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THE STRUCTURE OF HIGH-STRENGTH ULTRAHIGH-MOLECULAR-WEIGHT POLYETHYLENE FIBRES FABRICATED BY THE GEL-SPINNING METHOD

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In orientation drawing of UHMPE (ultrahigh-molecular-weight polyethylene) fibres, conformational rearrangements take place that enrich the conformation set of the polymer with T-isomers and impoverish it in G-isomers. The basic increase in the orientation of T-isomers is observed in the initial stages of drawing. In orientation drawing of UHMPE gel fibre, no significant increase was found in the concentration of molecular breaks, a necessary condition for effective strengthening of the fibre. Two types of crystallites (crystallites in folded and straightened chains) and a mesophase were found in samples of multifilament UHMPE fibres. There is a smooth transition from the structure of the folded-chain crystallite (FCC) type to a structure of the straightened-chain crystallite (SCC) type with an increase in the draw ratio due to formation of a rigid amorphous phase of straightened segments of the polymer chains.

One of the main problems of polymer technology is to develop new and to improve existing methods of obtaining polymeric materials with extreme properties, particularly with high strength indexes. Gel spinning is currently used as the most effective and industrially feasible method of strengthening flexible-chain polymers [1, 2]. It is possible to increase the strength of ultrahigh-molecular-weight polyethylene (UHMPE) fibres by one order of magnitude in the stage of orientation drawing of spun gel fibres (the most important stage of gel spinning). However, the strength values attained are no greater than 10% of the theoretical limit [3]. It is important to study the rearrangement of the molecular and supramolecular structure of the polymer that take place during drawing and to establish their correlation with the mechanical properties for further orientation strengthening of fibres.

We investigated the effect of orientation drawing on the structure of UHMPE fibres obtained by gel spinning and their elastic-strength properties. Comprehensive studies were conducted with such physical methods as Fourier IR spectroscopy, wide-angle x-ray diffraction, differential scanning calorimetry, and mechanical tests.

We studied multifilament fibres (280 filaments) made from UHMPE with a molecular weight of $M_w = 1.9 \cdot 10^6$ drawn at different ratios and at different temperatures. The fibres were fabricated from a 3% spinning solution of UHMPE in paraffin oil in the conditions of the experimental setup at the All-Russian Scientific-Research Institute of Synthetic Fibres [4]. Drawing of the fibres was divided into three stages. The fibre was initially drawn at a temperature of 110°C to ratio $\lambda = 3$. In the second stage, after shrinkage, the fibre underwent one-stage thermal orientation drawing at 125-128°C. Both drawing stages were conducted in solvent medium. The third drawing stage was conducted in air at 140-145°C.

The IR spectra of filament fibres laid in a monolayer parallel to each other on the frame holder were recorded in polarized light on an Equinox 55 Fourier IR spectrometer.

The molecular structure and rearrangements in the fibres were judged by the conformation- and decomposition-sensitive IR absorption bands.

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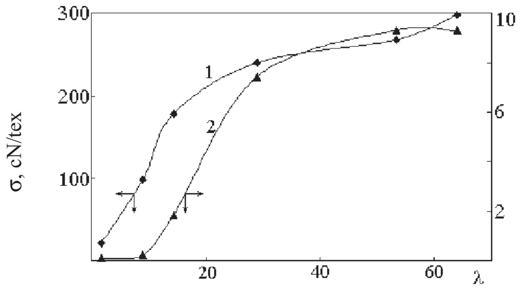

Fig. 1. Strength (1) and modulus of elasticity (2) vs. draw ratio for UHMPE fibres.

