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The effect of adding calcium stearate on wear-resistance of ultra-high molecular weight polyethylene

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Abstract

In order to find an effective solid lubrication filler for the composites based on ultra-high molecular weight polyethylene, tribotechnical properties of UHMWPE and its blends with calcium stearate (C36H70CaO4, CS) under dry friction, boundary lubrication and abrasion were studied. It is demonstrated that wear rate of UHMWPE-CS compositions under dry sliding friction decreases by more than 4 times as compared to pure UHMWPE while the mechanicals properties do not change substantially. Under abrasion conditions the wear rate of the stated composites rises with the increased content of the filler. The optimal filler weight fraction is determined in terms of ensuring maximum wear resistance. The wear mechanisms of UHMWPE-based polymer compounds with a solid lubrication filler under dry sliding friction conditions and abrasion are discussed.

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Keywords: ultra-high molecular weight polyethylene; filler; calcium stearate; wear-resistance; permolecular structure

1. Introduction

Antifriction polymer composite materials are widely used as friction units and sealing elements in various types of modern equipment and medicine that is determining by their reliability and durability [1-3]. Namely the usage of the composite materials based on ultra-high molecular weight polyethylene (UHMWPE) allows increasing the abrasion resistance of metallopolymeric tribounits in multiples. Recently UHMWPE-based micro- and nanocomposites have been developed dynamically [4-8]. For instance, when manufacturing solid lubrication composites, dispersed fillers, graphite and molybdenum disulfide, are added into a polymer matrix to expand the

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usability of antifriction composites in the highly-loaded friction units when liquid or paste lubricants do not endure operating conditions. When introducing polytetrafluoroethylene (PTFE) into a high molecular weight matrix as a solid lubrication filler, the range of biocompatible extrusionable polymers for medical needs (orthopedic implants) can be expanded [9,10]. The calcium stearate (C36H70CaO4, CS) can be used as a solid lubricant as well. Ca-stearate is the mixture of calcium salts of stearic and resin-based fatty acids and is used for processing plastic materials as a plasticizer and adhesive, or as an emulsifier, lubricant, and stiffener in medicine (pharmacy) [11,12]. Calcium stearate is nontoxic, biocompatible, and, consequently, applicable in medical materials. There are no data available where calcium stearate was used as a UHMWPE filler.

In developing UHMWPE-based composite materials, the focus is traditionally made on primary operating conditions such as abrasion, dry sliding friction, and friction under boundary lubrication.

In practical applications UHMWPE products can experience three types of wear; consequently, it is important to look for the fillers capable of solving several tasks simultaneously, including decreasing coefficient of friction as well as increasing abrasion resistance under exposure to the fixed abrading particles, dry sliding friction and friction in presence of lubrication medium.

2. The objective of the research

The objective of the study was to investigate the tribotechnical properties of the UHMWPE-Ca-stearate micro-composite as well as to perform comparative analysis of various solid lubrication fillers efficiency (calcium stearate, MoS_2, graphite, fluoropolymer) in developing UHWMPE-based composites with high wear-resistance under dry and lubrication sliding friction as well as abrasion wear.

3. Methods

The research was conducted with UHMWPE powder produced by Ticona (GUR-2122) with molecular weight of 4.0 mln and particles size of 5-15 μm, and calcium stearate CS (C36H70CaO4, particles size 1÷7 μm). Polymer composites specimens were formed by hot-pressing technique with pressure 10 MPa and temperature 200 ºC with subsequent cooling rate of 1.5 ºC/min. The mixing of UHMWPE and CS filler polymer powder was performed in the planetary ball mill MP/0.5*4 with preliminary dispersing of the components in ultrasonic bath.

The friction testing machine SMT-1 was used to determine the wear-resistance of the materials under dry sliding friction by the “block-on-ring” scheme with applied load of 68.8 N and roller rotational speed of 100 rpm in accordance with ASTM G99 (sliding speed was 0.32 mps). The sample dimensions were H×W×L=7×7×10 mm. The diameter of the counterface made of bearing steel 52100 was 62 mm. The samples friction surfaces were examined with the optical profiler "Zygo New View 6200". The friction track area was computed with the software "Rhino Ceros 3.0" by the manual selection of the abrasion surface contour (the wear track) followed by the automatic calculation of its area.

