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Comparison between self-reinforced composites based on ultra-high molecular weight polyethylene fibers and isotropic UHMWPE

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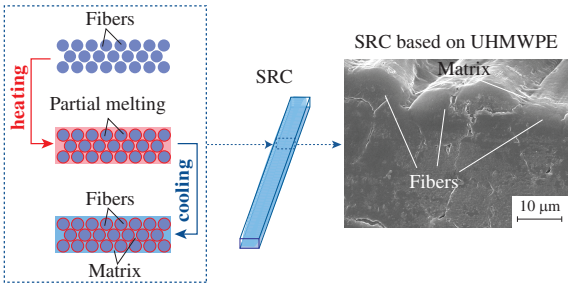
The self-reinforced composites based on ultra-high molecular weight polyethylene (UHMWPE) fibers and isotropic UHMWPE were comparatively analyzed. The composites were produced using a compression molding, which resulted in only partial surface melting of the fibers and promoted a good interfacial adhesion, while the fiber core remained highly oriented. It was demonstrated that the formation of such structure led to significantly higher performance properties of the composites as compared to those of the isotropic polyethylene.



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Nowadays, ultra-high molecular weight polyethylene (UHMWPE) is one of the most widely used high-performance thermoplastic polymers due to its molecular weight reaching up to 10^6–10^7 g mol^{-1}. For approximately three decades, UHMWPE has been employed as a bearing surface in total knee and hip joint replacement prostheses due to its good toughness, fatigue resistance, and biocompatibility. Despite these advantages, an osteolysis induced by UHMWPE wear debris is the major reason for a long-term failure in the total joint arthroplasty.[1] To improve the mechanical and tribological properties of UHMWPE, various methods including cross-linking,[2] surface modification,[3] and development of composites can be used. A wide range of fillers such as nanofillers, hard particles, and fibers were introduced in order to enhance the performance properties of UHMWPE.[4–8]

In recent years, a self-reinforcement has been proven as an efficient way to enhance the mechanical properties of polymers.[9–13] In self-reinforced composites (SRCs), both matrix and reinforcing phases consist of the same polymer. The SRC advantages include a high compatibility of the matrix and reinforcements, the capability of manifesting a good interfacial interaction, and a high recyclability as compared to traditional composites.[13–15] UHMWPE-based SRCs are of great interest since UHMWPE fibers possess excellent mechanical properties that are superior to all the known fibers in terms of specific tensile properties.[16] There are some difficulties related to manufacturing all-UHMWPE composites: the difference in melting temperatures of the oriented UHMWPE fibers and unoriented UHMWPE matrix is too small, the extremely high melt viscosity results in a negligible melt flow in SRC producing processes, *etc.*

In the present study, an approach based on the hot compaction of UHMWPE fibers was employed for the production of SRCs. The hot compaction† resulted only in a partial surface melting of UHMWPE fibers, while the molten part formed a matrix of the composite material during its cooling. This work was aimed at the investigation of structure and properties of the obtained SRC and at the comparison of its performance properties with those of isotropic non-reinforced UHMWPE.

Figure 1 shows a general approach for the SRC manufacturing. The proposed regime for the composites production results in a partial surface melting of the UHMWPE fibers and allows one to preserve the oriented structure of fibers.

The highly oriented structure of UHMWPE fibers enhances their mechanical properties. However, a relaxation process may occur at high temperatures, and molecular disorientation of the polymer chains can consequently be observed; while at low temperatures, the oriented structure is 'frozen'. The relaxation of oriented structure would result in a loss in the mechanical properties of fibers.[17,18] The SRC

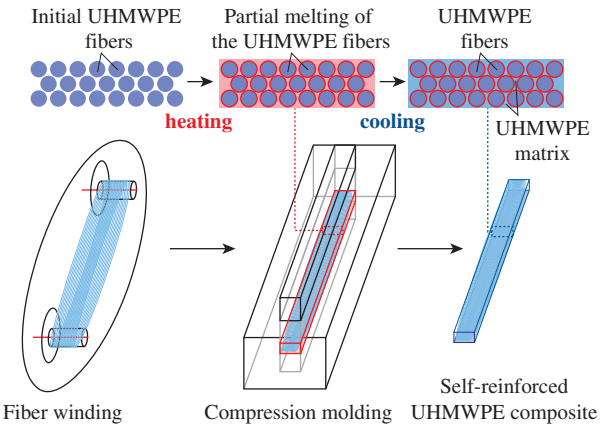

Figure 1 Schematic diagram of the SRC production.