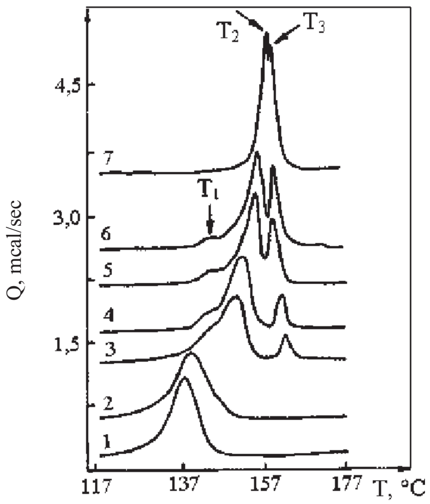

Fig. 2. DSC curves of UHMPE fibre with different draw ratios λ: 1) 1.9; 2) 5.7; 3) 11.5; 4) 15.5; 5) 28.4; 6) 33.6; 7) 75.0.

The optical density of the IR absorption band D was calculated with the equation in [5]

$$D = (D\text{II}+2\,D\perp)/3, \tag{1}$$

where $D|$ and $D\perp$ are the optical density in parallel and perpendicular polarization of light relative to the axis of drawing the fibre. To avoid the effect of the thickness of the sample, the density pertained to the bands of the standard D_o: 1894 cm^{-1} for 1710-1720 cm^{-1}bands, 2850 cm^{-1} for 720 and 730 cm^{-1} bands, and 1380 cm^{-1} for the 1350 and 1368 cm^{-1} bands.

The conformational rearrangements were judged by the change in the optical density of absorption bands with a frequency of 1350 (*GG*) and 1368 cm^{-1} (*GTG*) corresponding to twisting vibrations of CH_2 groups in the amorphous regions of the polymer and with frequencies of 720 (T_m, m = 2-7) and 730 cm^{-1} (T_m, $m > 7$) corresponding to rocking vibrations of CH_2 groups in amorphous and crystalline regions (*G* and *T* — *gauche*- and *trans*-isomers) [6]. The concentration of molecular breaks was estimated by the accumulation of acid (1710-1720 cm^{-1}) and aldehyde (1740 cm^{-1}) end groups [7, 8].

The degree of molecular orientation $<\cos^2\theta>$ for CH_2-group rocking vibrations was calculated with the IR dichroism $R = D|/D\perp$ with the equation in [5]

$$<\cos^2\theta> = (2 - R)/(2 + R), \tag{2}$$

and for CH_2-group twisting vibrations with the equation in [5]

$$^2\theta> = R/(2 + R), \tag{3}$$

where θ is the angle between the axis of the molecular segment and the axis of orientation.

