Molecular mobility in bulk and in near-surface nano-layers of ultra-high-molecular-weight polyethylene.

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Abstract. A comparative study of molecular dynamics in near-surface nanolayers and in a bulk of polyethylene is presented. Molecular mobility in near-surface nanolayers of polyethylene reactor powders and melt-crystallized films of various molecular weights prepared in different crystallization conditions were studied with the help of thermoluminescence technique using high frequency glow discharge Ar plasma for surface activation. Molecular mobility in a bulk of the same samples was investigated by the method of radio thermoluminescence, in which a deeply penetrating $\gamma$-quanta from $^{60}$Co radiation was used for activation of the bulk. A marked difference in a temperature position of the peaks on the glow curves of plasma-induced thermoluminescence and those of radiothermoluminescence corresponding to $\gamma$- and $\beta$-transitions was found to depend on crystallisation conditions and molecular weight. Quasi-independent segmental mobility ($\beta$-relaxation) in the near-surface nano-layers of UHMWPE reactor powder particles synthesized at low temperatures appeared to be unexpectedly unfreezed at the temperature higher than that in the bulk. It was supposed that this happened because of crystallization under the confinement conditions during low-temperature polymerization leads to formation of a specific surface structure.

1. Introduction

As known the structure of the near-surface layers and their properties differ significantly from those of the bulk and affects dramatically the behavior of solids in various thermal, mechanical and other fields. Investigation of the surface properties of solids is of particular interest now due to intensively developing physics of nano-sized objects, which are characterized by a very high surface-to-bulk ratio. A proper understanding of molecular mobility in the near-surface layers is also in high demand because the polymer mobility at an interface controls many technologically important processes such as welding [1], adhesion [2], melt-pressing[3, 4], and others. The enhanced molecular mobility at the polymer surface as compared to that in the bulk of the polymers prepared from the same powder was recently observed by X-ray photoelectron spectroscopy [5] and atomic force microscopy [6].

The knowledge of molecular dynamics in polymer near-surface nano-layers may be also gained with the help of a plasma-induced thermoluminescence technique (PITL). A large body of data related to molecular mobility in top-layers was obtained by PITL for a number of polymeric materials during the last decades [7-15]. It was found that the peaks on thermoluminescence glow curves correspond to relaxation transitions [7, 10, 11]. The main purpose of our investigation was to study the influence of crystallization conditions on relaxation properties of the near-surface nano-layers with the help of the...
PITL technique and to find the difference between molecular dynamics at the top-surface nanolayers and in a bulk by the means of a radiothermoluminescence technique (RTL).

2. Samples and experiment

The objects of investigations were ultra-high-molecular-weight polyethylene (UHMWPE) commercial reactor powder Stamylan (DSM, the Netherlands) with $M_w=2.5\cdot10^6$ g/mole, lab-scale UHMWPE reactor powder M30 (Institute of Organic Physical Chemistry, Minsk, Belorussia) with the same $M_w$ and high density polyethylene HDPE (OOO Plastpolymer, St. Petersburg) with $M_w=60\cdot10^3$ g/mole.

2.1. Sample preparation

The reactor powders were investigated as they were. In addition, both Stamylan and M30 UHMWPE reactor powders, as well as HDPE granules were isothermally recrystallized. To study the virgin surface structure of the melt-crystallized films the samples were prepared in two stages. At the first stage, films were obtained by pressing the reactor powder between two aluminum foils for 15 min under a pressure of 46 MPa at 180°C using a Carver-3912 lab-scale press (USA). At the second stage, the Al foil was removed from one side of the film, while the film with the other Al foil was placed in a small vacuum chamber pumped out to a forevacuum. The chamber was then mounted in a thermostat heated to 180°C, held for 2 hours and after this the isothermal crystallization of the films at 125°C during 6 hours was performed. Special attention was paid to preventing any contact of the free surface of the film with some other substance during crystallization in order to study the truly virgin surface.

2.2. Scanning electron microscopy

The morphology of reactor powders and melt-crystallized films from them were studied with the help of a scanning electron microscope JSM-7001F (Jeol, Japan). The samples were glued to conducting tapes on a sample holder coated with a layer of platinum 10-15 nm thick by sputtering in a Sputter coater PEKS, model 628, Gatan, USA.

