Effect of deformation on the parameters of solid-solid phase transitions in polytetrafluoroethylene

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The influence of hydroextrusion and orientation drawing on the parameters of solid-solid phase transitions in polytetrafluoroethylene has been studied by differential scanning calorimetry. A comparative analysis of the heat capacity peaks based on the theory of diffuse first-order phase transitions showed a significant increase in the period of the macromolecular helix from the nano-level in the original polymer to the micro-level in the oriented one. In the latter, the effect of the formation of a „superhelix" was found. An assumption was made about the mechanism for the supermolecular structure transformation leading to the observed effect.

Keywords: phase transition, polytetrafluoroethylene, supermolecular structure, hydroextrusion, orientation drawing, differential scanning calorimetry.

Among all the known polymers, polytetrafluoroethylene (PTFE) is characterized by the highest chemical resistance and biological inertness due to which it has found wide practical application in various fields including radio and electrical engineering, medicine, as chemical fibers, etc. [1]. An important aspect of employing materials of this type is the possibility of predicting their physical and mechanical properties, including strength characteristics. As it is known, the latter ones are determined by the structural peculiarities of the polymer [2].

In the temperature range of solid-solid transitions $(250-350\,\text{K})$, the PTFE structure undergoes considerable changes with increasing temperature. In the crystalline part of the polymer, a double phase transition (PT) takes place: first, there is observed a first-order transition from a structure with a triclinic unit cell existing at $T < T_1$ to a structure whose molecular packing is close to the hexagonal one. At a higher temperature $(T_2\ (T_2 > T_1))$, a second-order PT occurs which is associated with a change in the helical PTFE molecule conformation, namely, an increase in the helix period [3]. In this work, the effect of hydroextrusion and orientation drawing on the parameters of solid-solid PT in PTFE was studied by differential scanning calorimetry (DSC).

Thermodynamic parameters of the PTFE samples were determined with calorimeter DSC-500 produced by („Spetzpribor", Samara, Russia) in the nitrogen atmosphere at the scanning speed of $2\,\text{K/min}$. The temperature scale was calibrated to the melting points of ice $(273.1\,\text{K})$ and indium $(429.7\,\text{K})$, the heat flow scale was calibrated to the leucosapphire heat capacity. The measurements were performed in the temperature range of $250-640\,\text{K}$. The test sample weight was below $5\,\text{mg}$, which made lower the

sample thermal resistance and, hence, reduced the systematic error [4]. Based on the peak areas in the experimental dependence $C_p(T)$, the transition enthalpy ΔH and entropy ΔS were determined via relations $\Delta H_{exp} = \int C_p(T)dT$ and $\Delta S_{exp} = \int C_p(T)d(\ln T)$. The degree of crystallinity χ was calculated as $\chi = 100\Delta H_m/\Delta H_m^0$, where ΔH_m is the experimentally measured melting enthalpy, $\Delta H_m^0 = 69\,\text{J/g}$ is the melting enthalpy of the perfect PTFE crystal [3].

The PTFE samples furnished for calorimetric tests by „Formoplast" LLC were prepared in the following way.

1. As the original sample (sample No. 1), PTFE sample premelted at $620\,\text{K}$ and slowly cooled to room temperature T_{room} with the rate of $1\,\text{K/min}$ was used.

2. As a precursor for the next sample, there was used a polymer pre-subjected to hydroextrusion at the pressure of $52.7\,\text{MPa}$, extrusion drawing ratio of 2.8 and temperature of $393\,\text{K}$, which resulted in formation of rods from which films $< 0.5\,\text{mm}$ thick (sample No. 2) were cut.

3. After that, film No. 2 was uniaxially drawn at room temperature up to drawn ratio of ~ 9 with formation of a „neck" (sample No. 3).

The DSC curves measured in the temperature range of $250-330\,\text{K}$ are presented in Fig. 1; they allowed characterizing thermodynamic parameters of the endothermic doublet for each sample.

