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MOLECULAR MOBILITY IN NEAR-SURFACE NANO-LAYERS OF ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE AS REVEALED BY THERMOLUMINESCENCE ACTIVATED BY LOW TEMPERATURE Ar PLASMA

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ABSTRACT

Aiming at better understanding the properties of the near-surface nano-layers of UHMWPE reactor powders (RP) used for manufacturing high-performance fibers by solvent-free processing, a comparative study of the molecular mobility in the nano-layers of two different UHMWPE RP and its change after compaction and sintering is carried out with the help of thermoluminescence method. The dependence of the intensity of light quanta emitted by heated samples (previously evacuated, cooled to 77 K, and activated by low-temperature argon plasma) on the heating temperature (glow curves) is analyzed. The glow curves were recorded using a unique Nanoluminograph device, which exists in a single copy at Ioffe Institute. It was found that all the glow curves observed had the complicate profiles, which evidenced the overlapping of a number of relaxation processes. The Fityk software was used for deconvolution the experimental curves into elementary peaks. The length of the so-called kinetic unit of motion (the mobility of which is defreezing in the temperature interval of each elementary peak) was calculated. The influence of the behavior of the near-surface RP nano-layer during compaction/sintering on the achieved strength of the oriented final film threads is demonstrated.

KEYWORDS

Plasma-induced thermoluminescence; UHMWPE reactor powders; molecular mobility; near-surface nano-layers; high-performance film threads; relaxation properties.

МОЛЕКУЛЯРНАЯ ПОДВИЖНОСТЬ В ПРИПОВЕРХНОСТНЫХ НАНО-СЛОЯХ СВЕРХВЫСОКОМОЛЕКУЛЯРНОГО ПОЛИЭТИЛЕНА ПО ДАННЫМ ТЕРМОЛЮМИНЕСЦЕНЦИИ, АКТИВИРОВАННОЙ НИЗКОТЕМПЕРАТУРНОЙ ПЛАЗМОЙ АРГОНА

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АННОТАЦИЯ

В целях лучшего понимания свойств приповерхностных нанослоев реакторных порошков (РП) СВМПЭ, используемых для производства высокопрочных волокон безрастворным способом, методом термолюминесценции проведено сравнительное исследование молекулярной подвижности в нанослоях двух различных РП СВМПЭ и ее изменения после прессования и спекания. Проанализирована зависимость интенсивности квантов света, излучаемых нагретыми образцами (предварительно вакуумированными, охлажденными до 77 K и активированными низкотемпературной аргоновой плазмой) от температуры нагрева (кривые свечения). Кривые свечения записывались с помощью уникального прибора «Нанолюминограф», существующего в единственном экземпляре в ФТИ им. А.Ф. Иоффе РАН. Установлено, что все наблюдаемые кривые свечения имеют сложный профиль, что свидетельствует о наложении ряда релаксационных процессов. Программное обеспечение Fityk использовалось для разложения экспериментальных кривых на элементарные пики. Рассчитана длина так называемой кинетической единицы движения (подвижность которой размораживается в температурном интервале каждого элементарного пика). Показано влияние поведения приповерхностного нанослоя РП в процессе прессования/спекания на достигаемую прочность конечных ориентированных пленочных нитей.

КЛЮЧЕВЫЕ СЛОВА

Плазмоиндуцированная термолюминесценция; СВМПЭ реакторные порошки; молекулярная подвижность; приповерхностные нанослои; высокопрочные пленочные нити; релаксационные свойства.

Introduction

It is known that the properties of the surface of solids differ significantly from the properties of the bulk and largely determine the behavior of solids in various physical fields. The study of the surface of solids has recently become especially intensive due to the growing interest in nanoscale objects, and also, in particular, due to the intensive development of solid-phase methods for processing ultra-high molecular weight polyethylene (UHMWPE), the melt viscosity of which is so high that it makes it difficult to process it by traditional methods, such as extrusion or injection molding. At the same time UHMWPE is a large tonnage polymer due to its unique properties, such as high mechanical properties, low friction, high abrasive and chemical resistance etc. and wide practical applications such as bulletproof jackets and armours, fishing lines, ropes, sporting-goods, medical artificial joints, implants, suture material, etc.

