it has on the deformation of the spherulites.

Components of displacement vector for amorphous phase are represented as follows:

$$\mathbf{u}^{м} = \vec{\mathbf{e}}_r u_r^{м} + \vec{\mathbf{e}}_\theta u_\theta^{м} + \vec{\mathbf{e}}_\varphi u_\varphi^{м}. \qquad (24)$$

Components of displacement at each point of amorphous phase of polymer material can be represented as follows:

$$u_r^{м} = \frac{1-2\nu_{м}}{E_{м}} \cdot \frac{Q \cdot r}{3} - \frac{D_0}{r^2} + \left(\frac{C_2}{r^2} \cdot (10 - 8\nu_{м}) + \frac{2(1+\nu_{м})}{E_{м}} \cdot \frac{Q \cdot r}{3} - \frac{3D_2}{r^4} \right) \cdot P_2(\cos\theta),$$

$$u_\theta^{м} = \left((1-2\nu_{м}) \cdot \frac{2C_2}{r^2} + \frac{1+\nu_{м}}{E_{м}} \cdot \frac{Q \cdot r}{3} + \frac{D_2}{r^4} \right) \cdot \frac{dP_2(\cos\theta)}{d\theta}, \qquad (26)$$

$$u_\varphi^{м} = 0.$$

The unknown constants A_0, A_2, B_2, D_0, D_2, C_2 can be determined from the conditions of perfect contact of spherulites and amorphous matrix surfaces, which take place in case of contact of spherulites, ie when: $r = L_s/2 = a$:

$$u_\theta^{м} = u_\theta^{s};\ u_r^{м} = u_r^{s};\ \sigma_r^{м} = \sigma_r^{s};\ \sigma_\theta^{м} = \sigma_\theta^{s};\ \sigma_{r\theta}^{м} = \sigma_{r\theta}^{s}. \qquad (27)$$

Therefore, solving the system of equations (22)-(25), we can indicate the field of stress and strain of spherulites at any moment during uniaxial stretching of polymeric material.

There is the uniform tension of spherulites interaction Q in the systems of equations (23) and (25), that is not there in systems of equations (22) and (24). This can be explained as follows: the spherulites are influencing one another through the amorphous phase that surrounds them. As a result, in the amorphous matrix there is an additional stress that is caused by the interaction between the spherulites, because of the impact of specific load on polymeric material.

Satisfying the conditions for an ideal contact (27) at $r = d_s/2 = a$ and equating the coefficients of the Legendre polynomials, we obtain expressions for the unknown constants A_0, A_2, B_2, D_0, D_2, C_2 through the homogeneous stress interaction Q:

$$A_0 = Q\cdot\frac{-(1-\nu_м)}{2\left(E_s(1+\nu_м)+E_м(1-2\nu_s)\right)},$$

$$A_2 = 0,$$

$$B_2 = Q\cdot\frac{5(1-\nu_м)(1+\nu_м)(1+\nu_s)}{E_s(1+\nu_м)(8-10\nu_м)+E_м(7-5\nu_м)(1+\nu_s)},$$

$$C_2 = Q\cdot\frac{5r^3(1+\nu_м)(E_м(1+\nu_s)-E_s(1+\nu_м))}{6E_м\left(E_s(1+\nu_м)(8-10\nu_м)+E_м(7-5\nu_м)(1+\nu_s)\right)}, \qquad (28)$$

$$D_0 = Q\cdot\frac{r^3(1+\nu_м)(E_s(1-2\nu_м)-E_м(1-2\nu_s))}{3E_м\left(E_s(1+\nu_м)+2E_м(1-2\nu_s)\right)},$$

$$D_2 = Q\cdot\frac{r^5(1+\nu_м)(E_м(1+\nu_s)-E_s(1+\nu_м))}{E_м\left(E_s(1+\nu_м)(8-10\nu_м)+E_м(7-5\nu_м)(1+\nu_s)\right)}.$$

