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Transformation of the lamellar structure into nanofibrillar structure in the bulk oriented ultra high molecular weight polyethylene: mechanical and tribological properties

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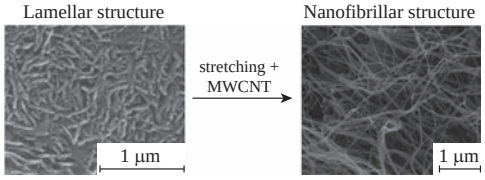
The possibility of a change in supramolecular structure of ultra high molecular weight polyethylene and its influence on the polymer mechanical and tribological properties has been demonstrated.



Polyethylene (PE) is a linear polymer which exhibits variable properties, depending on the relative position and packaging of macromolecules. High energy C–C bonds in the PE main chain make it very promising in terms of manufacture of highly oriented high-strength materials. Highly oriented films and fibers based on ultra-high molecular weight polyethylene (UHMWPE) have shown a tensile strength of 0.9–1.6 GPa[1,2] and even 4 GPa,[3] respectively.

Nowadays, there is a need for the production of bulk material with oriented structure and improved mechanical properties. Currently, the fabrication of bulk materials based on UHMWPE is achieved through self-reinforced highly oriented nanocomposite fibers or films creation.[4,5] Highly oriented fibers and films are often used as reinforcing fillers for different bulk polymeric matrices.[6,7] Therefore, development of technologies for the bulk materials with oriented structure and improved mechanical and tribological properties is a very promising direction of modern materials science.

UHMWPE is widely used in medicine, particularly in the manufacture of different implants, due to polymer high chemical stability.[8–11] However, UHMWPE in an isotropic state exhibits rather mediocre mechanical properties (tensile strength of 21 MPa, elastic modulus of 750 MPa). The development of bulk oriented materials based on UHMWPE allows one to create implants with improved properties. For example, the manufacture of an acetabular cup from bulk oriented UHMWPE polymer can increase the implant life time.

In the present study an introduction of multi-walled carbon nanotubes (MWCNT) into the UHMWPE matrix[†] was performed by solid phase mixing using a planetary ball mill at regimes similar to previously described.[12,13] The MWCNT were subjected to a fluorination with the gaseous fluorine at a pressure of 0.6–0.7 atm and a temperature of 150 °C for 2 h to improve their adhesion to the polymer matrix.[14,15]

Bulk oriented nanocomposites fabrication was carried out by the compression molding and low orientational stretching in several stages. At the first stage, monolithic materials with isotropic lamellar structure were obtained by the compression molding of UHMWPE/MWCNT mixture (T_{pres} = 180 °C, P = 25 MPa), Figure 1(*a*). A chaotic distribution of the lamellae in the bulk confirms its isotropic properties. UHMWPE with such a structure does not exhibit any outstanding mechanical properties (Table 1).

At the second stage, the samples were subjected to an uniaxial low orientational stretching at room temperature. The draw ratio was λ = 3. At the third stage, the samples after uniaxial low orientational stretching were subjected to the compression molding (T_{pres} = 130 °C, P = 25 MPa) and bulk oriented nanocomposites were fabricated. SEM images indicate the presence of nanofibrils with a diameter of 40 nm [Figure 1(*b*)]. According to modern concepts, nanofibrils with a size of 20–100 nm are considered as basic units, which do not undergo further fibrillization. The quality of the nanofibrillar structure may vary as defined by a ratio of an amorphous phase to a crystalline one. Therefore, nanofibrils exhibit different mechanical properties depending on the quality of their structure. For example, according to ref. 16 the theoretical strength of nanofibrils with a diameter of 100–150 nm can be as great as 19 GPa. In other words, the formation of nanofibrils with more perfect structure should be accompanied by a strong increase in the mechanical properties. In practice, this trend was confirmed by the fact that all highly oriented fibers and films based on UHMWPE possess nanofibrillar structure. However, the oriented PE-based materials require an elongation of $\lambda > 10$ to provide the nanofibrillar structure formation, which transfers them into the category of non-bulk materials. The

[†] UHMWPE powder (GUR 4120, Ticona GmbH) with molecular weight of 5×10^6 g mol^{-1} was used.

MWCNT produced by 'Nanotechcenter Ltd' (Tambov, Russia), with an external diameter of 8–15 nm, were used for the formation of bulk oriented nanocomposite. MWCNT content has been varied from 0.1 to 1 wt%.

Table 1 Tensile properties and wear resistance of UHMWPE-based materials.[a]

Material	Tensile strength/MPa	Elastic modulus/MPa	Elongation at break (%)	Wear resistance (h/L)
Isotropic UHMWPE	22±2	700±17	>200	5.30×10^{-9}
Oriented unfilled UHMWPE	94±9	767±11	71±4	3.62×10^{-9}
Bulk UHMWPE + 0.1% MWCNT	103±10	897±35	78±20	3.60×10^{-9}
Bulk UHMWPE + 0.5% MWCNT	122±2	867±61	48±3	3.43×10^{-9}
Bulk UHMWPE + 1% MWCNT	132±0.3	919±10	53±5	3.00×10^{-9}

[a]Tensile tests were performed in accordance with ASTM D638. Wear resistance was measured at the load of 19.2 N in the contact point.