At the end of the last century, a gel-technology method was developed for the processing of UHMWPE, which consists in the extrusion of a low-concentration ($< 5\%$) solution of UHMWPE in non-polar solvents, followed by orientation hardening of the resulting gel-fibers. [1]. The method was successfully commercialized by DSM (Netherlands) and Honeywell (USA) companies, producing high-strength high-modulus fibers Dyneema and Spectra, respectively, with strength of 3.0–3.6 GPa and Young’s modulus $\leq$ 180 GPa. At present, China, Japan and other countries already produce high-performance fibers via gel technology. However, the gel technology method is expensive and environmentally unsafe.

In 1987, an alternative solution-free method was proposed for obtaining high-performance fibers directly from products of polymer synthesis, the so-called reactor powders (RP) [2], which consists in powder monolithization followed by orientational hardening.

The first stage of solid-phase processing of UHMWPE is similar to powder metallurgy and consists in sintering the initial nascent RP in order to create strong interparticle boundaries between powder particles and form a mechanically integral precursor film for subsequent orientational hardening.

If in the gel-technology method the supramolecular structure of the reactor powder practically disappears and the molecules pass into the state of a Gaussian coil in solution, then in the solution-free method the structure formed during the synthesis is preserved and has a significant effect on the compactability and drawability of the polymer.

In the production of high-performance UHMWPE fibers using solventl-free technology, there are two key points: firstly, it is necessary to create a strong precursor for orientation drawing, and secondly, not to change the internal structure of the RP, since it is the specific disentangled structure of the RP that provides the highest achievable precursor draw ratio and obtaining, as a consequence, the ultimately high tensile strength and high modulus of the final product.

Needless to say, many different RP powders have been explored and many attempts have been made to commercialize solid-state processing.

Thejin-Aramid currently manufactures Endumax tapes from UHMWPE RP using solid state machining. However, its strength is somewhat less than that of Dyneema and Spectra fibers, and is equal to 2.5 GPa, although laboratory high-performance fibers with extremely high mechanical characteristics (4–5 GPa) have been obtained [3–7].

Obviously, the ability to form strong interparticle boundaries, which will not breakdown during orientation drawing catastrophically, depends on the molecular mobility in reactor particles near-surface nano-layers.

There are many different methods for studying the chemical and physical properties of a surface.

Surface morphology of typical crystalline polyolefins has been extensively explored by many research groups with the advent of modern microscopic techniques [8–10]. However, the relaxation processes in the near-surface layers are poorly investigated. At the same time, it is the molecular motion activated in the temperature ranges of the relaxation transition that determines such important properties of the polymer surface as diffusion, adhesion, the formation of chemical bonds at interfaces, etc., and also controls the healing of the grain boundaries during compaction and sintering. The needed information on relaxation properties of near-surface nanolayers of RP particles that characterize molecular mobility, which ensures the formation of cohesive bonds, can be obtained by the method of plasma-induced thermoluminescence (PITL). The application of glow discharge plasma for activation of solid surface layers was proposed by Lipatov et al. [11, 12] and put forward by Nikol’skii et al. as the technique for investigation of structural transitions in organic materials [13]. The PITL technique was used by many researchers [14–19]. Newly developed and patented research device Nanoluminograph [20, 21], whose action is based on thermoluminescence phenomenon, used in this work. Possibilities of thermoluminescence method for estimating the molecular packing in near-surface layers of polymers using this device were demonstrated in a number of papers [22, 23] and in a review [24]. The aim of the present work was to carry out a comparison study of relaxation properties of near-surface layers of two different UHMWPE reactor powders synthesized on different catalysts, their change after sintering, and the effect on the mechanical characteristics of oriented end filaments.

1. Research Methods

1.1. Objects of investigation

Two ultra-high-molecular weight polyethylene synthesized on different catalysts were chosen for investigation. These were UHMWPE reactor powder (UHMWPE-IVA6) with Mw = $3 \cdot 10^6$ g/mol synthesized on the metallocene catalyst F-95 in a slurry process in toluene at 30 °C (Institute of Macromolecular Compounds, St. Petersburg) and UHMWPE reactor powder (UHMWPE-R) with Mw = $2{,}5\cdot10^6$ synthesized on one-site metallocene F1 catalyst and kindly provided to us by Prof. S. Rastogi (Maastricht University).