Substituting the meaning of the coefficients from (28) for Eqs. (20), (21), (23) and (26), we obtain a solution of the boundary problem of uniaxial stretching of an isotropic unbounded amorphous medium containing spherulite. As a result, we will have the expressions for the components of the displacement vector **u** and the stress tensor $\mathbf{T}_\sigma$:

– for a spherulite

$$\sigma_r^s = E_s\cdot Q\cdot\left(\frac{1-\nu_м}{E_s(1+\nu_м)+E_м(1-2\nu_s)}+\frac{10\left(1-\nu_м^2\right)}{E_s(1+\nu_м)(8-10\nu_м)+E_м(7-5\nu_м)(1+\nu_s)}\cdot P_2(\cos\theta)\right),$$

$$\sigma_{r\theta}^s = E_s\cdot Q\cdot\left(\cdot\frac{5\left(1-\nu_м^2\right)}{E_s(1+\nu_м)(8-10\nu_м)+E_м(7-5\nu_м)(1+\nu_s)}\right)\cdot\frac{dP_2(\cos\theta)}{d\theta},$$

$$\sigma_\theta^s = E_s\cdot Q\cdot\left(\frac{1-\nu_м}{E_s(1+\nu_м)+E_м(1-2\nu_s)}-\frac{5\left(1-\nu_м^2\right)}{E_s(1+\nu_м)(8-10\nu_м)+E_м(7-5\nu_м)(1+\nu_s)}\cdot\left(4P_2(\cos\theta)+\frac{dP_2(\cos\theta)}{d\theta}ctg\theta\right)\right),$$

$$\sigma_\varphi^s = E_s\cdot Q\cdot\left(\frac{1-\nu_м}{E_s(1+\nu_м)+E_м(1-2\nu_s)}+\frac{5\left(1-\nu_м^2\right)}{E_s(1+\nu_м)(8-10\nu_м)+E_м(7-5\nu_м)(1+\nu_s)}\cdot\left(2P_2(\cos\theta)+\frac{dP_2(\cos\theta)}{d\theta}ctg\theta\right)\right),$$

(29)

$$u_r^s = Q\cdot r\cdot(1-\nu_м)\left(\frac{1-2\nu_s}{E_s(1+\nu_м)+E_м(1-2\nu_s)}+\frac{10\,(1+\nu_м)(1+\nu_s)}{E_s(1+\nu_м)(8-10\nu_м)+E_м(7-5\nu_м)(1+\nu_s)}\cdot P_2(\cos\theta)\right),$$

$$u_\theta^s = Q\cdot r\cdot\frac{5\left(1-\nu_м^2\right)(1+\nu_s)}{E_s(1+\nu_м)(8-10\nu_м)+E_м(7-5\nu_м)(1+\nu_s)}\cdot\frac{dP_2(\cos\theta)}{d\theta},$$

$$u_\varphi^s = 0.$$

(30)

– for an amorphous matrix

$$\sigma_r^{м}=Q\cdot\left(\frac{1}{3}+\frac{2}{3}r\left(\frac{E_s(1-2\nu_{м})-E_{м}(1-2\nu_s)}{E_s(1+\nu_{м})+2E_{м}(1-2\nu_s)}\right)+\left(\frac{1}{3}+\frac{E_s(1+\nu_{м})-E_{м}(1+\nu_s)}{E_s(1+\nu_{м})(8-10\nu_{м})+E_{м}(7-5\nu_{м})(1+\nu_s)}\cdot\left(\frac{5}{3}(10-2\nu_{м})-12\right)\right)\cdot P_2(\cos\theta)\right),$$

$$\sigma_\varphi^{м}=-Q\cdot\left(\frac{E_s(1-2\nu_{м})-E_{м}(1-2\nu_s)}{3[E_s(1+\nu_{м})+2E_{м}(1-2\nu_s)]}-\frac{E_s(1+\nu_{м})-E_{м}(1+\nu_s)}{E_s(1+\nu_{м})(8-10\nu_{м})+E_{м}(7-5\nu_{м})(1+\nu_s)}\times\right.$$

