# POLYMER COMPOSITE MATERIALS BASED ON ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE MATRIX FILLED BY ALUMINUM OXIDE POWDERS

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**Abstract**

*The paper presents the results of experimental investigation of formation microstructure and properties of ultra high molecular weight polyethylene (UHMW-PE), which are modified by ceramics $A1_2O_3$ particles by different particle size and method of obtaining.*

## Introduction

Product designing based on advanced composite materials, including polymeric base, is one of the most important conditions for improving the operational and economic performances of products and machines.

At present such polymeric composite materials (PCM) which are not inferior to aluminum and titanium alloys by their physical and mechanical properties have been developed, and their use reduces the weight of the product that is relevant to the aerospace industry, shipbuilding, mechanical engineering, mining and oil and gas industry.

Ultra-high molecular weight polyethylene (UHMWPE) can be used as the polymer matrix. UHMWPE is a material with high performance properties such as specific strength, stiffness, fatigue (cyclic) resistance, high wear-resistance at low temperatures (up-200°C), ultralow coefficient of friction, high impact strength and resistance to hostile environments, weather impacts and radiation exposures. The unique material properties, good processibility and a variety of application allow you to use it widely for the production of various parts in tribology applications, abrasive action and hostile environments.

To improve the performance specifications of the material (strength, hardness and melting temperature) the modification of UHMWPE with aluminum oxide is suggested.

The aim of the present investigation regularities of processes compaction and formation microstructure and properties ultra-high molecular weight polyethylene (UHMWPE), which are modified by ceramics $A1_2O_3$ particles by different particle size and method of obtaining.

In the work the following tasks were solved: the development of theoretical models describing the processes of consolidation and structurization of PCM, the study of morphology of the source powders, the research of the effect of agents $A1_2O_3$ on the technological and physical-mechanical characteristics of PCM.

This paper presents the results of research of materials based on: UHMWPE, polyethylene with a molecular mass of $9,2*10^6$ - $10.5*10^6$ g/mol, the average particle size of 70 microns and aluminum oxide $Al_2O_3$ with an average particle size of 0.01 up to 7 microns.

## Materials and testing methods

The main method of determining the size and the shape of the particles was the optical microscopy (ZEISS Observer, Zlm-Germany) and scanning electron microscopy (JEOL JSM-7001F, Japan). To obtain micrographs of the particles the direct methods were used – a study of the particles themselves, translucence of the particles which are placed onto a carbon film.

The uniform distribution of aluminum oxide powder was achieved by pre-mixing it with UHMWPE powder in the ratio 1:5 in a ball mill. The resulting mixture was added in the form of the batch before the final mixing. Powder compositions were pressed in a rigid die at a specific pressure of the mold pressing in the range of 2 to 7.5 MPa. Pressing was carried out in the required mass fractions with sintering at temperatures ranging from 50 to 200°C.

To obtain the samples a die mold with an external source of heat – micanite heating annular element made in Germany was used. A stand was designed to obtain samples of composite material with sizes 17x17x10 (mm) with the ability to perform compression with sintering at temperatures ranging from 50 to 300°C (Fig. 1).