The abrasion tests were conducted with the use of MI-2 tribometer (for testing the rubber wearing). The abrasion resistance was calculated under load of 0.15 MPa and disk sliding rate of 17.0 mpm regarding the couple of the samples fixed in a holder. The fixed abrading particles P 240 (sand paper) with grain size of 58.5 μm (GOST 426) were used. The volume abrasion was measured every 5 minutes by weighing the samples followed by the mass loss calculation. The testing technique corresponded to the requirements of ASTM G99 and DIN 50324. The tribotechnical properties were estimated through averaging of four samples.

The structural studies were conducted with the scanning-electron microscope LEO EVO 50 under accelerating voltage of 20 kV on the fracture (rupture) surfaces of notched specimen mechanically failing after exposure to liquid nitrogen. The mechanical properties were estimated through tensile tests carried out with the use of universal testing machine Instron 5582 by stretching the dump-bell samples with the number of ones of each type not less than 5 (GOST 11262-80).

4. Results and discussion

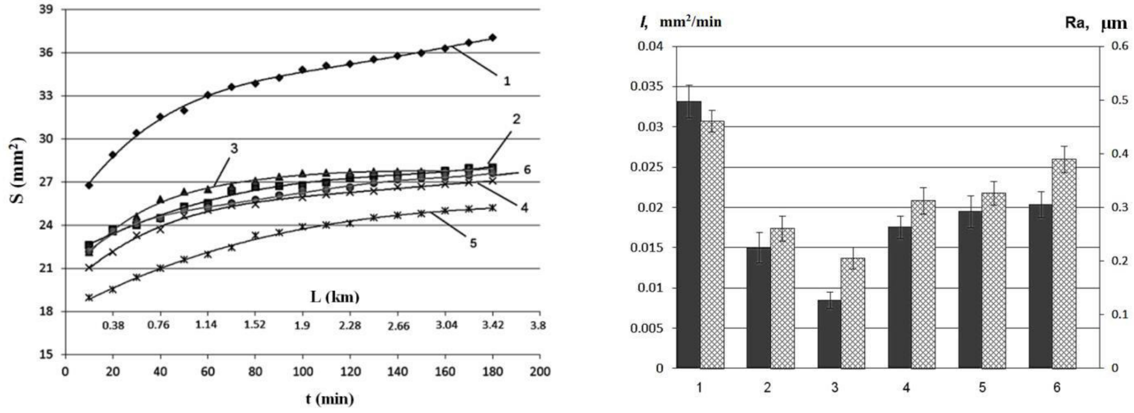
Table 1 shows the tribomechanical properties of UHMWPE and UHMWPEB + n wt. % of CS composites. The table illustrates that Shore D hardness of UHMWPE + n wt. % of CS composites decreases slightly as compared to pure UHMWPE. At first, the ultimate stress slightly increases (when weight fraction makes up to 3÷5 wt.%), and then it decreases. The value of elongation at failure changes slightly when the polymer is loaded with the filler weight fraction up to 3 wt.%. When UHMWPE is filled with Ca-stearate particles the blend density increases.

Table 1. Mechanical properties and coefficient of friction of UHMWPE-CS composites

Content of the filler, wt.%	Density, ρ, g/cm3	Shore D hardness	Ultimate stress σ_U, MPa	Value of elongation at failure, ε, %	Crystall. χ, %	Friction coef. *f*	
						D/friction	Water lubric.
0	0.936	59.5±0.6	32.3±0.9	485±23.6	56.5	0.120	0.079
1	0.935	58.9±0.7	34.7±1.0	484±25.0	44.2	0.099	0.072
3	0.937	58.3±0.5	35.0±0.9	461±24.3	42.5	0.100	0.075
5	0.940	57.5±0.6	35.1±0.9	411±19.5	41.0	0.111	0.095
10	0.941	57.3±0.5	28.8±1.0	402±15.6	38.1	0.123	0.105
20	0.955	56.4±0.6	28.8±1.1	366±17.9	37.5	0.135	0.107