2.3. Thermoluminescence

The molecular mobility at near-surface layers of both reactor powders and melt-crystallized films was investigated by the plasma-induced thermoluminescence technique (PITL) with the help of Nanoluminograph (PlasmaChem, GmbH, Germany) [16, 17]. The samples, preliminary evacuated and cooled down to 77 K, were activated by the low temperature, low power high frequency plasma of Ar glow discharge (13.56 MHz) for 1s. The pressure of Ar was $10^{-1}$ torr. The glow curves (temperature dependencies of luminescence intensity) were recorded at a heating rate of 10 K/min in the temperature range from 77 K to 300 K. As distinct from PITL the RTL technique uses deeply penetrating $\gamma$-quanta for activating luminescence, which allowed us to obtain information on molecular mobility of a whole bulk. The samples were exposed to $\gamma$-irradiation from $^{60}$Co source in the ampoule filled with liquid nitrogen (the dose was 0.2 kGy). Before exposure, the ampoule with samples was pumped out for 100 minutes at room temperature to remove oxygen and then only that it was filled with liquid nitrogen. The glow curves were recorded when the samples were heated with a heating rate of 10 K/min.

3. Results and discussions

The scanning micrographs of Stamylan reactor powder (SRP) and Stamylan film (SF) crystallized from this powder are presented in figure 1 (A and B, respectively). As expected, the surface structure of the powder formed during synthesis (figure 1A) differs significantly from the structure of the remelted powder (figure 1B). SRP is comprised of nodules, sub-nodulus and fibrillar entities while SF has lamellar structure, with the lamellae being collected in small clusters. In addition, there is a marked difference in the shape of PITL glow curves recorded for the samples investigated. Both curves have the complicated profiles, which consists of several elementary overlapping glow peaks.
There is lack of information on decomposing of the curves into elementary peaks. They can be only roughly decomposed into two peaks (low temperature (LT) peak in the region of 120-140 K and high temperature (HT) peak in the region of 200-260K. As known [7, 10, 11], the peaks on glow curves are caused by erosion of electron traps by micro-Brownian motion upon heating the activated samples and recombination of released electrons with counter ions. The intensification of the micro-Brownian motion occurs in the temperature regions of relaxation transitions, and therefore each peak on the glow curve can be attributed to a certain relaxation transition.

The LT peaks are attributed typically to γ-relaxation associated with unfreezing of torsion oscillation of 2-3 monomer units localized in the vicinity of conformational defects in the disordered regions. The positions of the HT peaks coincide with the temperature region of β-relaxation associated with unfreezing the quasi-independent segmental motion. While the positions of the γ peaks for the SRP and the SF samples almost coincide (figure 2 (1 and 2)), the positions of the β-peak for SRP sample (figure 2 (1)) markedly shifts towards higher temperature (246K). We suppose that it was caused by the fact that crystallization of SRP during synthesis occurred in confined conditions when one end of a growing molecule was still fixed on a catalyst particle while another part of the same molecule took part in crystallization process. It could result in generation of the stresses and formation of taut tie molecules. The presence of these molecules inhibited segmental mobility unfreezing and led to an
increase in the temperature of $\beta$-transition. On the contrary, SF samples were crystallized from a quiescent melt and obviously had no residual stresses in them. Thus, the inequality in crystallization conditions leads to dramatic difference in the surface molecular dynamics.

The comparative study of the relationship between molecular dynamics in the near-surface nano-layers and that in the bulk was carried out for two types of samples: an isothermally crystallized HDPE film (icr-HDPE) and UHMWPE M-30 reactor powder (see 2.1).

The classical lamellar structure formed during polymer crystallization near melting point is well seen in the SEM micrograph (figure 3).

Next to it the PITL and RTL curves are presented in figure 4.

