Relaxation transitions in UHMWPE near-surface layers as revealed by the thermoluminescence method

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Abstract. Aiming at finding the proper UHMWPE reactor powders convenient for solvent-free technology producing high-strength fibers, the comparative study of the near-surface layers of the commercial and lab-scale UHMWPE reactor powders was carried out with the help of the thermoluminescence method. The difference in the powder glow curves and changes in them after subjecting the powders to various processing (compaction and sintering) were observed. Decomposition of the curves was carried out using Fityk program. The energy activation of the electron trap erosion, and the relative content of the shallow and deep traps in the samples investigated were calculated. The association of these observations with the mechanical properties of the end sintered oriented product is discussed.

1. Introduction
At present a solution-free (“dry”) method for producing ultra-strong high-modulus film filaments of ultra-high molecular weight polyethylene (UHMWPE) directly from UHMWPE synthesis products (the so-called reactor powders) [1,2], an alternative to the expensive and environmentally non-friendly gel-technology that uses a low-concentration solution of UHMWPE in polar solvents is being actively developed in the world.

Some success in the implementation of the dry method has already been achieved, and the Dutch company Tejin-Aramid, already produces high-strength film tapes Endumax. However, its mechanical characteristics are lower than the characteristics of high-strength fibers produced by gel technology. The dry method consists in sintering powder particles into a monolithic film at a temperature below the melting temperature of the polymer and subsequent hardening of the monolithic film by orientational drawing. Along with the need to preserve the specific nature of the internal supermolecular structure of particles, which controls drawability the monolithic films, one should create cohesive bonds between particles. Otherwise the films being oriented could be break before reaching the maximum possible draw ratio which provides the highest mechanical properties of oriented filaments.

Obviously, the surface structure of the particles plays a key role here, since it is precisely the properties of the surface that affect the healing of interparticle boundaries. There are many methods for studying the fine structure of the surface, but only the method of plasma-induced thermoluminescence allows one to obtain information on the relaxation properties of near-surface nanolayers of reactor powder particles that characterize molecular mobility, which ensures the formation of cohesive bonds. The aim of this work is studying the UHMWPE reactor powders synthesized on different catalytic systems which have various compactabilities anddrawabilities.
2. Samples
Two UHMWPE reaction powders were selected for the study: one of them was well compacted UHMWPE powder with \( M_w = 3.5 \times 10^6 \) g/mole synthesized on one site F1 catalyst [3] and kindly provided by Prof. Sanjai Rastogi (Maastricht University, Netherlands). We refer to this powder as UHMWPE-R. The synthesis of UHMWPE reactor powder used by Tejin-Aramid Company for producing strong Endumax tapes by dry method is carried out on a similar catalytic system. Another one was poorly compacted UHMWPE powder with \( M_w = 3.0 \times 10^6 \) g/mole synthesized on supported Ziegler-Natta catalytic system in Boreskov Institute of Catalysis (Novosibirsk, Russia) used in gel-technology. This powder was designated as UHMWPE-553. It was of importance to clarify what factors are responsible for the difference in the near-surface structure of these reactor powders.

3. Experiment

3.1. Sample preparation
Three types of samples were investigated: starting powders, compacted and sintered.
Compaction was carried out in a Carver press (USA) in a special press-tool at room temperature under a pressure of 95 MPa for 15 minutes. The resulting compacts were sintered in the same press between two aluminium foils at 130°C under a pressure of 95 MPa for half an hour.

3.2. Thermoluminescence
Molecular mobility in the near-surface layers of the samples was studied by using a unique recently designed and patented Nanoluminograph device which is available only at the Ioffe Institute [4]. The powders were attached to the sample holder (a thin-walled copper cylinder) with Dottite conductive adhesive. Compacted and sintered specimens were merely attached to the holder with strong springs to ensure good thermal contact. The samples, preliminary evacuated (down to \( 10^{-7} \) torr) and cooled down to 77 K, were activated by the low temperature, low power high frequency plasma of Ar glow discharge (13.36 MHz) for 1s under the Ar pressure (\( 10^{-1} \) torr). Under these conditions, only a thin surface nanolayer of the sample was activated. The glow curves (temperature dependences of luminescence intensity) were recorded at a heating rate of 10 K/min in the temperature range from 77 K to 350 K. In order to minimize changes in the surface structure during its activation by the glow discharge the input power of the glow discharge was reduced to the minimum possible value limited by the sensitivity of the detection system (0.004 ± 0.001) W/cm³.

4. Results and discussions
It has been found that the glow curves of powders, as well of compacts and sintered samples prepared from them, noticeably differ from each other despite the fact that at least two peaks are clearly visible in all the curves: a low temperature peak (LT) in the region 100-170 K and a high temperature peak (HT) in the region 170-280 K (figure 1).