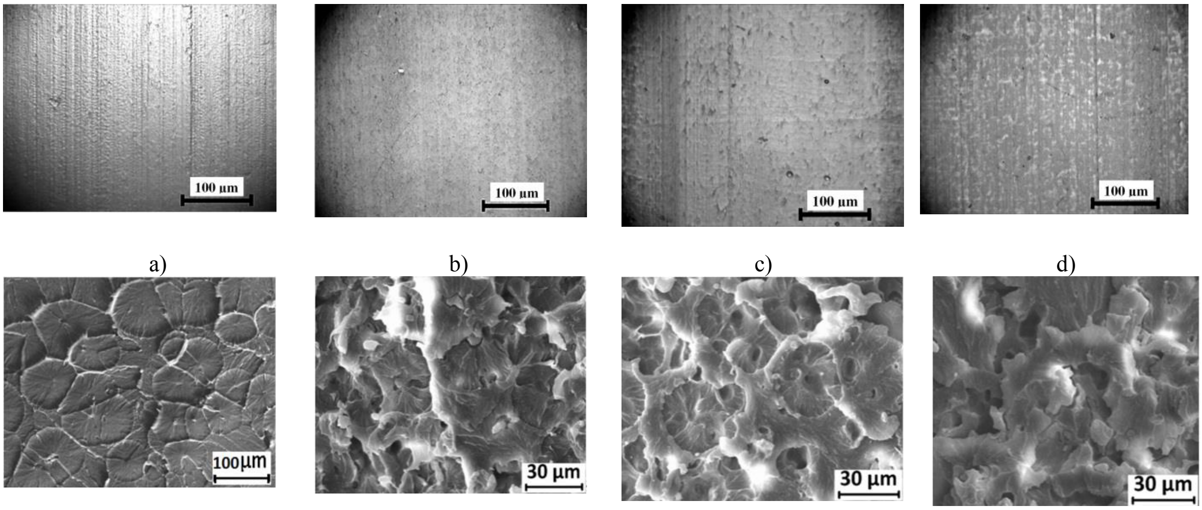
4.1. Dry sliding friction

The kinetic curves of the wear of UHMWPE samples and UHMWPE + n wt.% of CS composites (Fig. 1a) show that the wearing intensity is significantly lower than that of a pure UHMWPE. Fig. 1b demonstrates the diagram of the wear intensity at the stage of steady-state wearing (*I*, mm^2/min) of the above stated composites. Fig. 1b shows that the least wear intensity is registered for UHMWPE + 3 wt.% of CS compounds (the wear intensity is decreased 4 times as compared to pure UHMWPE). The wear track surface roughness in UHMWPE + 3 wt.% of CS composites is the least as well (Fig. 2) Therefore, while preserving the strength properties (ultimate stress, value of elongation at failure, table 1), UHMWPE + 3 wt.% of CS composites are characterized by quadruple increase of the wear resistance under dry sliding friction. The subsequent increase of calcium stearate content in the composition to 20 wt.% is ineffective in terms of rising the wear-resistance of UHMWPE + CS blends, though that content of the stated filler results in significantly increased wear-resistance as compared to that of pure UHMWPE. The coefficient of friction (Table 1) changes similarly with the filler weight fraction increase: at first, it decreases significantly (to 3 wt. % CS) and then it rises again.



a b

Fig.1. The kinetic curves of (a) wear intensity (I) and wear track surface roughness (Ra) of (b) UHMWPE and UHMWPE-CS composites: pure UHMWPE (1), UHMWPE + 1 wt.% CS (2), UHMWPE + 3 wt.% CS (3), UHMWPE + 5 wt.% CS (4), UHMWPE + 10 wt.% CS (5), UHMWPE + 20 wt.% CS (6) at the stage of steady-state wear under dry sliding friction.



a) b) c) d)

e) f) g) h)

Fig. 2. Micrograph of the wear track surfaces and the permolecular structure of UHMWPE (a, e), UHMWPE + 3 wt.% CS (b, f), UHMWPE + 5 wt.% CS (c, g), UHMWPE + 10 wt.% CS (d, h) under dry sliding friction.