1.2. Sintering

The reactor powders were pre-compressed at room temperature under a pressure of 95 MPa for 15 min to ensure close contact between the particles and avoid the formation of pores with entrapped air. Then, the compacts obtained were sintered at 130 °C under a pressure of 95 MPa for 30 min to obtain precursors for the orientation hardening.

1.3. Orientation hardening and tensile strength measurements

The sintered films were cut into the strips of 1 mm width. The strips were subjected to multi-stage zone drawing at a speed of 10 cm/min according to the scenario developed in Ioffe Institute.

The drawing process was stopped at various draw ratios to measure the tensile strength of the oriented filaments and plot the dependence of the tensile strength on the draw ratio. Strength measurements were carried out on a Shimadzu tensile tester (Japan) at room temperature with a clamp rate of 10 cm/min.

1.4.Thermoluminescence

The studies of thermoluminecence emitted by activated powders and sintered films under heating were carried out with the help of the above-mentioned unique Nanoluminograph device, which is the only one available in the Laboratory of Fracture Physics in the Ioffe Institute.

Thermoluminescence is a glow that occurs when a substance is heated, previously frozen and exposed to ionizing radiation. Charges generated by radiation can be stabilized in physical or chemical traps of various depths. Heating, activating the micro-Brownian movement of atomic groups and molecules, destroys the traps and releases the trapped charges. The released electrons recombine with the counter ions and light quanta are emitted.

For surface activation the low temperature low powerful plasma of Ar glow discharge (13.36 MHz) was used. The Ar pressure and the generator voltage were chosen in such a way to provide the reduced strength of electrical field E/P about $2\cdot10^3$ Vcm^{-1}/MPa (E is the electric-field strength, and P is the gas pressure). In this case, the calculated thickness of the activated layer comprises 5–10 nm. The consumed power W was 0.004 Wt/cm^3, and absorbed dose was about 0.2 kGy.

Particles of the reactor powders under investigation were glued by a Dottite conducting silver adhesive (used in electron microscopy) to a thin Al foil, which was attached to a thin-walled copper cylindrical holder. The studied films were fixed on the holder using thin copper wires wound on the holder with the film. After the chamber was evacuated to a residual pressure of $1.33\ 10^{-4}$ Pa and the holder was filled with liquid nitrogen, which cooled the sample at 77 K, argon was let into the chamber to a pressure of 13.3 Pa.

Then, a high-frequency glow discharge (13.56 MHz) was initiated for one second. In order to minimize a modifying action of the plasma on the sample, the discharge power in the experiments was decreased to 4±0.1 mW/cm^3. The chamber was evacuated again to the initial pressure of $1.33\ 10^{-4}$ Pa, and the isothermal luminescence was first recorded with a photomultiplier. When the luminescence intensity decayed to a level of photomultiplier noises, a heater of the holder was switched on and the luminescence intensity was measured as a function of the temperature (the so-called glow curves). The Hamamatsu R-6095 photomultiplier (Japan) operated in the one-electron pulse counting mode with a maximum sensitivity in the range 400–600 nm was used for measurements. To decrease the intrinsic noises, the photomultiplier was cooled down to 4–5 degrees of Centigrade; therefore, the intensity of the noise was no more that 20 imp/sec. The glow curves were registered in the temperature range from 77 to 300 K during linear heating of the sample at a rate of 10 K/min.

To avoid contamination of the surface of the samples during evacuation of the chamber, it was evacuated with an oil-free turbo molecular pump Hi CUBE-80 (Pfeiffer). In addition, the trap, installed directly in the chamber and used to freeze out various contaminants, was filled with liquid nitrogen before cooling the samples.

For all the samples investigated, the experiments were performed under identical conditions.

2. Results and Discussion

The glow curves from reactor powders UHMWPE-R and UHMWPE-IVA6 and from the films sintered from them are presented in Fig. 1 and Fig. 2, respectively. It is seen that glow curves from the both powders have very intensive luminescent peak in the temperature range 100–170K and the less pronounced peaks in a higher temperature region (190–280K).