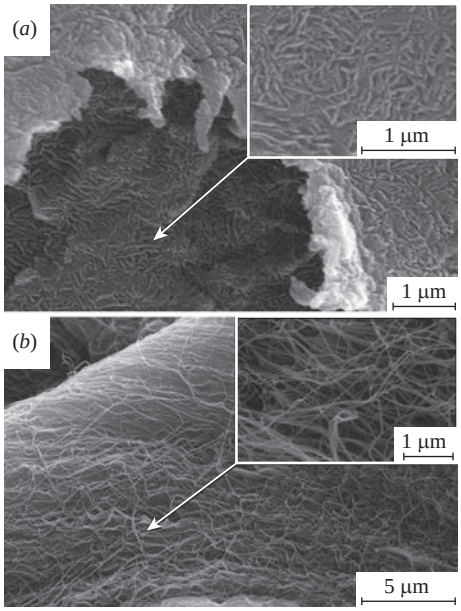


Figure 1 (*a*) Lamellar structure of isotropic UHMWPE nanocomposites; the sample surface was obtained by acids mixtures etching as described in ref. 18; (*b*) nanofibrillar structure of bulk oriented UHMWPE/MWCNT nanocomposites. The surface was studied after the tensile tests.

proposed method allows one to produce bulk materials with nanofibrillar structure in UHMWPE at a low draw ratio of $\lambda = 3$.

The presence of MWCNT in UHMWPE matrix is a cause of a nanofibrillar structure formation. An application of a draw ratio of $\lambda = 3$ to UHMWPE without nanotubes led to the formation of oriented structure without nanofibrils (Figure 2). The MWCNT can serve as crystallization centers in PE macromolecules.[3,17] The proposed bulk nanocomposites production technology provides the conditions for the UHMWPE lamellar structure crystallization on the nanotubes surface as it is shown in Figure 1(*a*). In the stretching process carried out at the second stage, nanotubes undergo significant movement with UHMWPE macromolecules, which leads to a transformation of the lamellar structure obtained on the MWCNT surface into the nanofibrillar structure [see Figure 1(*b*)]. The transformation is caused by the straightening of UHMWPE macromolecules packed in a lamellar structure. Remarkably, the fluorination of nanotubes plays a key role in the increase of the concentration of nanofibrils. Nanotubes functionalization improves the interfacial adhesion between the polymer matrix and fillers and therefore increases the filler nucleation ability.

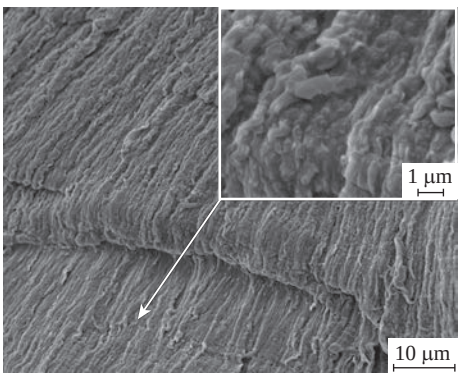


Figure 2 SEM micrograph of the oriented unfilled UHMWPE.

The transformation of the UHMWPE lamellar structure into the nanofibrillar one affects the composite mechanical and tribological properties. The results of the isotropic, oriented unfilled UHMWPE, and bulk nanocomposites tension measurements are collected in Table 1. The orientation of the unfilled UHMWPE resulted in a fourfold increase in the tensile strength as compared to the isotropic UHMWPE. The introduction of the fluorinated MWCNT into the UHMWPE polymer matrix led to nanofibrillar structure formation and further increase in the tensile strength up to 132 MPa for the bulk UHMWPE + 1% MWCNT (see Table 1). Elastic modulus of the fabricated composite weakly depends on the polymer matrix orientation and the filler concentration. The elongation at break is reduced.

The tribological study of composites in the mode of dry friction was carried out by cylinder-disk method at a sliding speed of 2.6 m s^{-1} and the load varied from 9.64 to 19.2 N. The friction coefficient and wear resistance were determined for a 3.35 km friction distance. Wear resistance was determined as the ratio between the depth of the wear spot (h) and the sliding distance (L). The friction coefficient decreases significantly in the case of the UHMWPE with oriented and nanofibrillar structures, oriented unfilled UHMWPE, and bulk UHMWPE with addition of 1 wt% of MWCNT (Figure 3). This effect was particularly evident at low loads. The friction coefficients of materials with different structures achieve the similar value with an increase of load to 16 N. Further increase of load led to a reduction of the friction coefficient in the case of the materials with oriented and nanofibrillar structures.

The UHMWPE-based materials wear resistance has been significantly strengthened after orientation, nanofibrillar structure formation and the increase in MWCNT content (Table 1). The maximum wear resistance has been observed for the bulk UHMWPE with addition of 1 wt% fluorinated MWCNT, which corresponds to an increase in wear resistance by 76% as compared to an isotropic UHMWPE.

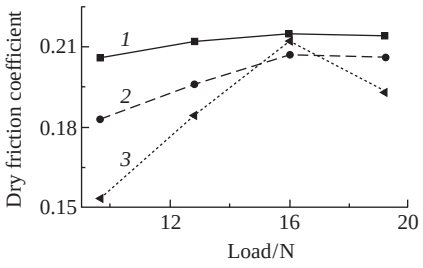


Figure 3 Dependence of friction coefficient on the load for (*1*) isotropic UHMWE, (*2*) oriented unfilled UHMWPE, and (*3*) bulk UHMWPE + MWCNT.

Bulk materials based on UHMWPE designed in this work can be recommended for an application in the low- and medium loaded friction elements, as well as acetabular cups for a total joint replacement.

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