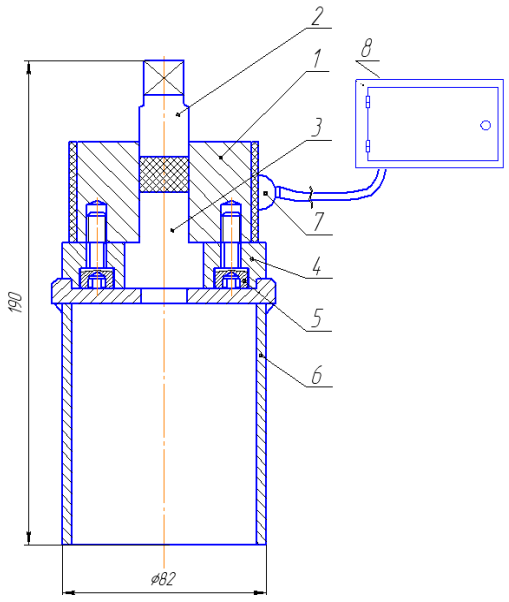


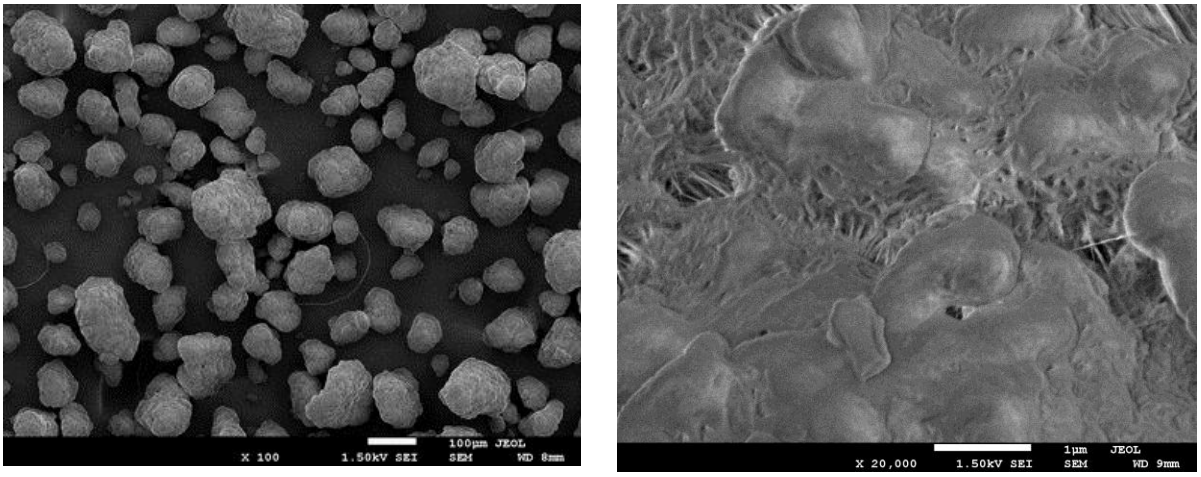

**Figure 1.** A sketch of the experimental design of thermo die mold (1-die, 2-upper punch,3- lower punch , 4- bolster, 5-fastening bolts, 6- crutch ejector, 7- heating ring, 8-electrical control cabinet.)

## Experimental results and there discussion

Firstly the morphology of the source powders, the formation of the structure of the samples obtained from the detached components of the composite under the influence of pressure and temperature were studied; the areas with a significant qualitative changes in the material, with the formation of the boundaries between particles (grains) that begin with intensive processes of mass transfer and with the formation of boundaries between powder particles and their agglomerates were determined.

Typical images of morphology of the source powders of the particles UHMWPE are presented in Fig.2. The particles have nearly spherical shape and rather narrow particle size distribution (no dust

fractions and large particles in size greater than 150 microns). It should be noted that the source powders of UHMWPE with an average size of about 70 microns are not monolithic, but they are composed of smaller micron-size agglomerates bonded with nanofibers. (Fig. 2. b).