$$\left.\times\left[\left(\frac{25}{3}(1-2\nu_{м})+3\right)\cdot P_2(\cos\theta)-\left(\frac{5}{3}(1-2\nu_{м})+1\right)\frac{dP_2(\cos\theta)}{d\theta}ctg\theta\right]\right),$$

$$\sigma_\theta^{м}=Q\cdot\left(\frac{2}{3}-\frac{E_s(1-2\nu_{м})-E_{м}(1-2\nu_s)}{E_s(1+\nu_{м})+2E_{м}(1-2\nu_s)}-\frac{2}{3}P_2(\cos\theta)-\frac{E_s(1+\nu_{м})-E_{м}(1+\nu_s)}{E_s(1+\nu_{м})(8-10\nu_{м})+E_{м}(7-5\nu_{м})(1+\nu_s)}\left(\frac{113}{12}P_2(\cos\theta)-\frac{8}{3}\frac{dP_2(\cos\theta)}{d\theta}ctg\theta\right)\right),$$

$$\sigma_{r\theta}^{м}=Q\cdot\left[\frac{1}{3}\frac{dP_2(\cos\theta)}{d\theta}-\frac{E_s(1+\nu_{м})-E_{м}(1+\nu_s)}{E_s(1+\nu_{м})(8-10\nu_{м})+E_{м}(7-5\nu_{м})(1+\nu_s)}\cdot\left(\frac{5}{6}(1+\nu_{м})-4\right)\cdot\frac{dP_2(\cos\theta)}{d\theta}\right].$$

(31)

$$u_r^{м}=Q\cdot r\cdot\left[\frac{1-2\nu_{м}}{3\,E_{м}}-\frac{(1+\nu_{м})(E_s(1-2\nu_{м})-E_{м}(1-2\nu_s))}{3\cdot r\cdot E_{м}(E_s(1+\nu_{м})+2E_{м}(1-2\nu_s))}+\frac{2(1+\nu_{м})}{3\,E_{м}}\cdot P_2(\cos\theta)-\right.$$

$$\left.-\frac{(1+\nu_{м})(E_s(1+\nu_{м})-E_{м}(1+\nu_s))}{E_{м}(E_s(1+\nu_{м})(8-10\nu_{м})+E_{м}(7-5\nu_{м})(1+\nu_s))}\cdot\left(\frac{5}{6}(1-8\nu_{м})-3\right)P_2(\cos\theta)\right],$$

$$u_\theta^{м}=Q\cdot r\cdot\left[\frac{1+2\nu_{м}}{3\,E_{м}}-\frac{(1+\nu_{м})(E_s(1+\nu_{м})-E_{м}(1-2\nu_s))}{E_{м}(E_s(8-10\nu_{м})(1+\nu_{м})+E_{м}(7-5\nu_{м})(1+\nu_s))}\left(\frac{5}{3}(1-2\nu_{м})+1\right)\right]\cdot\frac{dP_2(\cos\theta)}{d\theta},$$

$$u_\varphi^{м}=0.$$

(32)

To determine the homogeneous interaction stress Q, we use the method of successive regularization [11], which allows us express the potential energy of the elastic deformation U through the surface integral:

$$U=\frac{1}{2V}\sum_{k=1}\int_{V_k}\sigma_{ik}\varepsilon_{ik}\,d\upsilon=\frac{1}{2V}\sum\int_{S_0}\sigma_{in}u_i\,df_n\,, \tag{33}$$

where df_n is an element with normal n to the surface S_0, bounding the volume V; σ_{in}, u_i – the components of the stress tensor $\mathbf{T}_{\boldsymbol{\sigma}}$ and the displacement vector $\mathbf{u}$, acting on the surface S_0. Using the first representation of elastic energy through the average stress meanings $\overline{\sigma}_1$ and deformations $\overline{\varepsilon}_1$