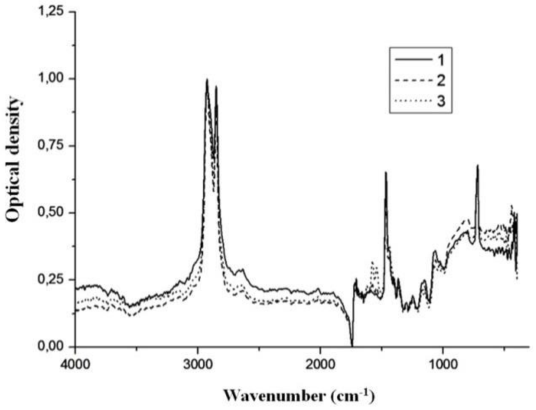


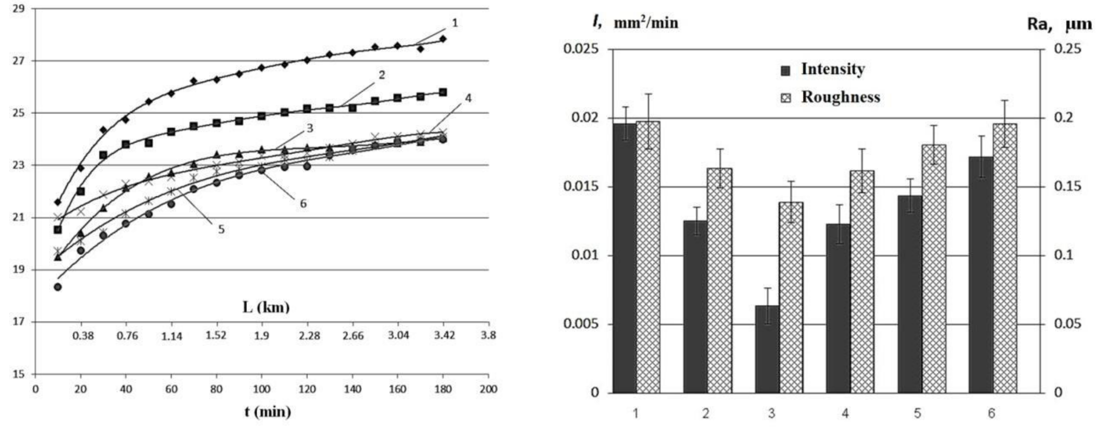
Fig. 3. IR spectra of pure UHMWPE (1) and UHMWPE + 3 wt.% CS (2) and UHMWPE + 10 wt.% CS composites (3).

The pattern for dependence of the wear track surface roughness (*R*a) on the filler content is similar to that of the wear intensity (*I*) of all examined composites (Fig. 1b), and the coefficient of friction as well (table 1).

To find the interrelation of the wear pattern under dry sliding friction, the formed structure and the Ca-stearate content in UHMWPE-based composites, the investigation was made of the wear surface topography (at the stage of steady-state wearing) and the permolecular structure of UHMWPE + n wt.% CS (Fig. 2). The investigation showed that the filling of UHMWPE with calcium stearate results in gradual changing of the permolecular structure; the formation of the spherolitic structure (size of spherolites decrease) is suppressed. Apparently, the permolecular structure becomes less homogeneous due to the filler particles holding back the spherolites increase in crystallizing. In the composites with high content of the filler, the spherolitic structure is almost not formed (Fig. 2h). The figures show that there is no adhesion between the filler and the matrix.

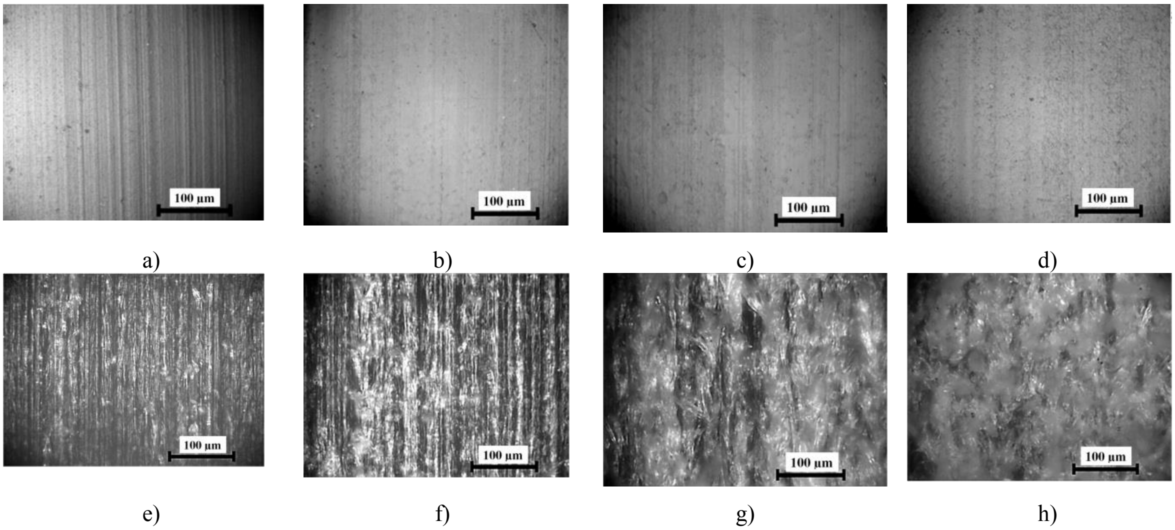
Microgroves present on the wear track surface of pure UHMWPE almost disappear in the composites with 3 wt.% of CS and are formed again with the further increase of the filler weight fraction (Fig. 2a-d).

