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A FRACTAL MODEL FOR THERMAL SHRINKAGE OF ORIENTED POLYMERS

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A relationship between the amount of thermal shrinkage and the structural parameters of polyethylene extruded in the solid state and polymerization-filled compositions based on it is studied. It is shown that thermal shrinkage is determined by the fractal dimension of the polymer structure and the degree of stretching of the molecular chain.

Investigation of thermal-shrinkage characteristics gives valuable information on the structural changes caused by orientation processes in polymers [1]. However, most papers devoted to this problem have studied only qualitative regularities of these processes. In recent years, fractal analysis [2] has been successfully employed for quantitative description of the relationship between the structure and properties of polymers. We used this approach to establish a relationship between the thermal shrinkage and structural parameters of specimens of superhigh-molecular-weight polyethylene (SHMWPE) and polymerization-filled compositions based on it, oriented by solid-state extrusion [3]. The processing method of [3], which combines transformation of the starting powder to a monolithic state and its orientational extrusion, yields high values of rigidity and strength of the articles produced [4].

In our experiments, SHMWPE with a molecular weight of $\sim 10^6$ and the polymerization-filled compositions SHMWPE–Al and SHMWPE–bauxite are used. The particle size of the filler is 10 μm, and the concentrations (by mass) are 70 and 45%, respectively.

Test specimens were prepared by solid-state extrusion by the following scheme [4]: preliminary compaction of a powder specimen in a cylindrical mold, free heating of the compacted specimen to 403 K (SHMWPE) or 393 K (compositions based on SHMWPE), extrusion through a die heated to the same temperatures using a high-pressure container. At the indicated temperatures, extrusion of a polymer workpiece through a die with an orifice diameter smaller than the diameter of the workpiece ensured production of monolithic specimens with a typical anisotropic structure oriented along the axis of extrusion [5]. The degree of extrusion elongation was varied using dies of different diameters and was calculated from the formula $\lambda = d_s^2/d_0^2$, where d_s and d_0 are the diameters of the specimen and the die opening, respectively. For comparison, specimens produced by pressing (pressing temperature 433 K and pressure 100 MPa) were tested.

Thermal shrinkage was studied on cylindrical extrudates of diameters 5–12 mm and length 15 mm after heating them in glycerin with exposure to each test temperature for 15 min. Since, upon heating, the length of such an oriented polymer specimen decreases with simultaneous increase in its diameter (recovery of the shape preceding extrusion), $\psi = (d_2 - d_1)/d_2$ (d_1 and d_2 are the extrudate diameters before and after exposure to the given temperature) was used as the parameter that reflects the shrinkage process.

Mechanical properties were measured for cylindrical specimens of diameter 4.5 mm and working length 30 mm under three-point bending. The tests were performed at 293 K and a maximum strain rate of $2.5 \cdot 10^{-3}$ sec^{-1}.

The number of specimens used to determine thermal shrinkage or mechanical properties was no less than five for each chosen value of λ. Here the spread of values of the strain–strength characteristics and the

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quantity ψ did not exceed 10%.

Ball [6] studied the elasticity of colloidal aggregates within the framework of fractal models and introduced two characteristic scales of length for the structure (a_T and ξ) assuming that the structure did not change for scales smaller than a_T and colloidal aggregates are homogeneous for scales larger than ξ. These assumptions made it possible to obtain a relation between the linear shrinkage ψ and the structural parameters of a polymer after gel formation:

$$\psi = (\xi/a_T)^{(d'_f - d_f)/d'_f}, \tag{1}$$

where d_f and d'_f are the fractal dimensions of the polymer structure before and after gel formation. As is known [7], unlike mathematical fractals, for real fractals, there are two natural limiting scales of length (in the model of [6], a_T and ξ correspond to them). The lower limit is associated with the finite size of structural elements, and the upper limit with the nonuniform tendency of d_f to the limit as a function of the linear scale. It has been established experimentally [8, 9] that the polymer structure is a fractal in the region of linear scales from $3 \cdot 10^{-8}$ to $5 \cdot 10^{-7}$ m. This range correlates well with the characteristic dimensions involved in the cluster model of [2], where the lower limit is the length of the statistical segment l_{stat} and the upper limit is the distance between the contacts R_{segment}. Since Eq. (1) includes only structural parameters and does not contain factors that indicate the character of the action, we can write