![Figure 3. SEM micrograph of icr-HDPE.](image)

![Figure 4. PITL (1) and RTL (2, solid line)) glow curves of icr-HDPE](image)

Both the LT and HT peaks are resolved in PITL glow curve (figure 4, the black curve). In accordance with the temperature position they also may be attributed to $\gamma$- and $\beta$-relaxation processes. The shape of RTL glow curve (figure 4, red bold line) differs from that of PITL. The temperature positions of $\beta$ peak shifts to higher temperatures insignificantly. This means that the near-surface layer is only slightly devitrified as compared to the bulk. What makes the main difference between top-surface and the bulk in this case is the ratio between intensities of the HT/LT peaks, which points to a greater contribution of $\gamma$-relaxation and allows one to conclude that long-time crystallization leads to ejection of molecular cilia and the majority of conformational defects to the near-surface layers. Their unfreezing actually contributes a lot to $\gamma$-process.

Quite another relationship between the segmental mobility in the bulk and in the near-surface layers is observed for M30 UHMWPE reactor powder. The structure of the M30 powder is homogeneous too (figure 3) but is comprised of nodules (figure 5). It also differs from the structure of Stamylan reactor powder (figure 1A). PITL and RTL glow curves demonstrate two well pronounced LT and HT peaks: $\gamma$-and $\beta$-relaxations (figure 6). However HT peak on PITL glow curve is observed at a significantly higher temperature (260 K) than that on the RTL glow curve (170 K). Analysis of the data obtained above for Stamylan suggests that the near-surface nanolayers in the Stamylan UHMWPE reactor powder are stressed due to the specific crystallization conditions. Probably, the stresses arising during the synthesis of M30 are even higher than those developing during the synthesis of Stamylan. This obviously happens because M30 is synthesized at lower temperature (30°C) than Stamylan (60°C) and many taut tie molecules are formed. The RTL data are the evidence of the dramatic difference in the segmental mobility at the surface and in the bulk.
The PITL and RTL data for the M30 reactor powder and the melt-crystallized HDPE film are summarized in Table 1. To obtain a more general picture of the relaxation properties of PE, the table also contains the temperatures of relaxation transitions for samples studied only by the PITL method.

Table 1. Temperatures of $\gamma$ ($T_\gamma$) and $\beta$ ($T_\beta$) relaxation transitions as determined by PITL(surface) and RTL(bulk) for PE of various $M_n$ crystallized under different conditions

| Polymer                        | Crystallization conditions                        | $T_\gamma$, K, PITL | $T_\gamma$, K, RTL | $T_\beta$, K, PITL | $T_\beta$, K, RTL |
|--------------------------------|--------------------------------------------------|---------------------|-------------------|-------------------|-------------------|
| UHMWPE-M30 reactor powder      | crystallization under confinement upon polymerization at 30°C | 120                 | 120               | 260               | 170               |
| Stamylan reactor powder        | crystallization under confinement upon polymerization at 60°C | 124                 | -                 | 246               | -                 |
| melt-crystallized HDPE film    | crystallization at 125°C, 6 hours, forevacuum     | 118                 | 135               | 211               | 216               |
| melt-crystallized Stamylan film| crystallization at 125°C, 6 hours, forevacuum     | 120                 | -                 | 210               | -                 |

4. Conclusions

The study using the PITL and RTL techniques has revealed a significant difference between the molecular mobility in the bulk and in near-surface nano-layers of the polyethylene samples which was found to depend on the molecular weight and crystallization conditions. It is worthy to note that the molecular mobility on the top-surface layers proved to be either greater or lower than in the bulk. A drastically higher temperature of $\beta$-relaxation in the near-surface layers than that in the bulk was observed in the UHMWPE reactor powders crystallized during slurry synthesis. This effect was, probably, associated, with the residual stresses on the taut tie molecules that could be generated during crystallization under confinement conditions. At the same time the quasi-independent segmental mobility unfreezing ($\beta$-relaxation) in the near-surface layers of melt-crystallized HDPE film appeared to occur at the temperature lower than that in the bulk. In addition, the $\gamma$-relaxation transition which is attributable to the mobility of molecular cilia and various conformational defects was also observed at
much lower temperature than in the bulk. The conclusion was made that the long-time crystallization near the melting point leads to pushing out of all the defects and impurities to the surface.

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