As the figure shows, all the curves exhibit the double endothermic effect in the room temperature range at T_1 and T_2. It is known [5] that PTFE undergoes an unusual solid-solid transition in the temperature range of $282-303\,\text{K}$ during which first there occurs a first-order transition from the structure with the triclinic unit cell to the hexagonal structure and then a second-order PT associated with variation in the helical chirality of the
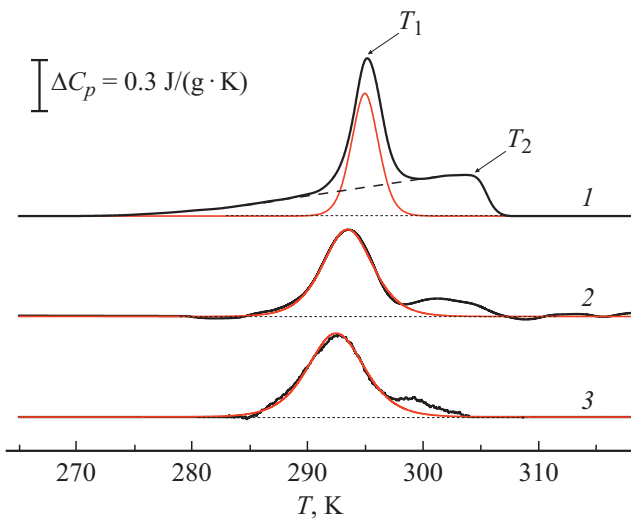
Figure 1. DSC curves of PTFE obtained during heating. The numbers of curves correspond to the sample numbers. Bold black lines represent experimental data, thin red curves were obtained by calculation. The colored figure is given in the electronic version of the paper.

PTFE crystal long-chain molecule, namely, with changing in the crystal symmetry element. The endothermic effect at temperature T_1 is associated with the first-order PT manifesting itself in the DSC curve as a symmetric relatively narrow diffuse Λ--like peak at temperature T_1, while the second-order PT appears in the DSC curve in the form of a broad diffuse λ-like peak at temperature T_2.

The first peak was analyzed according to the thermodynamic self-consistent field theory as applied to the Λ-like diffuse first-order PTs [6,7].

In the framework of this theory, the relation describing the temperature dependence of heat capacity has the following form:

$$\Delta C_p(T) = 4\Delta C_m \exp\left[B(T - T_1)/T_1\right]$$
$$\times \left[1 + \exp\left[B(T - T_1)/T_1\right]\right]^{-2}, \qquad (1)$$

where T_1 is the temperature of the first-order PT, ΔC_m is the maximal heat capacity at $T = T_1$, B — is the athermic parameter.

The heat capacity was calculated for each sample via (1) for each peak with T_1 and ΔC_m that are the maximal temperature and amplitude of a peak. Fig. 1 represents the calculations with thin red lines. The best agreement between the calculated and experimental dependences was observed at the parameter B values listed in the table.

Parameter B comprised in (1) bears the most interesting information on the PT physical nature since it is related with the peak of heat capacity $\Delta C_m = q_0 B/4T_1$ and transformation unit volume ω (the new phase nucleus) by expression $B = \omega \rho q_0/kT_1$, where q_0 is the transition heat, k is the

Boltzmann constant, ρ is the density. Parameter ω appears to be a structure−sensitive parameter since it defines the volumes of the new phase nuclei in the materials with diffuse PTs. Using the given relations, it is possible to find volumes ω (the PTFE crystal density is $\rho \sim 2\,\mathrm{g/cm^3}$ [3]). The calculations obtained via those relations are presented also in the table.

Comparing the ω values presented in the table, we can see that unit volumes of the new-phase nucleation regions associated with the solid-solid first-order transition are significantly smaller in samples No. 2 and 3 than in original sample No. 1. At the same time, extrusion and drawing lead to a considerable increase in the crystallinity. We assume that such an inconsistent behavior may be explained by an evolution of the polymer supermolecular structure (SMS) during treatment.

As per the crystallinity data presented in the table, the amorphous (disordered) part of the original polymer SMS sample is about a half of the polymer volume. The crystalline part is contained in microfibrils whose length along the macromolecule axis is several hundreds of nanometers, their cross dimension being several tens of nanometers (Fig. 2). Internal structure of the PTFE microfibrils has not been sufficiently studied yet. By analogy with the microfibril structure in well-studied polyethylene, crystalline regions inside each microfibril are assumed to alternate with disordered regions or regions with high content of defects. Indirect proof of this fact may be obtained by comparing the data on unit volumes ω presented in the table with microfibril volumes which significantly exceed ω. Hence, a single microfibril contains a considerable number of crystalline regions separated either by regions with a large number of defects forming the phase surface or by disordered regions. The latter consist of tie molecules connecting the neighboring crystallites and of irregular loops with different degree of coiling. In our opinion, on the surfaces of microfibril crystalline regions there get formed helical „motifs" repeating the helicity of an individual polymer macromolecule. This fact may affect the interaction between microfibrils and, hence, properties of materials fabricated from PTFE.

Extrusion and drawing lead to changes in the polymer SMS because stresses induce orientation of the amorphous-part microfibrils and individual macromolecules along the extrusion and drawing axis. Orientation of relatively rigid microfibrils are inevitably followed by bends and accumulation of internal defects under the action of shear stresses, which causes the observed decrease in ω. More flexible microfibrils in the polymer amorphous part form during orientation local areas with parallel packing, where „cold" crystallization occurs during orientation at T_{room}. Thus, seemingly contradictory combination of two processes is connected with changes in SMS in the amorphous and crystalline parts of the polymer.