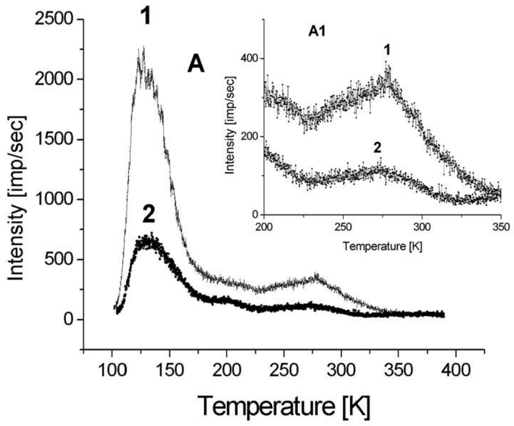

Fig. 1. “A” is the glow curves of virgin (1) and sintered (2) UHMWPE-R reactor powder
“A1” is the high-temperature parts of glow curves 1 and 2

Рис. 1. «A» кривая свечения исходного (1) и спеченного (2) UHMWPE-R реакторного порошка, «A1» –высокотемпературные части кривых свечения 1 и 2

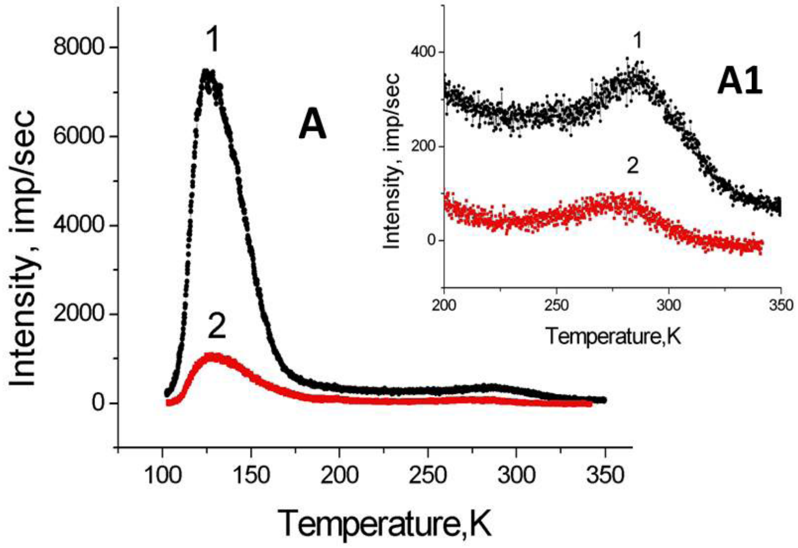

Fig. 2. “A” is the glow curves of virgin (1) and sintered (2) UHMWPE-IVA6 reactor powder
“A1” is the high-temperature parts of glow curves 1 and 2

Рис. 2. «A» кривая свечения исходного (1) и спеченного (2) UHMWPE-IVA6 реакторного порошка, «A1» –высокотемпературные части кривых свечения 1 и 2

Since polyethylene, as a non-polar polymer, has no electron affinity, dielectric cavities formed by segments of macromolecules located in a certain way in disordered regions can serve as electron traps in it [25, 26]. Defects in crystalline regions can also serve as traps, but their number is negligible. Since the thermoluminescence occurs due to the erosion of electron traps by thermal motion, as was mentioned above, the release of charges, their irradiative recombination, following the appearance of peaks on the glow curve is associated with relaxation transitions.

There are a lot of research works concerned with the relaxation transitions in polymers and a lot of confusions as regard to attribution the observed peaks to the definite type of relaxation. As is known, the defreezing of mobility in the region of 100–170 K is referred usually to as the so-called γ-relaxation, which corresponds to the defreezing of the mobility of several monomeric groups. The defreezing of mobility in the temperature range of 200–250 K is referred to as β-relaxation [13], corresponding to the appearance of quasi-independent mobility of individual segments of macromolecules, comparable in size to the Kuhn segment, which for PE is equal to the length of the trans-sequence, consisting of 8 methylene groups. The ratio of the luminescence intensities in the region of γ-and β- relaxation transitions for the UHMWPE-R powder is 5.96, and for the UHMWPE-IVA6 powder is 21.78. Thus, it can be concluded that the near-surface nanolayers of both investigated UHMWPE reactor powders contain mainly separate atomic groups and cilia of the molecular chains. However, IVA6 reactor powder contains much more of them. Obviously, this is the result of crystallization in confined conditions at low temperature, when the crystallization rate is close to the growth rate of molecules and all defects are pushed to the surface of the formed particles. After sintering, the ratio of peak intensities in the UHMWPE-R luminescence curves practically did not change ($I_\gamma/I_\beta = 5.9$), while in UHMWPE-IVA6 it decreased by a factor of 2 ($I_\gamma/I_\beta = 11.62$). Thus, the studied powders subjected to sintering behave differently.