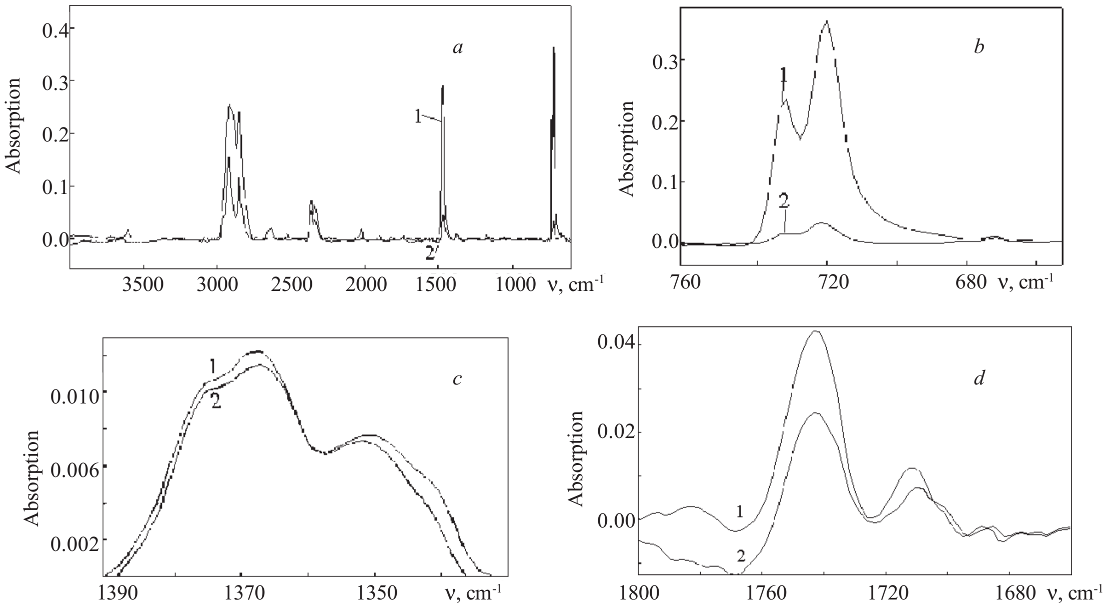

Fig. 3. IR spectrum of highly oriented UHMPE fibres ($\lambda = 64.1$) in polarized light: a) overall shape; b-d) individual regions of the IR spectrum; 1) parallel polarization; 2) perpendicular polarization.

The melting heat and average melting point of the drawn fibre were determined with a Perkin Elmer DSC-2 differential scanning calorimeter at the heating rate of 10°C/min. The measurements were conducted at a constant sample length (in isometric conditions). A rigid frame made from a 2×4 mm metal plate ≤ 0.5 mm thick with wide notches on the ends in the shape of a two-tine fork with a depth of 0.5-1.0 mm was used for realizing isometric conditions. The fibre was wound along the plate and then tightly wrapped with a thin copper wire in the transverse direction. The prepared sample was rolled in aluminum foil. One side of the package obtained was flattened for better contact with the instrument's sample holder [9].

The x-ray structural studies were conducted on a DRON-3M diffractometer (CuKα radiation, 0.1542 nm wavelength, Ni filter, exposure in flat holder) [9].

The degree of crystallinity of isotropic UHMPE powders was determined with the ratio of the intensity of reflections (110) and (200) to the overall intensity of the amorphous halo and the crystallite size was determined with the integral half-width of the corresponding reflections [9].

The mechanical characteristics of the fibre (strength and modulus of elasticity at 2% extension) were determined on an Instron 1122 tensile-testing machine with a clamp length of 150 mm and stretching rate of 50 mm/sec [10].

The changes in the mechanical characteristics of the UHMPE fibre in drawing are shown in Fig. 1. The dependence of the strength σ on the draw ratio λ is described by a curve with saturation. In the initial stages of drawing, the strength increased significantly, while it slowed slightly with an increase in the draw ratio. The modulus of elasticity of the fibres also increases with an increase in λ — somewhat slowly at λ from 0 to 10 and rapidly at higher values of λ. As a result of orientation drawing of UHMPE fibre with $\lambda = 64$, strength values of 298 cN/tex and a modulus of elasticity of 9300 cN/tex were attained as a result of orientation drawing of UHMPE fibre with $\lambda = 64$, which is almost one order of magnitude higher than for fibres drawn from high-density polyethylene (HDPE) [7].

Melting thermograms of gel fibres with different orientation draw ratios λ after the solvent was washed off are shown in Fig. 2. We can see that insignificant drawing (to $\lambda \leq 6$) had almost no effect on the character of the thermograms. At low λ, the folds of lamellar crystallites probably do not straighten, and lengthening of the fibre is basically due to straightening of chain segments binding adjacent microcrystallites in the gel fibre [9]. The structural model of the physical UHMPE gel that we used in the interpretation was taken from [11]. The only melting peak in the thermogram (T_1) at small λ should be assigned to crystallites in folded chains (FCC). The small shift of T_1 with an increase in λ in the high temperature region can be attributed to an increase in the fold length at the high drawing temperature and creation of a more oriented and stressed crystalline phase.

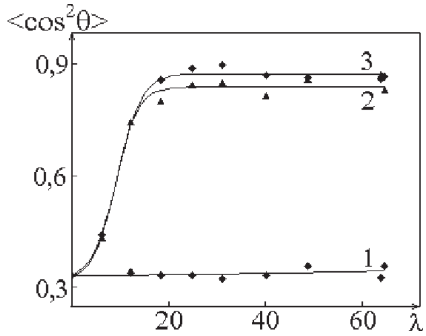

Fig. 4. Orientation of conformers vs. draw ratio: 1) *GTG* at 1368 cm^{-1}; 2) T_m at 720 cm^{-1}; 3) T_m at 730 cm^{-1}.