$$U=\frac{1}{2}\overline{\sigma}_1\overline{\varepsilon}_1\,. \tag{34}$$

and expressing the components of the displacement vector $\mathbf{u}^{M}$ in the spherical coordinate system through the average meaning of the deformation $\bar{\varepsilon}_1$, we find the elastic potential for the amorphous-crystalline body of the spherulite structure

$$\frac{1}{2V}\iint\limits_{(S)}\left[\sigma_r^{M}\,\bar{\varepsilon}_1\,r\left(\cos^2\theta-\nu_{M}\sin^2\theta\right)-\sigma_{r\theta}^{M}\,\bar{\varepsilon}_1\,r\left(1+\nu_{M}\right)\sin\theta\cos\theta\right]r^2\sin\theta\,d\theta\,d\varphi=\frac{1}{2}\bar{\sigma}_1\bar{\varepsilon}_1. \tag{35}$$

Substituting into the formula obtained the meaning of the stresses σ_r^{M} and $\sigma_{r\theta}^{M}$ from equation (31), integrating (35) on φ in the interval $0\le\varphi\le 2\pi$, and on θ in the interval $0\le\varphi\le\pi$ (thus reducing the unit cell to the concentric with the spherulite sphere with the radius r), we determine the homogeneous stress interaction Q between the spherulites through the given average stretching stresses $\bar{\sigma}_1$:

$$Q=\frac{\bar{\sigma}_1}{1+\frac{2}{3}\chi^2\left(\frac{\left(1-2\nu_{M}\right)\left(E_s\left(1-2\nu_{M}\right)-E_{M}\left(1-2\nu_s\right)\right)}{E_s\left(1+\nu_{M}\right)+2E_{M}\left(1-2\nu_s\right)}+\frac{\left(7-5\nu_{M}\right)\left(1+\nu_{M}\right)\left(E_s\left(1+\nu_{M}\right)-E_{M}\left(1+\nu_s\right)\right)}{E_s\left(1+\nu_{M}\right)\left(8-10\nu_{M}\right)+E_{M}\left(7-5\nu_{M}\right)\left(1+\nu_s\right)}\right)}. \tag{36}$$

The components of the stress tensor $\mathbf{T}_{\boldsymbol{\sigma}}$ and the displacement vector $\mathbf{u}$ can be found from Eqs. (29), (30), (31) and (32) by substituting for them the meaning of the interaction stress from Eq. (36). The components of the strain tensor $\mathbf{T}_{\varepsilon}$ are obtained from the following equation:

$$\begin{aligned}&\varepsilon_r=\frac{\partial u_r}{\partial r};\quad \varepsilon_\theta=\frac{1}{r}\frac{\partial u_\theta}{\partial\theta}+\frac{u_r}{r};\quad \varepsilon_\varphi=\frac{u_\theta}{r}ctg\theta+\frac{u_r}{r};\\ &\varepsilon_{r\theta}=\frac{1}{r}\frac{\partial u_r}{\partial\theta}+\frac{\partial u_\theta}{\partial r}-\frac{u_\theta}{r};\quad \varepsilon_{\theta\varphi}=\varepsilon_{\varphi r}=0.\end{aligned} \tag{37}$$

In the structure of a spherulite E, we replace the right side of equation (35) with the second energy representation [11], and the stresses σ_r^{M} and $\sigma_{r\theta}^{M}$ in the integrand function with the average stresses $\bar{\sigma}_1$:

$$\sigma_r^{M}=\bar{\sigma}_1\cos^2\theta,\qquad\qquad \sigma_{r\theta}^{M}=-\bar{\sigma}_1\sin\theta\cos\theta.$$

As a result, we get

$$U=\frac{\overline{\sigma}_1}{2V}\iint\limits_{(S)}\left(u_r^{м}\cos^2\theta-u_{r\theta}^{м}\sin\theta\cos\theta\right)r^2\sin\theta\,d\theta d\varphi=\frac{\overline{\sigma}_1^2}{2E}. \quad (38)$$