For a deeper understanding of the difference in their behavior, it is necessary to conduct a more accurate analysis of the glow curves. It should be recognized that the profile of all registered glow curves has a complex shape, which suggests the overlap of several elementary glow peaks and, accordingly, a number of different relaxation processes.

Both γ- and β-relaxation transitions can occur in a fairly wide temperature range, depending on the size of the molecular segment, the mobility of which is unfrozen at a given temperature [27]. There are several different explanations for relaxation processes occurring in different temperature ranges.The transition in the temperature range 105–120 K is attributed to small-scale motion, in particular, to the local relaxation of molecular ends and local bond rotational displacements involving several methylene groups in the amorphous regions or on the crystallite surfaces [28–31]. The relaxation in the temperature range 140–160 K is referred to as quasi-independent segmental mobility (the Arrhenius process), while the relaxation in the temperature range 240–270 K and higher is classified as the glass transition (cooperative segmental mobility, the non-Arrhenius nature) [31]. In flexible-chain polymers the elementary act in the Arrhenius process comprises in rotation of chain segments of length close to the Kuhn segment length upon overcoming the intermolecular barriers and involving single-barrier *trans-gauche* transitions.

By deconvolution of glow curves, it is possible to obtain more accurate information about the molecular mobility and fine structure of near-surface nano-layers of the investigated reactor powders and their changes during sintering. The results of deconvolution of the glow curves with the help of Fityk 3 1 software are presented in Fig. 3 and Fig. 4.

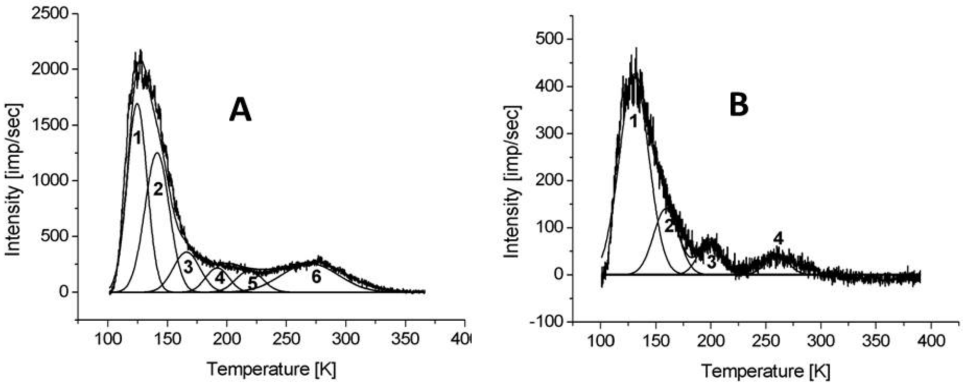

Fig. 3. Deconvolution of the glow curves of the virgin (A) and sintered (B) UHMWPE-R reactor powders

Рис. 3. Разложение кривых свечения исходного (A) и спеченного (B) UHMWPE-R реакторного порошка

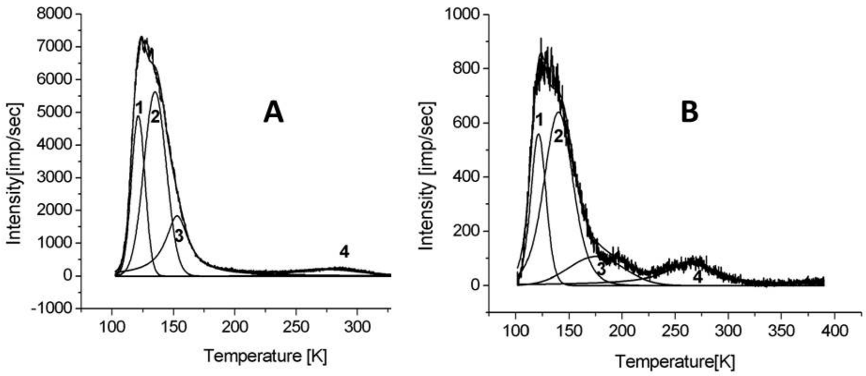

Fig. 4. Deconvolution of the glow curves of the virgin (A) and sintered (B) UHMWPE-IVA6 reactor powders

Рис. 4. Разложение кривых свечения исходного (A) и спеченного (B) UHMWPE-IVA6 реакторного порошка

It can be seen that the number of elementary peaks and their contribution to the total light sum, as well as their change after sintering, differ markedly.