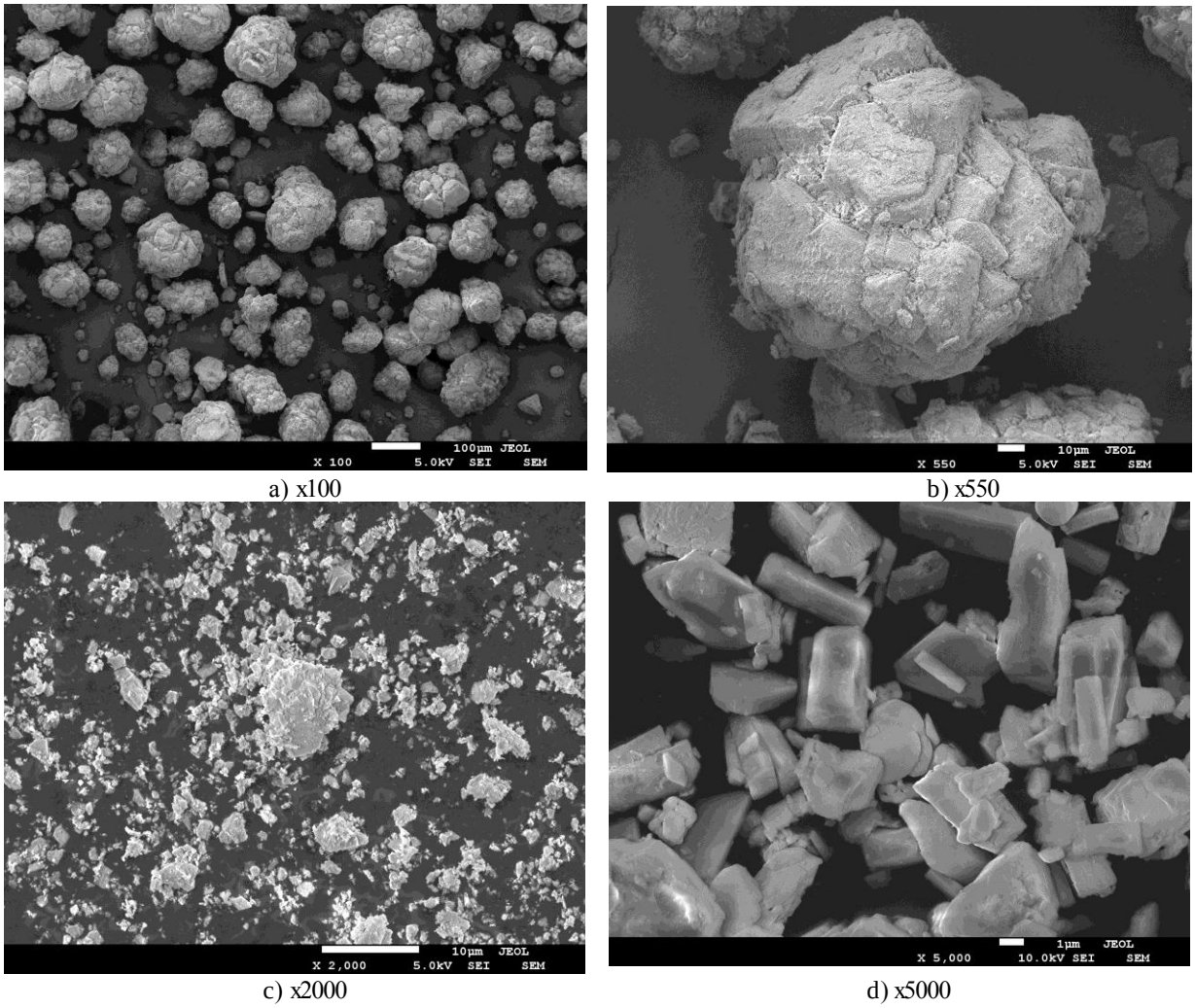

a) x 200 b) x 20000

**Figure 2.** Morphology of UHMWPE powder

Technical alumina, its powders were used in experimental studies (Fig. 3 a, b), according to grade G00 of GOST 6912-74 consists of agglomerates (sinters from the detached particles) with an average size of about 70 microns. Agglomerates are formed during the metallurgical redistribution, they have weak bonds between the particles (crystallites), and they can be easily destroyed with little external mechanical action. Therefore, the technological process has the preparation operation – chopping the source powders of alumina. In the planetary-type mill the powder particles are subjected to abrasive and shock action. Powders of alumina $Al_2O_3$ are crushed into smaller particles as a result of intensive treatment (energy up to 10g).

Fig. 3 c, d shows the micrographs of the powder particles of alumina grade G00 after being ground in a ball planetary-type mill. The micrographs were obtained on a raster electron microscope (JEOL JSM-7001F-Japan).