Substituting for (38) the values of the displacements $u_r^{м}$ and $u_\theta^{м}$ from (32), the value of the homogeneous interaction stress Q from (36) and solving expression (38) in relation to E, we find the elastic modulus of the amorphous crystal environment of the spherulite structure:

$$E=E_{м}\frac{1+\frac{2}{3}\chi^2\left(\frac{(1-2\nu_{м})(E_s(1-2\nu_{м})-E_{м}(1-2\nu_s))}{E_s(1+\nu_{м})+2E_{м}(1-2\nu_s)}+\frac{(7-5\nu_{м})(1+\nu_{м})(E_s(1+\nu_{м})-E_{м}(1+\nu_s))}{E_s(1+\nu_{м})(8-10\nu_{м})+E_{м}(7-5\nu_{м})(1+\nu_s)}\right)}{1-\frac{1}{3}\chi^2\left(\frac{(1+\nu_{м})(E_s(1-2\nu_{м})-E_{м}(1-2\nu_s))}{E_s(1+\nu_{м})+2E_{м}(1-2\nu_s)}-\frac{4(4-5\nu_{м})(1+\nu_{м})(E_s(1+\nu_{м})-E_{м}(1+\nu_s))}{E_s(1+\nu_{м})(8-10\nu_{м})+E_{м}(7-5\nu_{м})(1+\nu_s)}\right)}. \quad (39)$$

and for the bulk modulus of elasticity:

$$E_V=E_{м}\frac{E_s(1+\nu_{м})+2\chi^2E_s(1-2\nu_{м})+2E_{м}(1-\chi^2)(1-2\nu_s)}{3\left[E_s(1-\chi^2)(1-2\nu_{м})(1+\nu_{м})+\chi^2E_{м}(1+\nu_{м})(1-2\nu_s)+2E_{м}(1-2\nu_{м})(1-2\nu_s)\right]}. \quad (40)$$

The elastic properties of any isotropic material are due to two independent constants. The second constant, the bulk modulus E_V, is determined from the consideration of uniform expansion ($\sigma_x=\sigma_y=\sigma_z=\overline{\sigma}$) of an amorphous crystalline isotropic medium of a spheruline structure. Repeating the reasoning mentioned above, we obtain expressions for the stress characterizing the homogeneous interaction between spherulites Q:

$$Q=\frac{(1-2\nu_s)(1+\nu_{м})\left[E_s(1+\nu_{м})+2E_{м}(1-2\nu_s)\right]}{E_s(1+\nu_{м})+2\chi^2E_s(1-2\nu_{м})+2E_{м}(1-\chi^2)(1-2\nu_s)} \quad (41)$$

The effective constants E_V and E make it possible to determine other elastic constants of the amorphous crystalline polymer – the Poisson coefficient ν and the shear modulus G:

$$\nu = \frac{3E_V - E}{6E_V}; \qquad G = \frac{3E_V E}{9E_V - E}. \tag{42}$$

Expressions (39)...(42) make it possible to predict the elastic properties of amorphous crystalline polymers depending on the degree of crystallinity χ, and require in the first approximation the knowledge of the elastic properties of the amorphous phase $E_м$, $\nu_м$ and spherulites E_s, ν_s. If the elastic constants of different polymers in the amorphous state can be measured or taken from reference literature, then the use of the elasticity modulus of the crystal lattice of polymers E_c as the constant of the crystalline phase, as is done in most papers [16…21], in our opinion, is not entirely correct. Firstly, this is associated with the complex structure of spherulites [7], which is the third level of SMS, after crystallites and lamellas, in which both crystallites and lamellas, having a different orientation in space, are in the inter-amorphous interlayers, which makes it impossible to examine neither spherulites nor other structural formations as single crystalline morphoses. Secondly, in some works, for example [3, 4, 22], it has been established that the spherulites deform with the rest of the polymer mass as a single unit (Fig.2) [22], even in the case of large final deformations, stretching in the direction of the load and only slightly lagging behind the deformation of the macro sample. When the ratio between the elastic constants of crystallites E_c and the amorphous phase $E_м$ is, for example, for polyethylene $\sim 5 \cdot 10^3$ ($E_c / E_м = 250 \cdot 10^3 / 0{,}05 \cdot 10^3$ MPa) [16], this phenomenon would not be observed.