Fig. 3 demostrates the IR spectra of pure and Ca-stearate filled UHMWPE that clearly shows that in UHMWPE-CS composites one can observe the increased intensity of C-H (750 cm^{-1}) and C=C (1640 cm^{-1}) lines which in its turn indicates the appearance of additional chemical bonds in the polymer resulting in the increased ultimate stress σ_U of the filled composite (table 1) [13]. At the same time, Shore D strength is decremented by one due to soft filler CS.



a b

Fig. 4. The kinetic curves of (a) the wear intensity (I) and the wear track surface roughness (Ra) of (b) UHMWPE and UHMWPE-CS composites: pure UHMWPE (1), UHMWPE + 1 wt.% CS (2), UHMWPE + 3 wt.% CS (3), UHMWPE + 5 wt.% CS (4), UHMWPE + 10 wt.% CS (5), UHMWPE + 20 wt.% CS (6) under water lubrication (distilled water).



a) b) c) d)

e) f) g) h)

Fig. 5. The micrographs of the wear track surfaces of UHMWPE (a, e), UHMWPE + 3 wt.% CS (b,f), UHMWPE + 5 wt.% CS (c, g), UHMWPE + 10 wt.% CS (d, h) under lubrication (a-d) and abrasion wear (e-h)

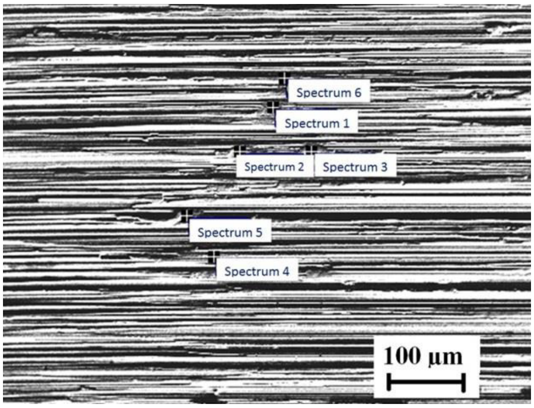
4.2. Friction under boundary lubrication

The results of the tests of the composites with water lubrication (distilled water) indicate that the filler under investigation (calcium stearate) serves as a solid lubricant under dry sliding friction conditions and in distilled water medium. In Fig. 4 one can see the kinetic curves (a) and the wear intensity as well as the wear surface roughness (b) of UHMWPE + n wt.% CS composites in lubrication medium. Fig. 4 shows that in presence of boundary lubricant, first, the wear intensity decreases both in pure UHMWPE and in UHMWPE-CS compounds. Second, the wear intensity of UHMWPE-CS composites in distilled water medium is lower than that of pure UHMWPE in the same medium. The wear surfaces roughness (*R*a) of the composites in lubrication medium is also lower than that of pure UHMWPE (Fig. 4 b).

The dependence of the coefficient of friction of the composites under investigation on the CS filler content in the lubrication medium is similar to that under dry sliding friction conditions (Table 1).

Fig. 5a-d display the wear track surfaces of UHMWPE and UHMWPE-CS composites under water lubrication conditions. It is seen that the wear surfaces of pure UHMWPE have narrow abrasion "microcratches" while there are none on those of composites. These results prove that calcium stearate serves as a solid lubricant in the wear of UHMWPE-based compounds under dry sliding friction conditions (similarity of the role of liquid boundary lubricant and solid lubricating in the filled polymer composites).

The microanalysis of the counterface surface proves the above-stated (Fig 6). The transfer film is not observed on the counterface and the increased carbon content on the counterbody surface indicates only the adjustment of its surface roughness by soft calcium stearate in tribounit.