We calculated the activation energy of the erosion of each elementary electron traps (E_{TL}) associated with correspondent relaxation transitions using formula $E_{TL} = kTm^2/(T'' - T_m)$, where T_m is the glow curve peak temperature, and T'' is the temperature at the half-width of the peak from its high-temperature side [29]. Using the approaches developed by V. A. Bershtein and V. M. Egorov [30] and admitting the equality of E_{TL} and E_{act} of relaxation transition values, we also estimated the number of monomer (CH_2–CH_2) units in the apparent kinetic units of motion L, mobility of which is defreezed in the region of correspondent relaxation transition. The calculation was carried out in accordance with the expression $E_{act} \approx (0.3\pm0.05)E_cN + B$, proposed by the authors, where E_{act} is the activation energy of the transition in kJ per mole of kinetic units of motion L, E_c is the cohesion energy (the intermolecular interaction energy per mole of monomer units equal to 9 kJ/mole), N is the number of monomer units (CH_2–CH_2) and B = 0.65 kcal/mole is the barrier to the internal rotation in flexible chains. The data obtained are given in the Table 1 and Table 2.

Table 1. Relaxation transition temperatures T, activation energies E_{TL} and length of kinetic units of motion L in the virgin and sintered UHMWPE-R reactor powders

Таблица 1. Температуры релаксационных переходов T, энергии активации и длины кинетических единиц движения L в исходных и спеченных реакторных порошках UHMWPE-R

Relaxation transition in virgin R-powder	Relaxation transition temperature T, K	Activation energy E_{TL}, kcal/mol	Number of CH_2 groups in kinetic units of motion	Length kinetic units, nm	Contribution to total sum TL in %
γ_1	124.23	3.14	3.86	0.5	33
γ_2	141.89	3.81	4.9	0.6	30.2
β_1	166.10	4.16	5.44	0.7	9.45
β_2	195.14	4.38	5.78	0.7	4.97
β_3	219.85	4.95	6.7	0.8	6.39
α	274.85	5.4	7.36	0.9	15.77
in sintered R-powder					
γ_1	130.45	1.94	2.0	0.2	67
β_1	159.46	3.73	4.8	0.6	19.2
β_2	198.33	5.8	8	1.0	8.2
α	260.01	10.3	14.7	2.0	5.34

Table 2. Relaxation transition temperatures T, activation energies E_{TL} and length of kinetic units of motion L in the virgin and sintered UHMWPE-IVA6 reactor powders

Таблица 2. Температуры релаксационных переходов T, энергии активации и длины кинетических единиц движения L в исходных и спеченных реакторных порошках UHMWPE-IVA6

Relaxation transition in IVA6-powder	Relaxation transition temperature T, K	Activation energy $E_{PITL,}$ kcal/mol	Number of CH_2 groups in kinetic units of motion	Length kinetic units, nm	Contribution to total sum TL in %
γ_1	121.25	4.25	5.6	0.7	24
β_1	134.97	4.6	7.2	0.8	26
β_2	153	5.43	7.4	0.9	45
α	275.74	6.4	8.9	1.0	5
in sintered IVA6-powder					
γ_1	126.36	2.45	2.79	0.3	52.28
β_1	150.36	3.00	3.64	0.4	31.17
β_2	196.47	6.44	8.97	1.0	8.9
α	264.27	6.6	9.36	1.2	7.6

To visualize changes in the content and size of apparent kinetic units of motion in the near-surface nanolayers of the studied reactor powders occurring during sintering, we plotted them in the form of histograms (Fig. 5).