Typical changes in the density of compacts depending on the temperature at pressures of 5 to 10 MPa are shown in the graphs in Fig. 4. The nonmonotonic character of the density change shows that there are certain temperature ranges, which correspond to different mechanisms of interfacial interaction. In the temperature range from 20°C to 70°C, the interaction between the fragments of the structure is limited only by the mechanical clutch and repacking of the particles. At temperatures between 70°C to 90°C it is likely to be liquid-like coalescence. Based on the graphs (Fig. 4, 5), during the following heating essential changes in the interaction between particles with the formation of contact necks and the boundaries between detached, fragments of the structure take place at the temperature of 90°C to 120°C. In particular, at temperature of 120°C ÷ 130°C there is no increase in the density of the compacts and the further increase in temperature and exposure are not necessary (Fig. 4). Moreover the data obtained during X-ray studies indicate that at temperature around 130°C the process of amorphous structure formation begins and at 140°C it practically ends (Fig. 5, curves 4, 5) with the production of glass phase. These hypotheses are indirectly confirmed by the study of compacts surfaces images obtained in these modes (Fig. 6). For this reason, we can assume that 120°C (<130°C) is necessary and sufficient heating temperature of PCM based on UHMWPE.




a) x100 b) x550

c) x2000 d) x5000

**Figure 3.** Morphology of the source powder of technical alumina grade G00

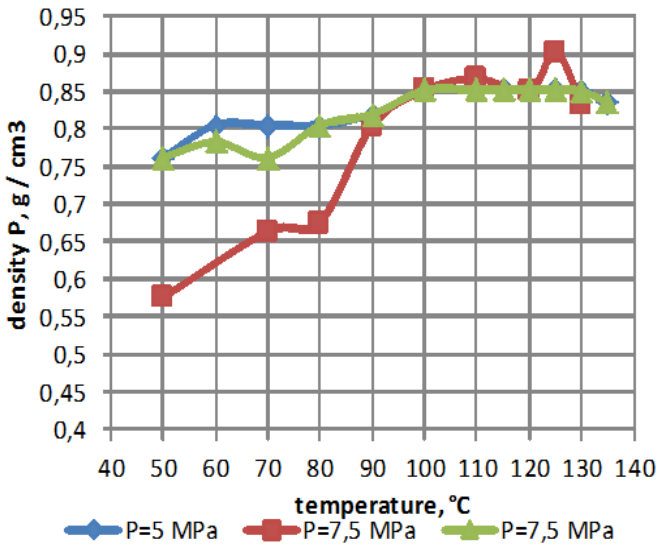



**Figure 4.** Dependence of the relative density of samples of UHMWPE on the heating temperature.

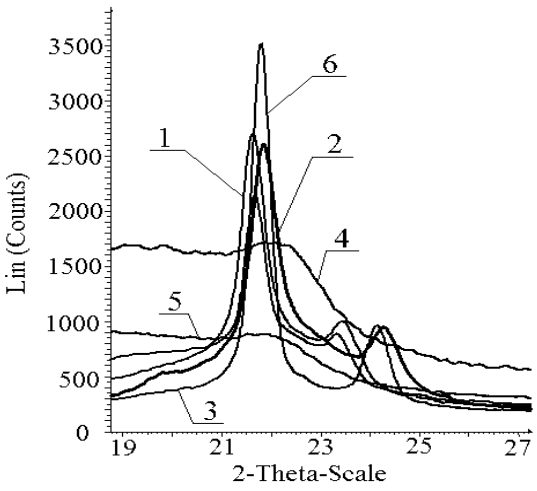



**Figure 5.** Diffractogram of UHMWPE materials at different temperatures. (1 – 20°C, 2 – 110°C, 3 – 120°C, 4 – 130°C, 5 – 140°C, 6 –20°C (cooling)).