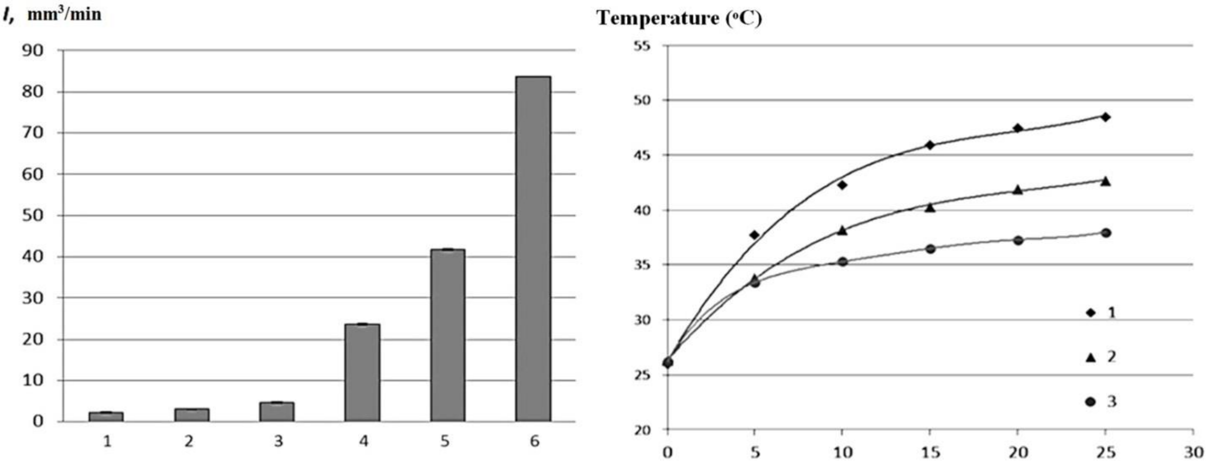


a

Spectrum	C (wt. %)	Ca (wt. %)	Cr (wt. %)	Fe (wt. %)
Spectrum	12.35	0.00	1.19	86.45
Spectrum	18.89	0.00	1.59	79.52
Spectrum	12.16	0.00	1.60	86.24
Spectrum	9.87	0.00	1.32	88.80
Spectrum	8.14	0.00	1.70	90.15
Spectrum	27.69	0.08	1.09	71.14

b

Fig. 6. The micrograph (a) and the results of microanalysis of the counterbody surface after the tests on UHMWPE + 20 wt.% CS composites under dry sliding friction (b).



a b

Fig. 7. The abrasion intensity (I) of UHMWPE and UHMWPE-CS composites (a): UHMWPE (1), UHMWPE + 1 wt.% CS (2), UHMWPE + 3 wt.% CS (3), UHMWPE + 5 wt.% CS (4), UHMWPE + 10 wt.% CS (5), UHMWPE + 20 wt.% CS (6) at the stage of steady-state wear under abrasive wear. P 240. (b) The kinetic curves of the temperature change of the wear surfaces of UHMWPE samples (1) and those of UHMWPE + 3 wt.% CS (2), UHMWPE + 20 wt.% CS (3) under dry sliding friction.

4.3. Abrasion

The paper analyses the effect of calcium stearate on UHMWPE-based microcomposites abrasion resistance. Fig. 7a demonstrates the diagram of the abrasion intensity of all investigated compounds with the abrasive grain size 240 (58,5 µm). Fig 7a shows that the abrasion intensity rises if UHMWPE is filled with Ca-stearate, the larger filler content (10÷20 wt.%) resulting in multiple increase of the abrasion (13÷17 times, columns 5 and 6). Fig. 5e-h illustrates the micrographs of the abrasion surfaces of UHMWPE (Fig. 5e) and UHMWPE-CS composites (Fig. 5f-h). Fig. 5 shows that, first of all, the fixed abrading particles cut the soft filler determining the low abrasion resistance of the composites. Second, calcium stearate cannot "protect" the matrix due to immense difference in the filler and the abrading grains sizes (1÷7 μm versus 58,6 μm).