† A commercial GUR 4120 UHMWPE powder (Ticona, Germany) possessing the molecular weight of 5×10^6 g mol^{-1} and an average particle size of 120 μm was used for the preparation of isotropic UHMWPE. This powder was compression molded at 180 °C and a pressure of 20 MPa. Continuous UHMWPE fibers SGX (Dyneema, Netherlands) having an average diameter of 15 μm were used for the preparation of SRC. The composites were compression molded at 155 °C and 50 MPa.

Table 1 Mechanical properties of the isotropic UHMWPE and SRC.

Material	Density/ g cm^{-3}	Tensile tests			Flexural tests	
		Tensile strength/ MPa	Young's modulus/ GPa	Elongation at break (%)	Flexural strength/ MPa	Young's modulus/ GPa
Isotropic UHMWPE	0.93±0.1	21±2	0.75±0.1	>300	22±1	0.7±0.1
SRC	0.97±0.1	460±12	21.1±0.8	⩽5	110±7	15±0.6

preparation process is always a compromise between some loss of oriented phase, including the associated loss of mechanical properties, and the development of good consolidation due to the increase in the melted and recrystallized phase. Both of these factors affect the SRC strength and stiffness. Table 1 summarizes the properties of the isotropic UHMWPE and SRC. The flexural and tensile properties[‡] of SRC are significantly higher than those of the isotropic UHMWPE. The longitudinal tensile strength reaches 460 MPa, Young's modulus is more than 21 GPa, whereas for the isotropic UHMWPE, the tensile strength and Young's modulus are as low as 21 MPa and 0.75 GPa, respectively. In addition, a significant decrease in the elongation at break was observed. The flexural strength of SRC is 5 times higher as compared to that of the isotropic UHMWPE. However, it should be noted that the SRC transversal tensile strength is about 20 MPa, *i.e.* comparable with isotropic UHMWPE. This occurs since the produced SRCs are unidirectional composites, and their transversal tensile strength is determined by the strength of fiber-matrix interface formed by the isotropic UHMWPE. To obtain high transversal and longitudinal tensile strength for reinforcement, it is necessary to use UHMWPE fabrics or prepare quasi-isotropic laminates.

The observed difference in mechanical properties arises from structural features[§] of the SRC and isotropic UHMWPE. The first one is characterized by a spherulitic supramolecular structure formed by lamellar crystals. The spherulitic structure of polymer [Figure 2(*a*,*b*)] determines its isotropic properties. The freeze fractured surface of SRC [Figure 2(*c*)] exhibits distinct fiber boundaries, and there is a melted material enough to fill the gaps and connect the fibers with each other. Due to a high processing pressure, the transverse section of fibers becomes nearly ellipse. The structure of SRC broken surface after the tensile tests [Figure 2(*d*)] is characterized by a pronounced oriented fibrillar structure. The SRC fracture occurs mainly due to a debonding at the fiber/matrix interface,

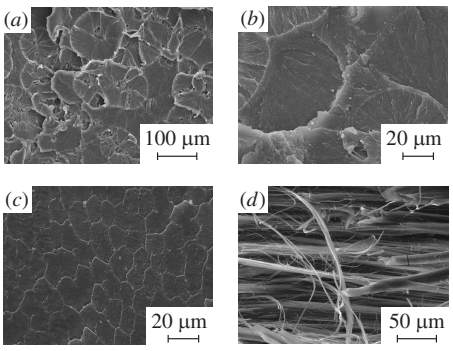

Figure 2 The freeze fractured surface of the (*a*), (*b*) isotropic UHMWPE and (*c*) SRC, and (*d*) SRC fracture surface after the tensile tests.

[‡] Tensile and flexural properties of the isotropic UHMWPE and SRC were studied using a Zwick/Roell Z020 universal test machine according to ISO 527 and ISO 178. For the tests, the rectangular samples (80×10×2 mm) were used. For each type of material, at least 5 samples were tested.