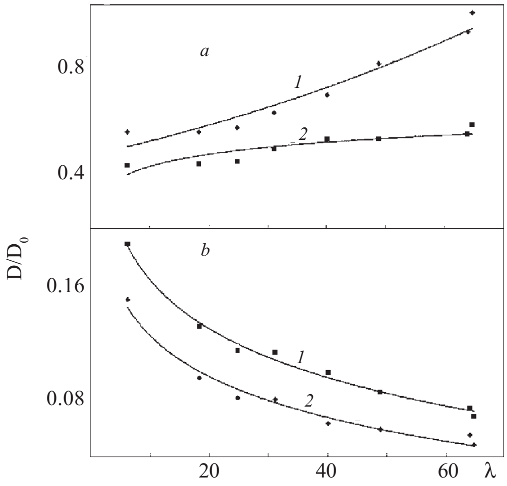

Fig. 5. Relative content of different conformers in UHMPE fibre vs. draw ratio: a) T_m at 720 (1) and 730 cm^{-1} (2); b) *GTG* at 1370 cm^{-1} (1) and *GG* at 1350 cm^{-1} (2).

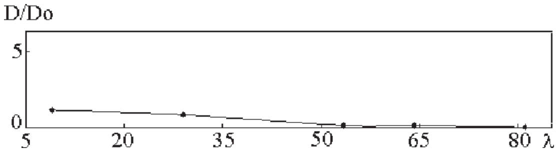

Fig. 6. Content of terminal carboxyl groups in UHMPE fibre vs. draw ratio.

A further increase in the draw ratio qualitatively altered the shape of the DSC curves. At λ ≥ 11 (Fig. 2), there were three peaks (T_1, T_2, T_3) in the thermograms, two very pronounced, and one, less intensive, in the form of a shoulder on the ascending branch of the curve related to the average melting peak.

The values of T_1 and T_2 increase with an increase in λ, and T_3 decreases slightly. Peaks T_1 and T_3 appear at λ ≥ 11. Beginning with this value of λ, according to the data from low-frequency Raman spectroscopy in [12], the length of the straightened chain segments forming the rigid amorphous phase between lamellar crystallites in folded chains increases significantly and the modulus of elasticity of the fibre also increases (see Fig. 1). We can hypothesize that at λ ≥ 11, straightened chain segments joining two neighboring FCC appear in the microfibril. Beginning with λ ≥ 11, straightened chain crystallites (SCC) appear in the sample, related to the second melting peak T_2. With a further increase in λ, the length and volume of the

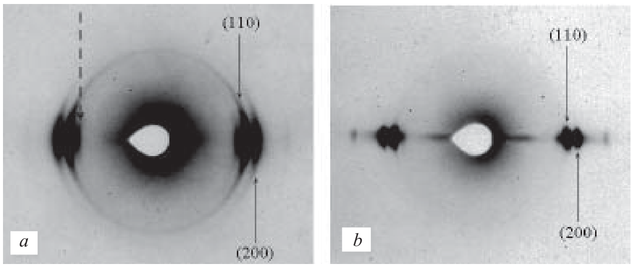

Fig. 7. X-ray photographs of fibres with draw ratios of 13.4 (a) and 55 (b).

SCC in the fibre increases due to unfolding of the folds in FCC, as confirmed by the increase in the intensity of peak T_2, its shift to the high-temperature region, and the decrease in the intensity of peak T_1 characterizing FCC. For highly oriented samples, melting peak T_1 is almost absent.