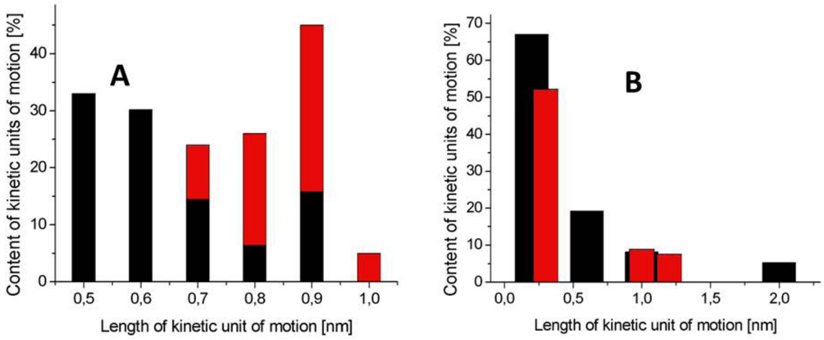

Fig. 5. Content of kinetic units of motion of different length in the near-surface layers of virgin (A) and sintered (B) reactor powders. Red bars are the UMWPE-IVA6 samples, black bars are the UHMWPE-R samples

Рис. 5. Содержание кинетических единиц движения различной длины в приповерхностных слоях исходных (A) и спеченных (B) реакторных порошках. Образцы UMWPE-IVA6 -красные столбцы, образцы UHMWPE-R – черные столбцы

First, one should admit that in the virgin R-powder there are a lot of short kinetic units of motion (0.5–0.6 nm) that do not exist in the IVA-6 powder. Their existence can be explained by the presence of microcavity and pores in powder particles. The cilia located at the boundaries of the pores begin to move first. These micro-cavities and pores are probably located in the interlamellar space or even in crystallites. The appearance of an intermolecular cavity in a crystallite may be a consequence of the formation of a dislocation that has arisen at the end of the macromolecule.

The pores in the IVA6 reactor powder (if any) are clearly smaller and require higher activation energy to allow mobility of cilia or small conformational defects at the pore boundaries. In addition, UHMWPE-IVA6 virgin powder has longer kinetic units of motion (L = 1.0 nm) than UHMWPE-R and more of them.

After sintering, the situation is changed. The number of short kinetic units increases in both sintered powders, while the longest kinetic units of motion (L = 2.0 nm) appear in the sintered UHMWPE-R sample. We assume that these can be taut tie molecules passing from one lamella to another, formed under the action of shear stress. Obviously, the presence of such structural units on the surface of sintered specimens (precursors for orientation hardening) will have a negative effect on the mechanical properties of the drawn films.

Indeed, a preliminary comparative study of the mechanical characteristics of films obtained from sintered powders UHMWPE-R and UHMWPE-IVA6 shows the advantage of the latter.

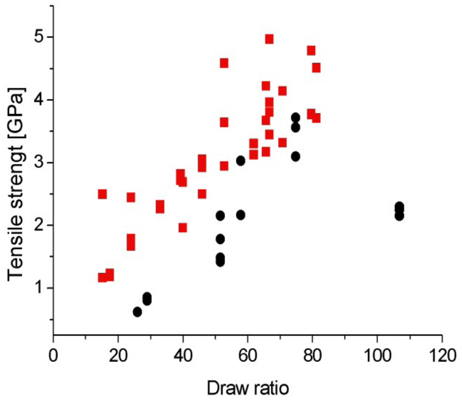

Fig. 6. Dependence of tensile strength on draw ratio for the films sintered from UHMWPE-R reactor powder (black spheres) and from the UHMPE-IVA6 (red squares)

Рис. 6. Зависимость разрывной прочности от степени вытяжки для пленок, спеченных из реакторного порошка UHMWPE-R (черные кружки) и из реакторного порошка UHMPE-IVA6 (квадраты)

Conclusions

The molecular mobility in the near-surface nanolayers of virgin and sintered two UHMWPE reactor powders synthesized on F1 an F95 metallocene catalysts was studied using the

Nanoluminograph device, which made it possible to obtain unique information on the relaxation properties of these layers. The deconvolution of the observed glow curves carried out with the help of Fityk 3.1. software. The activation energies of depletion of the detected electronic traps associated with the corresponding relaxation transitions are calculated as well as the lengths of the apparent kinetic units of motion, of which mobility is unfrozen in the temperature ranges of these transitions The influence of relaxation properties of the near-surface layers on mechanical properties of the investigated polymers is shown.

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