[§] Structure of the materials was investigated using a VEGA 3 TESCAN scanning electron microscope in the secondary electron image mode. The samples were coated with a thin layer of carbon in a sputter coater. The freeze fracture surfaces and SRC fracture surface after tensile tests were used.

while the 'splitting' of fibers has also been observed. The diameter of fibers in the composite varies from 10 to 12 μm. Considering that the average diameter of initial fibers was 15 μm, it can be concluded that the developed method enables melting only the surface layer of fibers. Such a partial melting promotes the good interfacial adhesion, while the fiber core remains highly oriented. The obtained structure ensures enhanced mechanical properties of the SRC as compared to those of the isotropic UHMWPE.

The major long-term limitations of UHMWPE performance as an orthopedic bearing surface are wear and creep deformation.[19] To increase a lifetime of the orthopedic implants, wear and creep resistance of UHMWPE should be significantly improved. The coefficient of friction (COF) is more stable for the SRC, while isotropic UHMWPE exhibits an unstable behavior of its COF (Figure 3).[¶] One can see jumps on the COF curve in the case of isotropic UHMWPE, and the curve reaches a plateau only after 80 min of testing. There is also a big difference between the initial and final COF values for the isotropic UHMWPE as compared to the SRC. An increase in the contact load leads to an increase in the COF and wear rate for the both materials. The COF at the end of tests rose from 0.098±0.002 to 0.108±0.003 for isotropic UHMWPE, and from 0.047±0.001 to 0.061±0.002 for the SRC with increasing the load from 5 to 20 N. Regardless of the applied load, the COF for the SRC is almost 2 times lower. The wear of SRC was also lower than that of isotropic UHMWPE: 0.028±0.003 and 0.015±0.002 mm at the load of 5 N and 0.029±0.002 and 0.020±0.002 mm at 20 N for UHMWPE and SRC, respectively. An increase in the wear resistance is usually associated with an improvement in the bulk properties, such as hardness and stiffness, which can lead to a change in the wear mechanism from adhesive to fatigue type. It is assumed that a high strength of UHMWPE fibers in the SRC results in the plastic deformation of surface layer under the cyclic frictional loading reducing. The fibers can also inhibit a crack propagation in the subsurface and reduce the delamination wear.[20]

The wear surface morphology of isotropic UHMWPE indicates that the adhesive wear is a predominant wear mechanism, and some flakes and asperities of UHMWPE formed due to the unidirectional shear stress can be observed (Figure 3). As the sliding goes on, a part of the adhesive transfer film peeled off and produced a lot of abrasive particles, which would stick on the UHMWPE surface or become free debris. While the wear tracks of SRC were smoother, it contained a low amount of the wear particles. In traditional composites, an increase in the wear rate is observed at fibers contents above 30 vol%,[21] which is caused by chipping the fibers and the formation of solid wear particles, accompanied by higher COF values and more intense wear. In the SRC, the reinforcing fibers are the same material as the polymer matrix and are non-abrasive towards the matrix material. Additionally, due to the same nature of the polymer matrix and fibers in the SRC, the formation of a stronger and more uniform interface is possible in contrast to the traditional composites. This results in a reduced crack nucleation and a propagation at the fiber-matrix interface, which is the main reason of fatigue wear.

The time dependences of the creep strain[††] of the isotropic UHMWPE and SRC indicate a general trend for the creep of materials: at the initial stage of experiment, the creep deformation developed rapidly, which includes an instant elastic response and

[¶] Tribological tests in the dry friction mode were carried out using a CETR-UMT-3 test machine in the linear reciprocating motion regime of a stainless steel ball with a diameter of 6.3 mm. The contact load was varied from 5 to 20 N, and the speed was 10 mm s^{-1}. The test duration was 10000 cycles, whereas each cycle corresponded to the sliding distance of 10 mm. For each type of material, at least 3 samples were tested.

[††] Creep tests under static tensile load were performed at load of 2.5–10 MPa for isotropic UHMWPE and 5–150 MPa for SRCs, the test duration was 300 min. For the tests, the rectangular samples 80×10×2 mm were used. For each type of material, at least 3 samples were tested.

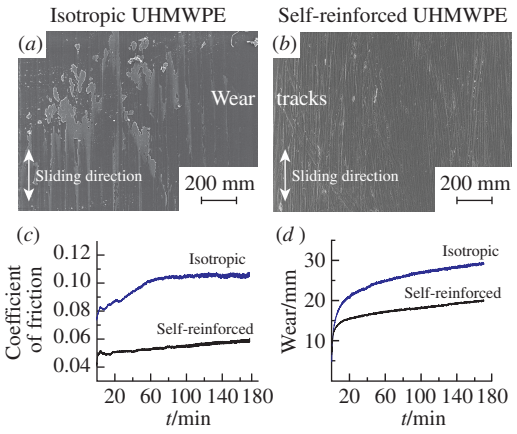

Figure 3 Wear tracks of the (*a*) isotropic UHMWPE and (*b*) SRC, (*c*) coefficients of friction, and (*d*) wear.