Melting peak T_3 appears at the same time as peak T_2 (at $\lambda \geq 11$) and is only manifested in conditions of isothermal heating. Visual observations of a plate with the sample removed from the instrument showed that isothermal heating of the fibre in the temperature region from T_2 to T_3 is initially accompanied by breaking of individual filaments and then the entire fibre. The filaments break at $T > T_2$ because of high internal stresses of an entropic nature. With an increase in λ, the length and number of straightened chain segments in the fibre that form SCC and the mesophase increase significantly. This in turn causes a significant increase in internal stresses, a decrease in the fibre breaking temperature, and shifting of melting peak T_3 to low temperatures (see Fig. 2). Due to breaking of the fibre, the isometric conditions are perturbed and the crystallites still retaining structural ordering or passing into the mesophase rapidly begin to melt. At a high draw ratio ($\lambda = 75$), the melting intervals of structural formations with average values of T_2 and T_3 overlap significantly, which indicates a more homogeneous structure of the fibre. We can thus assume that the longest SCC not destroyed before the fibre breaks melt at T_3. Melting peaks T_2 and T_3 probably totally overlap in the case of a highly oriented sample consisting of ideal SCC.

The overall shape (a) of the polarization IR spectrum of highly oriented UHMPE fibre ($\lambda = 64$) and its individual structure-sensitive regions (b-d) are shown in Fig. 3. The IR spectrum shows that some of the absorption bands are strongly polarized. This primarily relates to "crystallinity" bands (1894, 1473, and 730 cm^{-1}).

Drawing of UHMPE fibres is accompanied by an important change in the degree of orientation of the conformers (Fig. 4). Straightened *T*-segments in both crystalline and amorphous regions of the polymer are especially effectively oriented during drawing (curves 2 and 3). Folded *GTG*-conformers in amorphous regions change their orientation much less significantly (curve 10. A comparison of the orientation behavior in drawing of different types of polyethylene — low (LDPE) or high (HDPE) density [7] and UHMPE — shows their qualitatively similar curves. The degree of orientation of *T*-segments increases rapidly at low λ, attaining the limiting value. In further drawing, the degree of orientation of straightened molecular segments almost does not change. For folded *gauche* conformers, the degree of orientation weakly and monotonically increases in the entire region of drawing.

The analysis of the conformational composition of UHMPE fibre shows that in comparison to LDPE or HDPE [7], these samples had a high degree of crystallinity even before orientation drawing began. This is indicated by the high intensity of the IR absorption bands at 730 and 1894 cm^{-1} (long *T*-segments) and lower intensity of the IR bands for folded conformers at 1350 and 1370 cm^{-1}. In orientation drawing of UHMPE fibres, the T_m-conformers in amorphous regions increase significantly (Fig. 5a, curve 1) and the content of T_m-conformers in crystalline regions increases less significantly (curve 2). For *GG*- and *GTG*-conformers, a monotonic decrease in the number of folded conformers is observed with an increase in λ (Fig. 5b, curves 1 and 2). Based on the data obtained, we can conclude that the conformational composition of the polymer is enriched with straightened *trans*-segments with an increase in the draw ratio, especially in amorphous regions, due to a decrease in the number of folded conformers.

Figure 6 shows the concentration of terminal carboxyl groups (the number of these groups is proportional to the concentration of molecular breaks in the polymer chain) as a function of the orientation draw ratio. These curves show that in drawing even to a high ratio ($\lambda = 75$), the concentration of molecular breaks does not increase markedly, while their content increases in the initial stages of drawing in ordinary PE [8, 13]. In other words, in orientation drawing of UHMPE gel fibre,