As noticed above, the endothermic effect at temperature T_2 is induced by the second-order PT caused by variation in conformational entropy ΔS. The latter is related to the
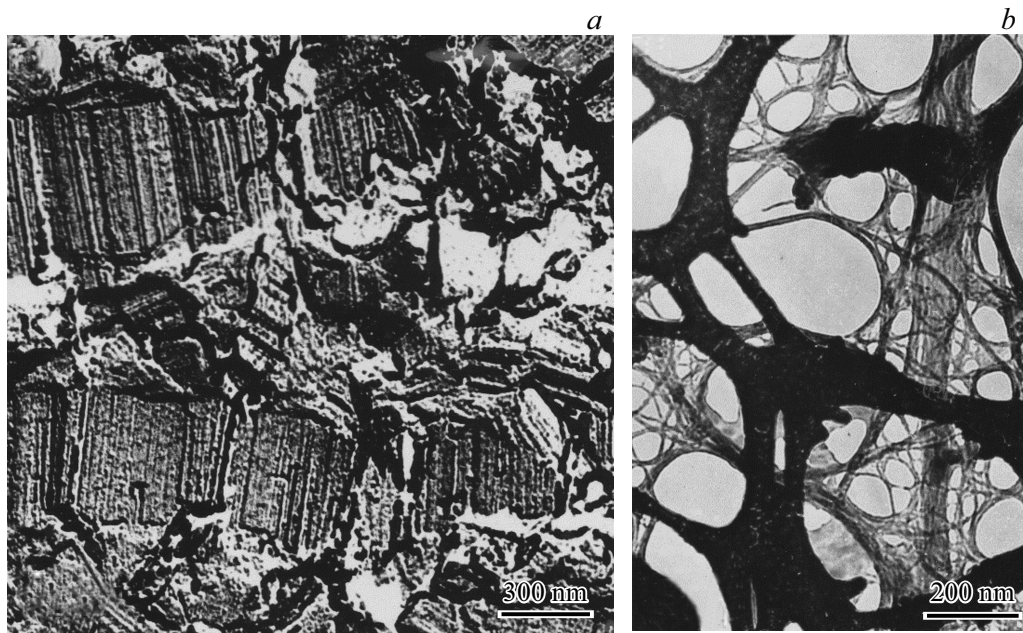
Figure 2. Electron-microscopic images of the Teflon strainless structure (*a*) and of the ultrasound-dispersed oriented Teflon (*b*).

Thermodynamic parameters of solid-solid transitions in PTFE samples

Sample No.	T_1, K	ΔC_m, J/(g·K)	B	ΔH_1, J/g	ω, nm^3	T_2, K	ΔH_2, J/g	ΔS, J/(K·g)	Z	χ, %
1	294.3	0.85	450	2.22	185	304.4	6.28	0.0160	14−15	51
2	293.5	0.52	205	2.98	130	301.2	0.84	0.0028	~ 90	68
3	292.5	0.5	180	3.25	105	298.8	0.20	0.0006	> 400	75

chain helix period for one mole of N_a –CF$_2$– links by expression $\Delta S = (N_a k \ln 2)/Z$, where Z is the number of –CF$_2$– links per helix period [8]. Using experimental values of ΔS presented in the table, it is possible to estimate Z for the samples under study. It turned out that estimation of Z for the original sample No. 1 gives $14-15$ links of the CF$_2$ groups in one helix period, which agrees well with literature data [3].

As shown in Fig. 1 (curve *2*), intensity of the transition at T_2 in sample No. 2 decreases considerably. A similar effect was observed on PTFE samples subjected to γ radiation and doping with silicon dioxide [9]. Because of a decrease in the PT entropy, the estimation of Z via the above-presented relation gives $Z \sim 90$, which means that the helix period has multiply increased as compared with the original sample.

The DSC curve for the drawn film still exhibits the transition at T_1, while the transition at T_2 for sample No. 3 almost fully disappears and manifests itself only in the form of a small „preshoulder" of the T_1 peak on the high-temperature side (curve *3* in Fig. 1). In this case, it is rather difficult to estimate Z, since the magnitude of the transition thermal effect is comparable with the instrument measurement error. Estimation of this quantity provides

values $Z > 400$ which indicate that the original helical polymer molecule approaches the conformation of the „flat zigzag" type, and the helicity appears no longer on the nano- but on the macroscopic scale. For the „flat zigzag" conformation, the above-described conformational transition at T_2 is to be absent since, when $Z \to \infty$, conformational entropy is $\Delta S \to 0$.