Figure 1. Glow curves for the UHMWPE powders (A), compacts (B) and sintered compacts (C). Blue curves refer to UHMWPE-553 and black curves to UHMWPE-R.
The peaks, however, have the complex shapes which imply the overlapping of several processes that occur when a sample is heated. It is generally accepted that the emission of light quanta occurs due to recombination of electrons released from electron traps with counter ions. However, polyethylene is a nonpolar polymer and has a negative electron affinity. Therefore, the question arises, what are electron traps in polyethylene. As follows from the literature [5], the traps in non-polar polymers can be only stacking faults, molecular cavities, adjacent molecules formed in a certain way, conformational defects such as kinks, molecular loops and all kinds of irregularities. Since the activation energy of thermoluminescence $E_{TL}$ is close to the activation energy $E_{act}$ of the relaxation processes determined by other methods [6], the peaks are supposed to be caused by the erosion of electron traps due to intensification of the micro-Brownian motion in the thermal range of corresponding relaxation transitions [6]. The LT peaks can be attributed to the small-scale motion $\gamma$-relaxation, while the HT peaks can be due to the quasi-independent segmental mobility ($\beta$-relaxation). Taking into account the complex peak profile, we made an attempt to decompose some of them into several peaks using the Fityk 0.9.8 program. The example of decomposition is presented in figure 2A.

**Figure 2.** An example of decomposition of the glow curve using the Fityk program (A) and temperature calculation of the activation energy $E$ for one of the peaks (B).

The activation energy was calculated by the formula $E_{TL} = kT_m^2/(T'' - T_m)$, where $T_m$ is the peak temperature, and $T''$ is the temperature at the half-width of the peak from its high-temperature side [6]. The peak areas (S arb. units), the total amount of luminescence ($\Sigma$, arb. units) and the contribution of each peak to the total amount of luminescence (content, %) were also estimated. The results obtained are presented in Table 1 for UHMWPE-R and in Table 2 for UHMWPE-553.

**Table 1.** Results of the analysis of the glow curves for powder, compacts and sintered compacts of UHMWPE-R

| Processing         | Peak 1 | Peak 2 | Peak 3 | Peak 4 | $\Sigma_{TL}$, arb.u. |
|--------------------|--------|--------|--------|--------|----------------------|
| Powder             | $T_{inK}$ | 129.3  | 164.08 | -      | 277.1                |
|                    | $E_{TL}$, ev | 0.084 | 0.08   | -      | 0.29                 |
|                    | S, arb.units | 11735 | 25737  | -      | 14631                |
|                    | Content, %   | 22.5  | 49.4   | -      | 28.1                 |
| Compact            | $T_{inK}$ | 126.9  | 159    | -      | 280                  |
|                    | $E_{TL}$, ev | 0.06  | 0.13   | -      | 0.45                 |
|                    | S, arb.units | 55110 | 10948  | -      | 11288                |
|                    | Content, %   | 71.2  | 14.2   | -      | 14.1                 |
| Sintered compact   | $T_{inK}$ | 130.45 | 159.5  | 198    | 260                  |
|                    | $E_{TL}$, ev | 0.095 | 0.16   | 0.31   | 0.48                 |
|                    | S, arb.units | 14024 | 4003   | 1713   | 1116                 |
|                    | Content, %   | 67.2  | 19.2   | 8.1    | 5.5                  |

| UHMWPE-R:          |        |        |        |        | 53102.45  |
|-------------------|--------|--------|--------|--------|-----------|
| UHMWPE–R:         |        |        |        |        | 71346.0   |

The peaks, however, have the complex shapes which imply the overlapping of several processes that occur when a sample is heated. It is generally accepted that the emission of light quanta occurs due to recombination of electrons released from electron traps with counter ions. However, polyethylene is a nonpolar polymer and has a negative electron affinity. Therefore, the question arises, what are electron traps in polyethylene. As follows from the literature [5], the traps in non-polar polymers can be only stacking faults, molecular cavities, adjacent molecules formed in a certain way, conformational defects such as kinks, molecular loops and all kinds of irregularities. Since the activation energy of thermoluminescence $E_{TL}$ is close to the activation energy $E_{act}$ of the relaxation processes determined by other methods [6], the peaks are supposed to be caused by the erosion of electron traps due to intensification of the micro-Brownian motion in the thermal range of corresponding relaxation transitions [6]. The LT peaks can be attributed to the small-scale motion $\gamma$-relaxation, while the HT peaks can be due to the quasi-independent segmental mobility ($\beta$-relaxation). Taking into account the complex peak profile, we made an attempt to decompose some of them into several peaks using the Fityk 0.9.8 program. The example of decomposition is presented in figure 2A.
Table 2. Results of the analysis of the glow curves for powder, compacts and sintered compacts of UHMWPE–553

| Processing   | Peak 1 | Peak 2 | Peak 3 | Peak 4 | ΣTL, arb.u. |
|--------------|--------|--------|--------|--------|-------------|
| Powder       | Tm,K  | -      | -      | 169    | 47625       |
|              | ETL, ev | -      | -      | 0.3    |             |
|              | S, arb.units | 34052.3 | -      | -      | 13573       |
|              | Content, % | 71.5   | -      | -      | 28.5        |
| Compaction   | Tm,K  | -      | -      | 260    | 81649.8     |
|              | ETL, ev | -      | -      | 0.19   |             |
|              | S, arb.units | 59632 | -      | -      | 22017       |
|              | Content, % | 73.0   | -      | -      | 2.9         |
| Sintering    | Tm,K  | 131    | 195.88 | -      | 260         |
|              | ETL, ev | 0.062  | 0.18   | -      | 0.26        |
|              | S, arb.units | 25612 | 5838   | -      | 5230.6      |
|              | Content, % | 69.82  | 15.9   | -      | 14.2        |

