Surface modification of articles made from ultrahigh molecular weight polyethylene

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Ultrahigh molecular weight polyethylene (UHMWPE) is one of the few polymers used in the endoprosthetics of joints. UHMWPE has performed reliably as a friction material in the moving links of total hip joint endoprostheses (THJEs). Attempts to replace it with other polymeric materials has yet to prove successful. The “UHMWPE–CoCrMo alloy” friction pair has been used hitherto in most THJE constructions (Figure 1) on account of its minimal cost, low friction coefficient, adaptability during manufacture, simplicity of assembly, and good alignability and biocompatibility. UHMWPE can be readily modified, and it can be given prescribed structure and properties during processing \[1–4\]. Furthermore, the use of readily deformable UHMWPE ensures walking “comfort”, since it compensates for impact loads on the acetabulum. However, even the use of high-quality UHMWPE does not solve problems of THJE wear. The creation of implants capable of simulating the structural features of living tissue is urgent \[5\]. In our view, technical realisation of this idea assumes the creation on the friction surface of the polymer insert of the THJE of a microporous transition layer \[6–10\]. Certain technological features of formation of a microporous structure on the surface of articles made from UHMWPE are set out in the present work.

MATERIALS AND EXPERIMENTAL

On the international market, UHMWPE is represented by base grades and different composites. UHMWPE grades Hostalen Gur 4120 and Chirulen DIN 58836C produced by the German company Hoechst AG were used in the experiments. The physicomechanical and technological characteristics of the materials used in the work corresponded to certificate data \[11\].
The selection of the modifying components was dictated by features of their molecular structure, making it possible to interact effectively with UHMWPE on the physicochemical level. Furthermore, the group of reagents was limited to the list of substances permitted by the Ministry of Health for contact with living tissues. Medical vaseline oil (MVO, GOST 3164–78), which is used as a component of a number of artificial lubricants widely employed in orthopaedic practice, was used as the modifier for UHMWPE [12, 13].

The solvents hexane (TU 6-09-3345–78) and ethyl alcohol (GOST 118300–87) were used in the experiments.

Specimens were moulded from powder and block UHMWPE. The specimens of powder UHMWPE were moulded by “hot” pressing at a temperature of 170°C with holding under a pressure of 10–12 MPa until complete cooling of the specimens. Specimens were obtained from block material by machining. Composites based on powder UHMWPE and MVO were moulded at T = 160°C. In the oil concentration range 0–6 wt.%, dosing of the oil in the composite was carried out in steps of 0.2 wt.%, while in the range 10–50 wt.% it was carried out in steps of 5 wt.%. In the development of the technology for moulding of porous material, specimens of initial UHMWPE were held in plasticisers at different temperatures (60–170°C) for a time ranging from several minutes to several days. After modification, the process liquid was removed from the specimens. For this, the specimens were washed with hexane in a Soxhlet apparatus and dried in the chamber of a VUP-4 unit at a pressure of 100–200 MPa.

Structural investigations of specimens were carried out using Amplival and MPSU-1 microscopes in reflected and transmitted polarised light, and JSM-50A and Hitachi-3000N electron microscopes.

The porous structure of the specimens was studied by the computer processing of images obtained by electron microscopy, determining the quantitative indices using Global Lab Image software. The method provides objective criteria for assessing the porosity of specimens in the form of numerical parameters [14].

RESULTS

Technology for the production of microporous material based on UHMWPE was optimised according to criteria of the porosity and strength of specimens moulded by pressing a composite of UHMWPE and plasticiser with different ratios of the components. When MVO is introduced into UHMWPE, the mobility of the macromolecules is increased, which facilitates the crystallisation of the polymer. This is indicated by the effect of antiplasticisation of the UHMWPE, to which extrema at an MVO content of 2–5% correspond [6]. Further increase in the MVO content leads to weakening of the interaction of macromolecules and is accompanied with a monotonic reduction in the strength of the specimens. A sharp fall in strength at an MVO content of over 40% was due to the intense formation of a pore system in the polymer matrix.

In order not to lower by plasticisation the strength of material not taking part in friction, an investigation was made of the possibility of local modification of UHMWPE specimens by heat treatment in MVO on the side of the friction surface. With such modification, a layer is formed on the surface of specimens that consists of a porous polymer matrix containing liquid in the pores. The structure of specimens modified in such a way is similar to the structure of specimens made from a mixture of UHMWPE and MVO (Figure 2).

The method proposed in the present work for producing a porous layer on specimens of UHMWPE was based on concepts of phase transformations in polymer–plasticiser systems, leading to the formation of gels of high molecular weight compounds [15]. When heated, the MVO diffuses into the surface layer of the specimen which is converted into the state of a colloidal solution. During cooling, by virtue of the high viscosity of the colloidal solution, complete phase separation does not occur. The phase with a high polymer concentration retains its spatial continuity and forms a porous matrix. The liquid is immobilised in pores of the matrix.

An analysis of the porous structure of UHMWPE gels (Figure 3) showed that pores in the polymer matrix comprise communicating capillaries emerging on the...

Figure 2. Structure of the cross-sections of specimens (×1000) obtained by heat treatment of UHMWPE in MVO at T = 125°C (a) and at T = 150°C (b), and by pressing of mixtures of 30% UHMWPE + 70% MVO (c) and 50% UHMWPE + 50% MVO (d)
The length of the capillaries corresponds on average to the thickness of the gel-like layer of the polymer insert. The diameter of the cross-section of pores in the matrix lies in the range $1 - 10 \mu m$, which is consistent with the parameters of the porous system of cartilage [16]. In an examination of sections of experimental specimens, a gradual reduction in filling by liquid (oil) of the polymer matrix is observed, and the communicating system of pores gradually disappears.