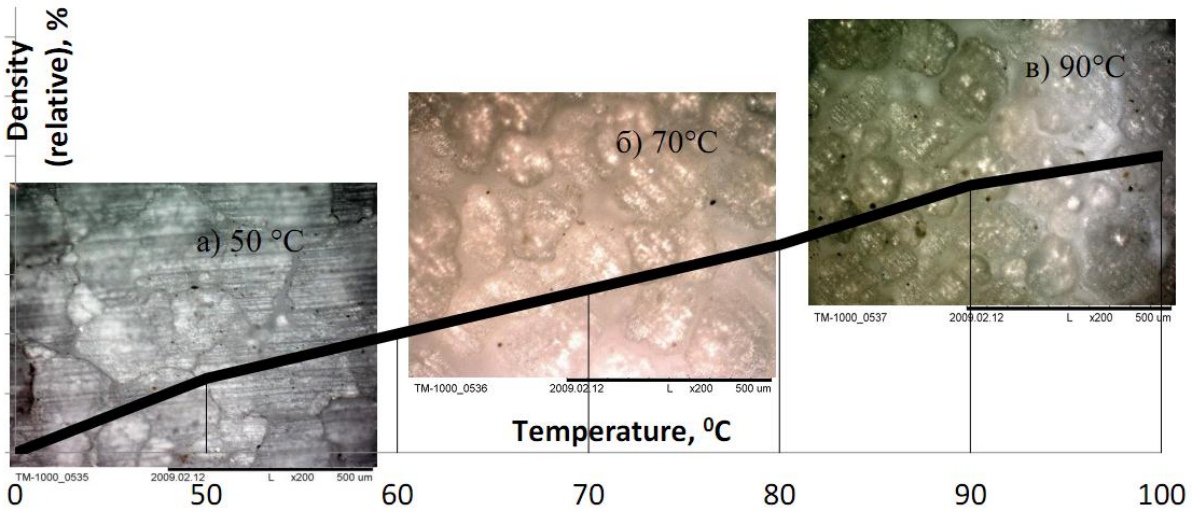
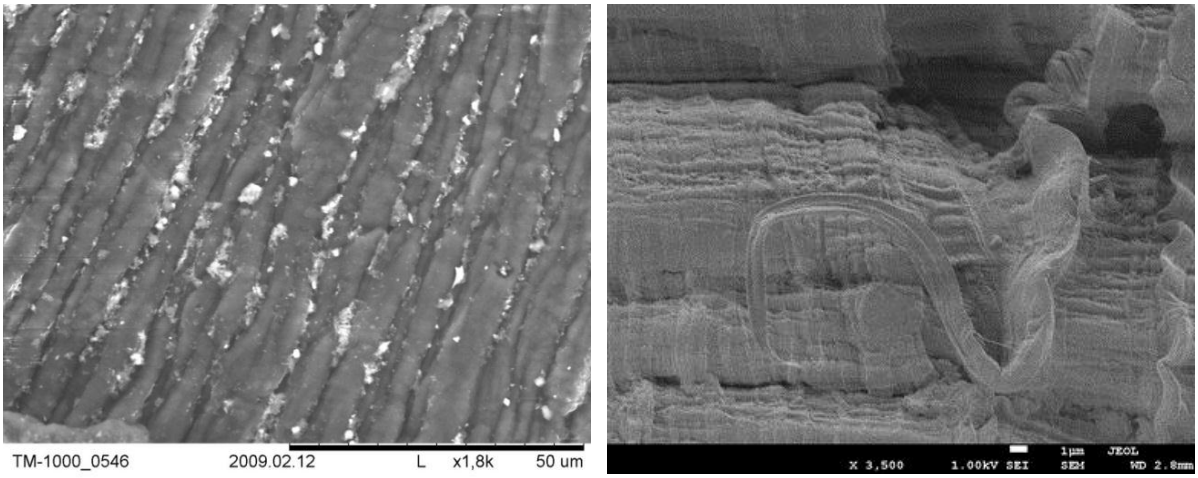