$$\psi = (R_{\text{segment}}/l_{\text{stat}})^{(d'_f - d_f)/d'_f}. \tag{2}$$

The ratio $R_{\text{segment}}/l_{\text{stat}}$ is the self-similarity coefficient Λ_i of the polymer structure. Hence, the identity [10]

$$\Lambda_i = R_{\text{segment}}/l_{\text{stat}} = L_{\text{segment}}/R_{\text{segment}} \tag{3}$$

is valid. Here L_{segment} is the length of the macromolecule region between the contacts and l_{stat}, l_{segment}, and R_{segment} are the successive scales of the length of the polymer structure [10].

Since the ratio $L_{\text{segment}}/R_{\text{segment}}$ is the maximum degree of elongation of the molecular chain λ_{m} between the contact nodes [11], Eq. (3) reduces to the form

$$\xi/a_T = \lambda_{\text{m}}. \tag{4}$$

The quantity λ_{m} is easily determined by the procedure of [1]:

$$\lambda_{\text{m}} = L/L_0. \tag{5}$$

Here L is the length of the specimen after thermal shrinkage and L_0 is the length of the specimen before extrusion. Since in filled compositions only the polymer matrix is deformed, the true value of λ_{m} is higher for them. The effect of the filler can be taken into account by introducing the corrected value of molecular elongation

$$\lambda_{\text{m}}^{\text{c}} = \lambda_{\text{m}}/1 - \varphi_{\text{fill}}, \tag{6}$$

where φ_{fill} is the volumetric degree of filling. The fractal dimension of the polymer structure d_f is connected with the Poisson ratio μ by the relation [2]

$$d_f = (d-1)(1+\mu). \tag{7}$$

Here d is the dimension of the space in which the fractal is placed (in our given case, obviously, $d = 3$). In turn, this quantity can be estimated from results of mechanical tests using the relation [12]

$$\frac{\sigma_{\text{yield}}}{E} = \frac{1-2\mu}{6(1+\mu)}, \tag{8}$$

where σ_{yield} is the yield stress and E is the elastic modulus. Formulas (1)-(8) allow one to obtain dependences of the structural parameters of the polymers studied and the quantity ψ on the degree of extrusion elongation.

Figure 1 shows curves of $d_f(\lambda)$ for the polymerization-filled compositions SHMWPE-Al and SHMWPE-bauxite (points 1 and 2). Obviously, extrudates show significantly larger values of d_f compared with the values of the reference specimens, which practically do not change with increase in λ. The value

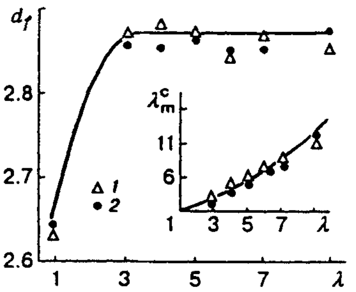

Fig. 1

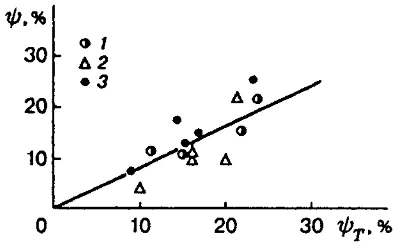

Fig. 2

$\mu \approx 0.43$ corresponds to $d_f \approx 2.86$, as is typical of polymers in a yield state [2]. Consequently, the structure of the extrudates studied is essentially a "frozen yield" structure, i.e., a state with a high resistance against shear (large values of elastic moduli) but with a structure similar to a yielding structure.

The curve of $\lambda_m^c(\lambda)$ given in Fig. 1 shows that the degree of molecular elongation increases monotonically with increase in λ. The function $\psi(\lambda)$ exhibits the same behavior.

A comparison of the experimental values of ψ and the values of ψ_T calculated from Eq. (1) (Fig. 2) shows a certain correlation between them for all the materials studied [SHMWPE, SHMWPE-Al, and SHMWPE-bauxite (points 1-3)].

The results obtained in this paper lead to the conclusion that the thermal shrinkage of SHMWPE extrudates and filled compositions based on it is determined by two parameters: d_f, which characterizes the change in the hypermolecular structure during the extrusion process, and λ_m, which describes structural changes at the molecular level.

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