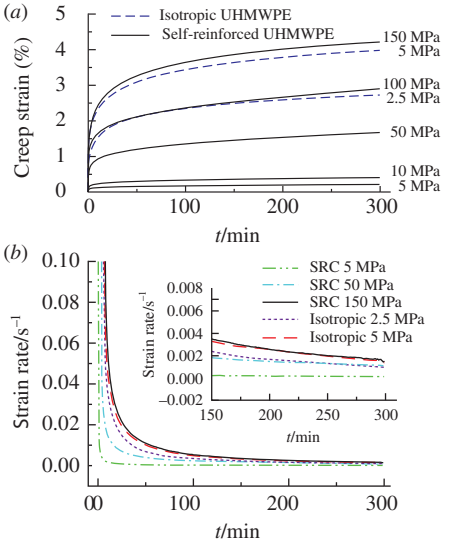

Figure 4 (*a*) Creep strain and (*b*) strain rate of the isotropic UHMWPE and SRC at various loads.

the rapid viscoelastic response to the applied load [Figure 4(*a*)]. After this short period, the creep developed into a stage where the creep strain propagated at a continuously reduced rate. The creep strain of isotropic UHMWPE at the end of the tests was 2.72±0.16% at the minimum load of 2.5 MPa [see Figure 4(*a*)]. A twofold increase in the applied load (up to 5 MPa) results in the strain growth up to 3.98±0.18%. At the same time, the creep resistance of SRC is much higher, and at the same load (5 MPa), the strain was only 0.21±0.05%. For the isotropic UHMWPE, the creep strain at the maximum load of 10 MPa was 11±0.8% (not shown in Figure 4), and it was only 4.2±0.25% for the composites even at the load of 150 MPa.

Figure 4(*b*) shows creep strain rates for the isotropic UHMWPE and SRC at various loads. Time dependences of the creep strain rates indicate that it decreases with an increase in the test duration. First of all, an initial rapid elongation was observed at the beginning of creep test, which is clearly time-independent for all materials. Then during the primary creep stage, the strain rate is relatively high, but it slows down upon increasing the strain, which may be due to the slip page and re-orientation of polymer chains under the applied persistent stress. After a certain period, the strain rate eventually reaches a minimum and becomes nearly constant, which is known as the secondary or steady-state creep. At this step, the viscous flow is activated, and a dynamic equilibrium between the polymer structure evolution and external load is subsequently reached. The duration of this step is relatively long. It can also be seen that the steady-state creep starts after various test durations at various loads. For example, it takes less than 10 min for the SRC strain rate to nearly become a constant at the load of 5 MPa, while at 150 MPa, it is barely constant at the end of test (300 min). Comparison of the strain rates for the isotropic UHMWPE and SRC at the same loads (5 MPa) shows that the strain rate of obtained composites is an order of magnitude lower (1.48×10^{-4} s^{-1}) than that for the isotropic UHMWPE (1.56×10^{-3} s^{-1}). It is known that the creep of polymers is mainly associated with a viscoelastic deformation due to conformational changes and slipping of macromolecules relative to each other. These processes mostly occur in the amorphous phase, since the intermolecular forces in amorphous regions are much lower than those in crystalline parts. Therefore, oriented structure and high crystallinity of the UHMWPE fibers result in the lower creep deformation and creep rate under a static load onto the SRC as compared to the isotropic UHMWPE.

In summary, novel fibers were produced using the hot compaction approach applied to the UHMWPE-based SRCs. The hot compaction at high mold temperature and applied pressure (155 °C and 50 MPa) resulted in the partial surface melting of UHMWPE fibers, during the cooling of molten part it recrystallizes and forms a matrix of the composite material. In terms of the mechanical properties such as coefficient of friction, wear rate, and creep resistance, the designed SRCs are far superior to the isotropic UHMWPE. The obtained composites can be a competitive alternative to the UHMWPE prostheses for the bearing surface in the total knee and hip joint replacement.

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