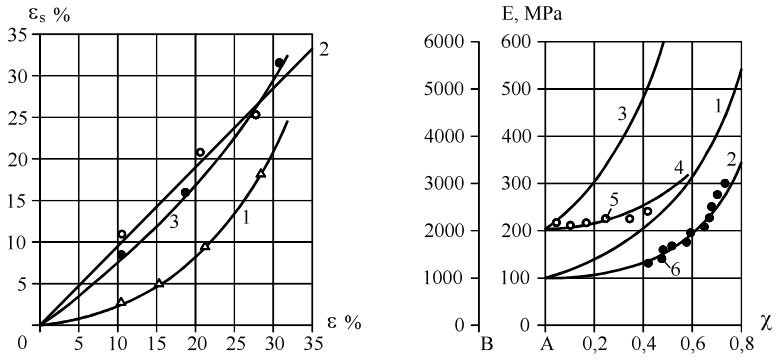


Figure 4 – Dependence of deformation of spherulites ε_s on the deformation ε of polypropylene film (curves 1, 3) at T = 20 (△, 1; ○, 2) and T = 90 (●, 3)

Figure 5 – Dependences of the elastic modulus E of polyethylene (●, scale of values of A) and polypropylene (○, scale of meanings of B) on the degree of crystallinity χ

1-4 - data obtained in the work; 5, 6 - results from [23, 21], respectively

As elastic constants of spherulites E_s, it is proposed to use the values of the elastic constants determined from Eqs. (39) ... (42) for the degree of crystallinity of $\chi_{\max}$, corresponding to the maximum possible for a given polymer, under the assumption of the ideal structure of the spherulites, When substituting, for example, in Eq. (39) the quantities E_c as E_s^*. The obtained meanings of the elasticity modulus E^* was subsequently used as the elasticity modulus of spherulites E_s in the prediction of elastic properties.

Summary & Conclusions

The verification of the model described above was carried out on polyethylene and polyethylene terephthalate, which are representatives of highly crystalline and intermediate crystalline polymers. The dependence of the polyethylene modulus of elasticity (curves 1 and 2, the scale of meanings *A*) and polyethylene terephthalate (curves 3 and 4, the scale of meanings of *B*) on the degree of crystallinity of χ, were shown in Fig. 4. Curves 1 and 3 were obtained in the approximation of the ideal structure of spherulites ($E_c = E_s^*$), and curves 2 and 4 were obtained using the results of the first approximation ($E_s = E^*$) as E_s and ν_s. The initial data for the construction of curves 2 and 4: for polyethylene $E_s = 1020$ MPa, $\nu_s = 0{,}2$, $E_{\text{M}} = 77$ MPa, $\nu_M = 0{,}39$; for polyethylene terephthalate $E_s = 8239$ MPa, $\nu_s = 0{,}2$, $E_{\text{M}} = 2000$ MPa, $\nu_M = 0{,}39$.

The analysis of data in Fig. 5 showed a satisfactory coincidence of the predicted and measured meaning of the Young's modulus, the largest spread of meaning does not exceeded 12% for polyethylene terephthalate and 15% for polyethylene.

Thus, the presented model satisfactorily reflects the spheruline structure of amorphous-crystalline polymers, even in the approximation of homogeneous interaction. The elastic constants *E, K*, obtained as a result of the construction of the model, are used as input data for the construction of the SMS mode, formed in the process of orientational drawing of amorphous crystalline polymers of the spheruline structure.

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