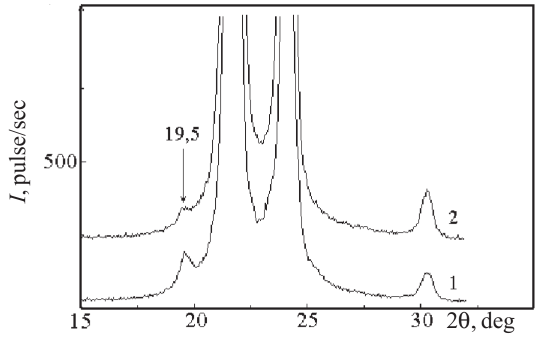

Fig.8

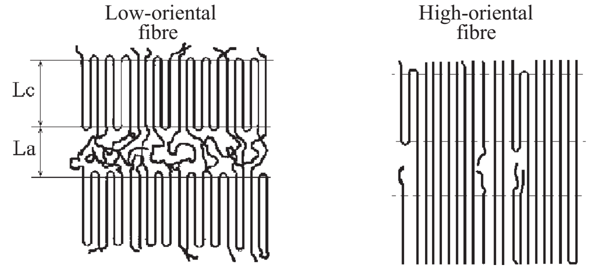

Fig.9

Fig. 8. Equatorial diffractograms of a fibre with a draw ratio of 55 before (1) and after annealing in isometric conditions at 140°C (2).

Fig. 9. Structural model of low- and high-oriented UHMPE fibre fabricated by gel spinning: L_c and L_a — longitudinal dimension of crystallite and amorphous phase, respectively.

more favorable conditions are created for effective orientation and strengthening of the polymeric material in comparison to ordinary drawing of PE.

In studying the change in the supramolecular structure of UHMPE fibre in orientation drawing by wide-angle x-ray scattering, the x-ray photograph of a fibre with $\lambda = 13.4$ (Fig. 7a) exhibited two narrow equatorial reflections (11) and (200) corresponding to orthorhombic crystallites well oriented in the direction of the axis of drawing (*C*-texture). There was also weak scattering with a relatively wide azimuthal intensity distribution corresponding to a system of isotropic or weakly oriented PE crystallites [9]. With an increase in the draw ratio of the fibre to $\lambda = 55$, the azimuthal half-width of reflections (11) and (200) decreases significantly (Fig. 7b), and the scattering with wide azimuthal distribution disappears. As a consequence, the degree of orientation of PE crystallites with *C*-texture increases even more.

It should be noted that in addition to the reflections corresponding to the orthorhombic cell of PE, the x-ray photos of these fibres (Fig. 7) exhibit additional equatorial scattering noted by the dashed arrow. To identify the nature of this scattering, the equatorial diffractograms of fibre samples with $\lambda = 55$ were analyzed before and after they were annealed in isothermal conditions at 140°C (Fig. 8). Note that this scattering is in the form of a reflection with an angular position of $2\theta = 19.5°$, which could coincide with the angular position of reflection (001) of the monoclinal phase of PE [9] or the angular position of the maximum scattering from the oriented amorphous phase. During isothermal heating of a fibre with $\lambda = 55$ to 140°C (which is much higher than T_m of the monoclinal phase), the intensity of the equatorial reflection with $2\theta = 19.5°$ decreases slightly and is preserved up to 20°C on subsequent cooling (curve 2). The azimuthal half-width of the analyzed reflection did not change in annealing. All of the above and the absence of any thermophysical changes in the 100-120°C temperature region in the thermograms of fibres with different draw ratios (see Fig. 2) suggests that the scattering with an angular position of 19.5° is not due to formation of the monoclinal phase of PE. We can hypothesize that drawn PE fibres contain regions in which oriented chains have packing close to the packing of the molecules in the amorphous phase. The degree of orientation of the chains in these regions (responsible for the appearance of the reflection with $2\theta = 19.5°$) increases with an increase in the draw ratio of the fibre, and their thermal stability is higher than for the FCC of the initial isotropic sample. All of the above is totally confirmed by the findings of Raman spectroscopy in [12], which indicate the existence of a rigid amorphous phase between the intrafibrillar crystallites of drawn PE fibre formed from very extensive straightened chain segments [9].

The change in the structure of the UHMPE fibre in orientation drawing can be very schematically represented as shown in Fig. 9. In orientation drawing of UHMPE gel fibre, FCC change into SCC due to straightening of the folds of the lamellar crystallite, which in turn increases the crystalline continuity in the direction of the axis of the fibre and ensures high elastic-strength properties of the finished fibre. We should also note that in a highly oriented fibre, the notion of the large period loses meaning, since the density of the amorphous and crystalline phases are almost equalized, as the data from optical spectroscopy, x-ray diffraction, and differential scanning calorimetry indicate.

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