By electron microscopy it was established that variation in the temperature and time conditions of modifying treatment of UHMWPE in MVO makes it possible to control the thickness of the microporous layer in a wide range: from unit to hundreds of micrometres (Figure 4). The temperature and duration of treatment of UHMWPE with plasticiser are equally effective factors of structure formation.

Figure 5 presents images of the modified surface of experimental specimens after the removal of the plasticiser. It can be seen that specimens produced under different conditions have an identical structure [17].

![Figure 3](Image)

**Figure 3.** Surface structure of gel based on UHMWPE and MVO: 1 – polymer matrix; 2 – pores containing liquid

![Figure 4](Image)

**Figure 4.** Change in the thickness of the modified layer as a function of the heat treatment time at temperatures of (a) $125^\circ C$, (b) $130^\circ C$, and (c) $140^\circ C$.
Table 1 gives data on the absorption of plasticiser by polymeric material during heat treatment. The nature of change in the mass of specimens indicates that there is a temperature-dependent UHMWPE and MVO compatibility limit that must be overcome by increasing the heat treatment time.

Absorption by the polymer of the plasticising liquid leads to change in the geometric dimensions of the specimens (Figure 6). The increase in dimensions of specimens in the plasticiser is dependent on the temperature and time of heat treatment. The limiting dimensions of the specimens and the rate at which they approach a constant value increase with increasing temperature.

The compressive strength of cylindrical specimens of UHMWPE, the end faces of which have been heat treated in MVO, decreases as a function of the heat treatment time (Table 2). It can be seen that the rate of decrease in strength increases with increasing heat treatment temperature. This seems to be the result of intermolecular plasticisation of UHMWPE, which extends to a considerable part of the volume of the specimen.

A UHMWPE specimen with a microporous structure is a non-equilibrium system, a specific property of which is syneresis – the spontaneous separation of liquid phase. One of the causes of syneresis is the relaxation of the stresses arising in the polymer matrix during pore formation. The dependence of syneresis on the plasticiser content is non-linear; the specific form of the kinetic dependence is determined by the nature of the polymer and plasticiser, and by the ratio of the components of the gel [18].

Investigations carried out on specimens containing 10–50 wt.% MVO confirmed the non-linearity of the kinetic dependences of syneresis. The maximum separation of liquid phase occurred 100–200 h after gel formation and reached 1 wt.% of the specimen. The amount of separating liquid then decreased exponentially, approaching zero after 40–45 days.

After heat treatment in MVO, the specimens were washed with solvents in order to extract the process liquid. It was established (Figure 7) that the solvent

<table>
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<tr>
<th>Temperature $T$, °C</th>
<th>Heat treatment $t$, h</th>
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<td>125</td>
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<td>140</td>
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<td>0.85</td>
<td>1.53</td>
<td>2.18</td>
<td>2.62</td>
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**Figure 5.** Surface of UHMWPE specimens after treatment with plasticiser under different temperature and time conditions: (a) $T = 130$°C, $t = 45$ min; (b) $T = 125$°C, $t = 120$ min

**Figure 6.** Dependence of the thickness of UHMWPE films on the temperature and duration of heat treatment in MVO: 1 – 170°C; 2 – 150°C; 3 – 140°C; 4 – 125°C

**Table 2.** Compressive strength of UHMWPE specimens as a function of the modification conditions

<table>
<thead>
<tr>
<th>Temperature of heat treatment $T$, °C</th>
<th>Compressive strength $\sigma$ (MPa) with different heat treatment times $t$</th>
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<tr>
<td></td>
<td>10 min</td>
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<td>125</td>
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(hexane) is volatilised almost entirely from the specimens (at room temperature) for 30 days. The use of vacuum drying made it possible to shorten the solvent evaporation time to 24 h. An alternative method is drying in an oven at a temperature of 60°C for a week, but this method may accelerate the ageing of the polymer.

On cross-sections of specimens subjected to extraction (Figure 8) it can be seen that only the surface layer, which is a microporous reservoir for drugs, is modified.

To ensure biocompatibility and to control wettability of the investigated surface of specimens, the latter, after extraction of the process liquid, was subjected to plasma treatment [9, 19]. The results of investigation made it possible to develop a process for the manufacture of UHMWPE inserts for THJEs with a modified friction surface (Figure 9).

The production layout for the modification of the polymeric elements of THJEs fits well into the process of their manufacture, without requiring any special expensive equipment. It can be hoped that the use of modified inserts in THJEs will increase their efficiency.

The author is grateful to a group of colleagues under the leadership of Professor L. S. Pinchuk who took part in the development of the technology for the modification of UHMWPE.

Figure 7. Kinetics of the change in mass of hexane Δm found in the porous polymer matrix of specimens during drying: 1 – in atmosphere at room temperature; 2 – in chamber of VUP-4 unit

Figure 8. Cross-section of a UHMWPE specimen with a microporous layer after extraction of the plasticiser: 1 – UHMWPE with initial structure; 2 – surface of specimen; 3 – microporous layer

Figure 9. Production layout for modification of polymer inserts of THJEs
REFERENCES


(No date given)