**Figure 6.** Metamorphoses of the microstructure of compacts during heating

Taking into account obtained values of temperature defined points (corresponding to the beginning of mass carry processes, the formation of contact necks between the individual powder particles (entities) of about 90°C) on the samples of pure UHMWPE, sintering must be carried out at this temperature range in isothermal mode at a curing of 0.5 ÷ 1.5 hours, it depends on the size of the part. In a sufficient degree, it can contribute to the completion of mass carry processes, homogenizing by volume with the formation of more streamlined, uniform, non-porous structure.
In the defined point of the temperature at 90°C it is proposed to make the additional compaction (increase in pressure from 20 to 50 of the initial depending on the size of parts in height). At the same time, this allows us to accelerate the processes of compaction and homogenizing, to structure the material with the formation of the elongated along one axis "grain" of the matrix material, to provide uniform distribution of $Al_2O_3$ inclusions in the amount of matrix.




a) x 1800 b) x 3500

**Figure 7.** The nature of the fracture surface of specimens after impact test

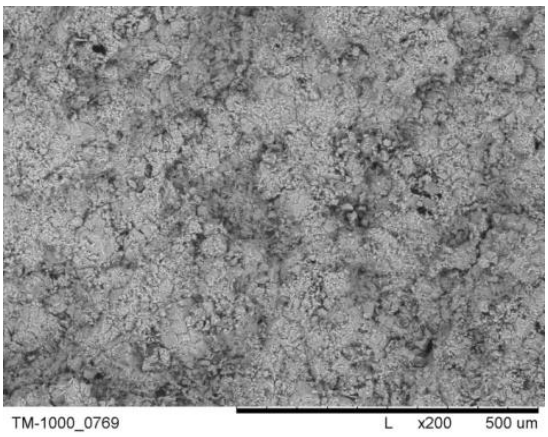
Images of the fracture structure of materials, received on the proposed technological modes shown in Fig. 7, show quite peculiar structure of the submicron and micron fragments in the form of elongated grains (fibers) with an average diameter 5mkm. Image of fiber-inside structure obtained at high magnification in a scanning microscope is illustrated in Fig. 7 b, it shows that the structure

of micron fibers has much more complex morphology (such as twisted nanofibers into bundles), which requires a more detailed, additional research and analysis.

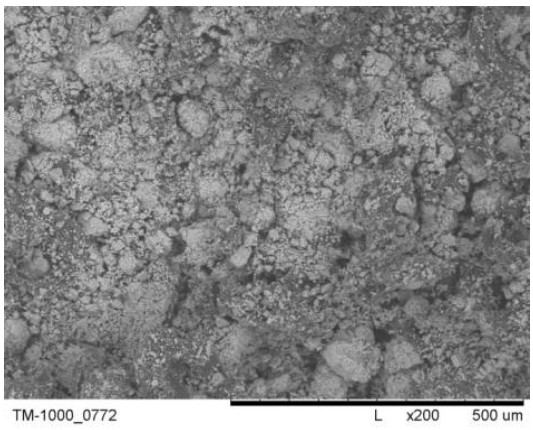
The second part of the research is to create PCM based on UHMWPE with different aluminum oxide content, to determine the effect of agent of aluminum oxide of different dispersion and ways of getting on the technological and physical and mechanical properties of the composite, the optimum area of additives and process conditions providing increase of hardness and wear resistance of PCM.

The uniform distribution of alumina powder was achieved by pre-mixing it with UHMWPE powder in the ratio of 1:5 in a ball mill. The resulting mixture was added to the batch before the final mixing. Powder mixtures were pressed in a rigid die of the mold at a specific pressure of 7.5 MPa with the synchronous sintering in air at a stepping heating mode with the curing of 1.5 hours at temperatures corresponding to different mass carry mechanisms.

