Surface Structure of Nascent Particles of Ultrahigh Molecular Weight Poly(ethylene) Reactor Powders

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Abstract—A comparative investigation of the surface structure of three ultrahigh molecular weight poly(ethylene) (UHMWPE) reactor powders that differ by their ability to be processed to high-performance fibers is carried out with a JEOL 6300 scanning electron microscope and a nanoluminograph, which makes it possible to study thermoluminescence of ultrathin near-surface layers of solids. The activation energies of relaxation processes in near-surface layers of nascent particles and the sizes of kinetic units of motion, for which the mobility is defrozen in the temperature range of the corresponding transitions, are calculated from the glow curves. The possible location of kinetic units in supermolecular formations resolved in micrographs and their influence on the dissolution of the reactor powder are discussed.

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1. INTRODUCTION

In the 1970s, ultrahigh molecular weight poly(ethylene) (UHMWPE) fibers with record high values of the tensile strength (3.2 GPa) and the initial modulus (approximately 160 GPa), which exceeded the mechanical characteristics of fibers produced from other flexible-chain polymers by one order of magnitude, were produced using the specially developed gel technology [1, 2]. The demands for these high-strength and high-modulus fibers are extremely high, and the range of their application is very wide: from reinforcing elements in bulletproof vests, armor products, and motorboat bodies to tow lines, ropes, fishing lines, etc. At present, these materials have been manufactured using the gel technology on an industrial scale by several leading foreign companies (in the United States, Holland, and Japan).

Although the gel technology was developed more than 30 years ago, a noticeable progress in the improvement of mechanical characteristics of produced fibers is absent. However, the theoretical modulus of a macromolecule in the trans-zigzag conformation is considerably higher. It amounts to 260–300 GPa, and the theoretical strength at 0 K is ten times smaller than the elastic modulus, i.e., 20–30 GPa [3]. Despite the fact that the theoretical strengths estimated at room temperature according to the thermal-fluctuation concept developed by Zhurkov are lower (15–18 GPa) [4], they remain substantially higher than the mechanical characteristics achieved to date for lab-scale and large-scale poly(ethylene) (PE).

Therefore, the potentialities of this material are far from exhausted. The fact that the natural unique properties of the poly(ethylene) molecule are not achieved can be associated with a rather complex procedure for manufacturing fibers according to the gel technology and inadequate understanding of the physical processes occurring at each stage of the production.

The gel technology is a complex multistage process consisting of three main stages: the dissolution of a reactive UHMWPE powder at an elevated temperature in a solvent (decalin, xylol, kerosene, mineral oil, etc.), the production of fibers with the formation of a gel, and one-stage or two-stage orientation drawing of fibers.

The possibility of achieving high orientation elongations and, hence, good mechanical characteristics, as a rule, is attributed to a loose entanglement network formed in semidilute UHMWPE solutions [1, 2, 5, 6]. In this case, “by default,” it is implied that the initial structure of the reactor powder is completely destroyed because molecules passing into the solution tend to take the shape of a statistical coil and the entanglement network density is determined by their mutual overlap, which depends on the solution concentration, the solvent type, the character of stirring,
the molecular mass, and the molecular-mass distribution.

However, it turns out that not all UHMWPE reactor powders are suitable for their use in the gel technological process for manufacturing high-strength fibers. For example, the use of the UHMWPE reactor powders synthesized at the Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk, Russia) has demonstrated that, under the same conditions of the gel process, the dissolution of a number of powders leads to the formation of homogeneous solutions, which make it possible to produce gel fibers that can be drawn to large orientation elongations. The dissolution of other powders also results in the formation of good solutions; however, the produced fibers are characterized by a poor drawability. Finally, third powders cannot be used even for preparing homogeneous solutions. These observations suggest that the gelation depends, in some way, on the structure of the nascent polymer.

Since the dissolution of any solid compound begins with the surface, it is primarily important to compare the structures of the surfaces of nascent particles of reactor powders.

One of the methods for investigating the surface of polymers is scanning electron microscopy, which with the use of modern scanning microscopes provides a means for visualizing the surface morphology with a resolution of no worse than 2–7 nm depending on the accelerating voltage. Information on the molecular packing in ultrathin surface layers of nascent particles and the molecular mobility in these layers of the polymer can be obtained by analyzing the thermoluminescence excited in the near-surface layer of the polymer by an ionizing radiation source.

In this work, both these methods were used in order to perform a comparative study of the surface structure of three UHMWPE reactor powders with different abilities to be processed to high-performance fibers and to reveal the influence of the surface structure on the properties of the solutions formed.

### Table 1. Characteristics of the catalytic systems and parameters of the synthesis and synthesized reactor powders

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Catalyst type</th>
<th>Diameter of catalyst particles (d), (\mu)m</th>
<th>(T_{pol}), °C</th>
<th>Monomer pressure, atm</th>
<th>Cocatalyst content, mol/g</th>
<th>(M_{\eta}), (10^6) g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>TS-D-71</td>
<td>3.5</td>
<td>45</td>
<td>1.2</td>
<td>7.4</td>
<td>3.0</td>
</tr>
<tr>
<td>449</td>
<td>TS-D-95</td>
<td>4.0–6.0</td>
<td>50</td>
<td>1–4</td>
<td>5.4</td>
<td>4.42</td>
</tr>
<tr>
<td>385</td>
<td>TS-42</td>
<td>11.2</td>
<td>58</td>
<td>2.0</td>
<td>13.2</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Note: \(M_{\eta}\) is the viscosity-average molecular mass.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

2.1. Materials

For our investigations, we chose UHMWPE reactor powders with the viscosity-average molecular masses \(M_{\eta} = 10^6\) g/mol (PE-385), \(3 \times 10^6\) g/mol (PE-550), and \(4.4 \times 10^6\) g/mol (PE-449), which were synthesized using titanium–magnesium supported catalysts at the Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences. The synthesis conditions and the catalyst characteristics are listed in Table 1.

2.2. Electron Microscopy

The structure of nascent particles of the reactor powders was investigated on a JEOL 6300 scanning electron microscope. In order to prevent the accumulation of a charge on the particle surface, particles were placed on special conducting substrates and coated by a thin layer of gold (no more than 10 nm) via cathode sputtering. With the aim of decreasing the degradation effect of the scanning electron probe on the polymer samples, examinations were carried out at an accelerating voltage of no higher than 5 kV. At this voltage, the microscope resolution was no worse than 5 nm.

2.3. Thermoluminescence

The molecular mobility was studied using a recently designed and patented nanoluminograph. The design and principle of operation of the nanoluminograph are described in detail in the patent [7] and our earlier works [8, 9].

Particles of the powders under investigation were cemented by a Dottite conducting silver adhesive used in electron microscopy to an Al thin foil, which was attached to a cylindrical holder cooled by liquid nitrogen in a vacuum chamber. After evacuation of the chamber to a residual pressure of \(1.33 \times 10^{-4}\) Pa and cooling of the sample to 77 K, argon was allowed to fill the chamber to a pressure of 13.3 Pa. Then, a high-frequency glow discharge (13.56 MHz) was ignited for one second. This discharge served as a surface excitation source. In order to minimize the modifying action...