In addition to variations in the thermodynamic parameters of solid-solid transitions in sample No. 3, formation of an unusual helix on the entire sample scale was visually revealed (Fig. 3, *a*). The period of this helix significantly exceeds the macromolecule helix period in the microfibril crystalline part. Formation mechanism for the macroscopic helix or „superhelix" is unclear. In the framework of this study, it is possible to assume that formation of the macroscopic helix is connected with specific features of the mechanism of microfibril interaction and „packing" in the process of the „neck" formation during drawing.

Previously it was noticed that on the surfaces of microfibril crystalline regions there get formed helical „motifs" repeating the helicity of the individual polymer macro-molecule (Fig. 3, *b*). As a result, when microfibrils are stacked in parallel, a variational cohesive Van-der-Waals
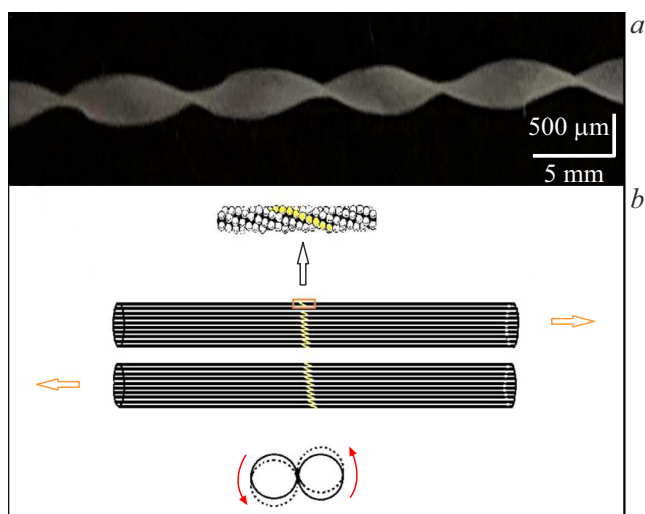
Figure 3. Optical microphotograph of PTFE sample No. 3 demonstrating the „superhelix" (*a*), and schematic diagram of the mechanism for its formation (*b*).

interaction takes place (a weaker one between microfibril regions with mismatched helicity „motifs", a stronger one between regions with matched „motifs").

Formation of the „neck" and significant elongation of the sample occur due to slipping of microfibrils with respect to each other. If the „motifs" of neighboring microfibrils coincide, the slippage will be accompanied by their slight rotation about the axis, which resembles the mechanism of longitudinal motion in the helical gear. In our opinion, those minor turns between individual microfibrils underlie formation of the macroscopic „superhelix". Since the number of contacts is of the statistic character, the distance between the „strong" contacts is expected to significantly exceed the helix period in the individual polymer macromolecule. In this case, the period of this „superhelix" will be defined by not only the polymer macromolecule helix period but also by the kinetic parameters of drawing, namely, temperature and time. Nowadays, additional investigations are needed to reveal the procedure of the „siperhelix" formation.

Conflict of interests

The authors declare that they have no conflict of interests.

References

[1] Yu.K. Mashkov, Z.N. Ovchar, V.I. Surikov, L.F. Kalistratova, *Kompozitsionnye materialy na osnove politetraftoretilena* (Mashinostroenie, M., 2005). (in Russian)

[2] V.R. Regel, A.I. Slutsker, E.E. Tomashevsky, *Kineticheskaya priroda prochnosti tverdykh tel* (Nauka, M., 1974). (in Russian)

[3] B. Wunderlich, *Macromolecular physics* (Academic Press, N.Y., 1980), vol. 3.

[4] V.A. Bershtein, V.M. Egorov, *Differential scanning calorimetry of polymers: physics, chemistry, analysis, technology* (Ellis Horwood, N.Y., 1994), p. 253.

[5] E.S. Clark, in *Physical properties of polymers handbook*, ed. by J.E. Mark (Springer, N.Y., 2007), p. 619–624. DOI: 10.1007/978-0-387-69002-5_38

[6] M.E. Fisher, *The nature of critical points* (University of Colorado Press, 1965).

[7] G.A. Malygin, Phys. Usp., **44** (2), 173 (2001). DOI: 10.1070/pu2001v044n02ABEH000760.

[8] V.M. Egorov, P.N. Yakushev, Phys. Solid State, **60** (9), 1874 (2018). DOI: 10.1134/S1063783418090093.

[9] V.M. Egorov, P.N. Yakushev, M.A. Arsent'ev, A.S. Smolyanskii, Phys. Solid State, **62** (8), 1506 (2020). DOI: 10.1134/S1063783420080132.

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