Using the approaches developed by V.A. Bershtein and V.M. Egorov [7] and admitting the equality of $E_{TL}$ and $E_{act}$ of relaxation transition values, we estimated the number of monomer (CH$_2$–CH$_2$) units in the apparent kinetic units of motion for the LT peaks, the mobility of which is defreezed in the region of $\gamma$-transition. The calculation was carried out in accordance with the expression $E_{act} \approx (0.3 \pm 0.05) E_c N + B$, where $E_{act}$ is the activation energy of the transition in kJ per mole of kinetic units, $E_c$ is the cohesion energy (the intermolecular interaction energy per mole of monomer units equal to 9 kJ/mole), $N$ is the number of monomer (CH$_2$–CH$_2$) units and $B = 0.65$ kcal/mole is the barrier to the internal rotation in flexible chains. It turned out that the number of monomer units in the kinetic units of motion in the powder, compacted and sintered samples of UHMWPE-R is higher than those of 553-samples (4; 3.6; 2.4 and 2.22; 1.9 and 1.2, respectively). Besides, to make the results of the glow curve analysis more visual, we plotted graphs of the dependence of the total sum of luminescence, as well as of the relationship between shallow and deep traps on the processing method of the powders studied (figure 3).

Figure 3. Dependence of total sum of thermoluminoscence (A) and relationship between shallow (LT-peak) and deep (HT-peak) electron traps (B) on the method of powder processing.

If the dependences of total luminescence on the method of powder processing (figure 3A) are very similar for the powders studied (if not the same), then a catastrophic difference is observed in the
dependences of the ratio of shallow and deep traps (figure 3B). It looks as if nothing happened to the powder UHMWPE-553 during compaction. This coincides with our experience: unlike the UHMWPE-R powder, which forms a mechanically coherent film after compacting, the compacted UHMWPE-553 powder is very fragile and brittle. Sintering makes the relationship between shallow and deep electron traps the same for both powders. However, one might think that this is an apparent identical property because this reflects the processes occurring on the surfaces of individual particles, but not at their boundaries. This assumption is confirmed by the difference in drawability of the sintered samples. The sintered precursors were subjected to a multi-stage zone drawing method developed at the Laboratory of Strength Physics at the Ioffe Institute. It turned out that the films prepared from UHMWPE-R powder could be stretched in almost 100 times, while the UHMWPE-553 powder films broke down when the draw ratio reached 20. This naturally affects the mechanical characteristics of the oriented films. Figure 4 shows the dependence of strength on the degree of drawing of the films sintered from the UHMWPE-R (red squares) and UHMWPE-553 (black stars) powders.

![Figure 4. Dependence of tensile strength on draw ratio of the sintered films.](image)

It is worth to note that the use of multi-stage zone drawing made it possible to obtain oriented films from UHMWPE-R powder with strength of up to 3.7 GPa, which is much higher than the strength of Endumax tapes (2.5 GPa).

We believe that the absence of longer kinetic segments of motion impedes coalescence of particles during compaction and a mechanically coherent film is formed.

It is also noteworthy that the temperature of the high-temperature peak, which characterizes usually the defreezing mobility in the region of $\beta$-relaxation, is higher for the UHMWPE-R powder and compact (277 K and 280 K) than that for the UHMWPE-553 samples (169 K and 260 K). Such a high temperature of the HT peak may be due to the presence of taut tie molecules and may be attributed to the cooperative motion of these segments ($\alpha$ relaxation).

5. Conclusion

A comparative study of the near-surface properties of two UHMWPE reactor powders differing in their ability to monolithization and orientational drawing was carried out with the help of the thermoluminescence method. It was found that the surface characteristics of powders in thermomechanical fields vary in different fashions. An analysis of the glow curves showed that in a poorly compacted UHMWPE-553 powder the kinetic units of motion responsible for $\gamma$-relaxation are
shorter than in the UHMWPE-R powder. The latter has probably a number of taut tie molecules as follows from the higher temperature of the HT peak. This is the evidence of a difference in the conformations of molecules in the disordered regions of the reactor powders investigated. A poor compactability of the UHMWPE-553 powder is due to the absence of molecular loose loops and irregular conformers. The film filaments obtained by multi-stage zone drawing from sintered UHMWPE-R powder demonstrate extremely high mechanical properties.

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