5. Results and discussion

The paper deals the comparative analysis of the wear-resistance of UHMWPE-based composites with the solid lubrication fillers (calcium stearate, molybdenum disulfide, graphite, fluoropolymer). Taking into account the previous publications of the authors, Fig. 8 contains the wear intensities of UHMWPE-based compounds with the optimal content of the solid lubrication fillers [9,13], from which it can be seen that the wear-resistance of UHMWPE + 3 wt.% CS composites is close to that of UHMWPE + 10 wt.% PTFE and is considerably higher than those of UHMWPE + 3 wt.% C and UHMWPE + 3 wt.% MoS_2. The authors showed in [9] that due to the layered lattice structure, molybdenum disulfide and graphite as fillers form the transfer microlayer of high strength on the counterface; and in tribounits under dry sliding friction conditions, due to the mutual transfer of molybdenum disulfide or graphite flakes (scales), those fillers decrease the friction and abrasion of the machine elements and products. In [10] it was found that PTFE filler forms the transfer film on the counterbody lowering the coefficient of friction and serving as a solid lubricant in the abrasion of UHMWPE-PTFE compounds.

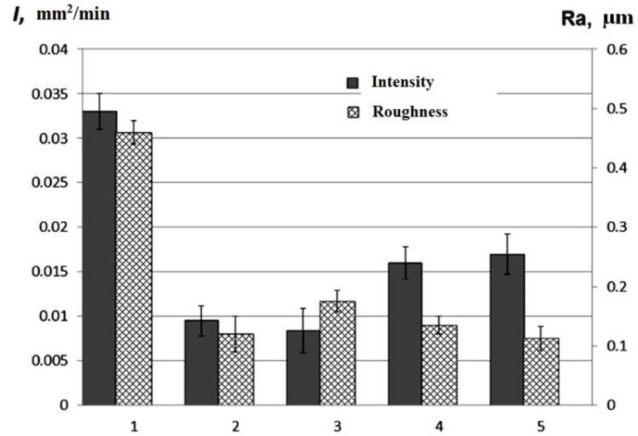


Fig. 8. The wear intensity and the wear surface roughness of UHMWPE (1), UHMWPE + 10 wt.% of PTFE (2), UHMWPE + 3 wt.% of CS (3), UHMWPE + 3 wt.% of C (4), UHMWPE + 10 wt.% of MoS_2 (5) at the stage of steady-state wear under dry sliding friction.

In terms of increased wear-resistance and preserved mechanical properties, calcium stearate was proved to be the most effective microfiller for high molecular weight matrix, decreasing the temperature of the sample (product) surface in tribounits (Fig. 7b). For this reason UHMWPE-CS compounds (to 3 wt. % of CS) can be used as biocompatible materials in medicine, namely in orthopedy.

Under abrasion conditions the cutting of the matrix and soft filler CS by the fixed abrading particles is the case that is why UHMWPE-CS compounds abrasion resistance results from the filler durability and the formed permolecular structure. Since in the abrasion the relatively soft calcium stearate cannot "protect" the matrix from the impact of the fixed abrading particles, UHMWPE-CS composites are not suitable for using under abrasion conditions. Soft filler polytetrafluoroethylene behaves similarly under abrasion conditions [10].

In abrasion the graphite and molybdenum disulfide (as the solid lubricants) role of increasing the wear-resistance of UHMPWE-based polymer compounds is cancelled out in part due to the inadequacy of the fillers and abradant granularity, therefore the abrasion resistance of the compounds with solid fillers depends on the abradant grain size and the formed permolecular structure durability.

6. Conclusion

The optimal weight fraction of calcium stearate filler (3 wt.%) is determined, that provides the increase of the wear resistance by more than 4 times under dry sliding friction. The stated effect is followed by the decrease of the coefficient of friction up to 1.2 times.

Calcium stearate serves as a solid lubricant in UHMWPE-based composites under dry sliding friction and in presence of lubrication medium.

UHMWPE-based compounds with soft microfiller, calcium stearate, are not suitable for using under abrasion conditions.

The comparative analysis of UHMWPE solid lubrication microfillers (soft ones being calcium stearate, fluoropolymer; and solid ones being molybdenum disulfide, graphite) in terms of preserving the mechanical properties, decreased coefficient of friction and increased wear-resistance under all three investigated abrasion types demonstrated that the most effective filler under dry sliding friction is calcium stearate. All examined UHMWPE-based composites with the solid lubrication fillers can be efficiently used for the friction units in absence of lubrication medium in engineering applications and in medicine, namely in manufacturing of endoprosthesis.

Acknowledgements

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