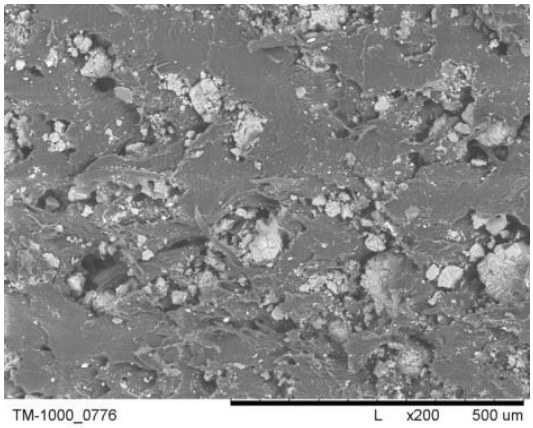
It was discovered experimentally that agents of aluminum oxide in the range from 25 to 80 wt % lead to the increase of compacts porosity, and as a result to the embrittlement of the composite material. Fracture surfaces of the samples were studied by optical microscopy (ZEISS Observer. Zlm-Germany) (Fig. 8). It makes it possible to formulate some conclusions: it is necessary to reduce the concentration of aluminum oxide in order to decline the porosity of samples, to increase the uniformity of distribution of particles of aluminum oxide in UHMWPE powder, to improve the adhesion between the particles of alumina and UHMWPE.




a) 20% UHMWPE -80% $Al_2O_3$




b) 50% UHMWPE -50% $Al_2O_3$




c) 70% UHMWPE -30% $Al_2O_3$

**Figure 8.** The nature of the fracture surface of the sample.

Based on theoretical and experimental data obtained at the stage of preliminary prospecting, the further studies were performed on the samples containing aluminum oxide less than 22%. (containing 0.5, 10, 15, 20% $Al_2O_3$).

We used the pre-cladding of aluminum oxide powders as the processing method which allows to improve the adhesion between polymer and aluminum oxide. Cladding process was carried out as follows: we stirred powders of aluminum oxide in 4% aqueous solution of polyvinyl alcohol (PVA), the resulting mixture was subjected to drying at temperature of 90°C for 2 hours, then the mixture was rubbed through a sieve with a mesh size of 300 microns. Granular clad aluminum oxide powders are well mixed with UHMWPE in required proportions, they are poured into a mold, without sticking and with uniform density in the amount of compaction.

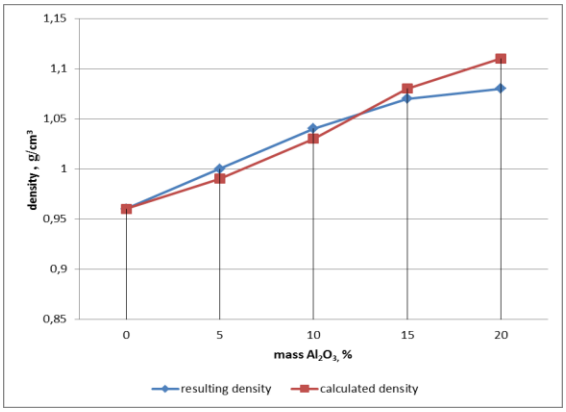
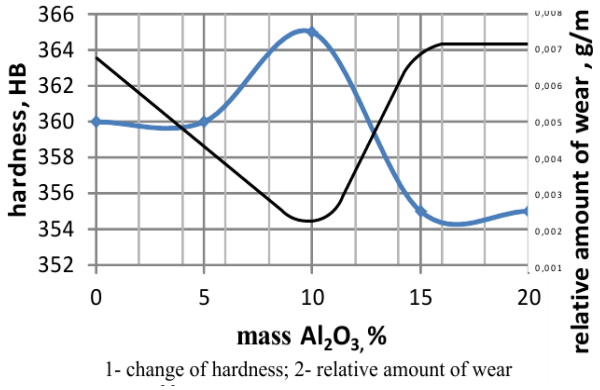



**Figure 9.** Dependence of changes in the density of compacts of PCM on the content of aluminum oxide




1- change of hardness; 2- relative amount of wear

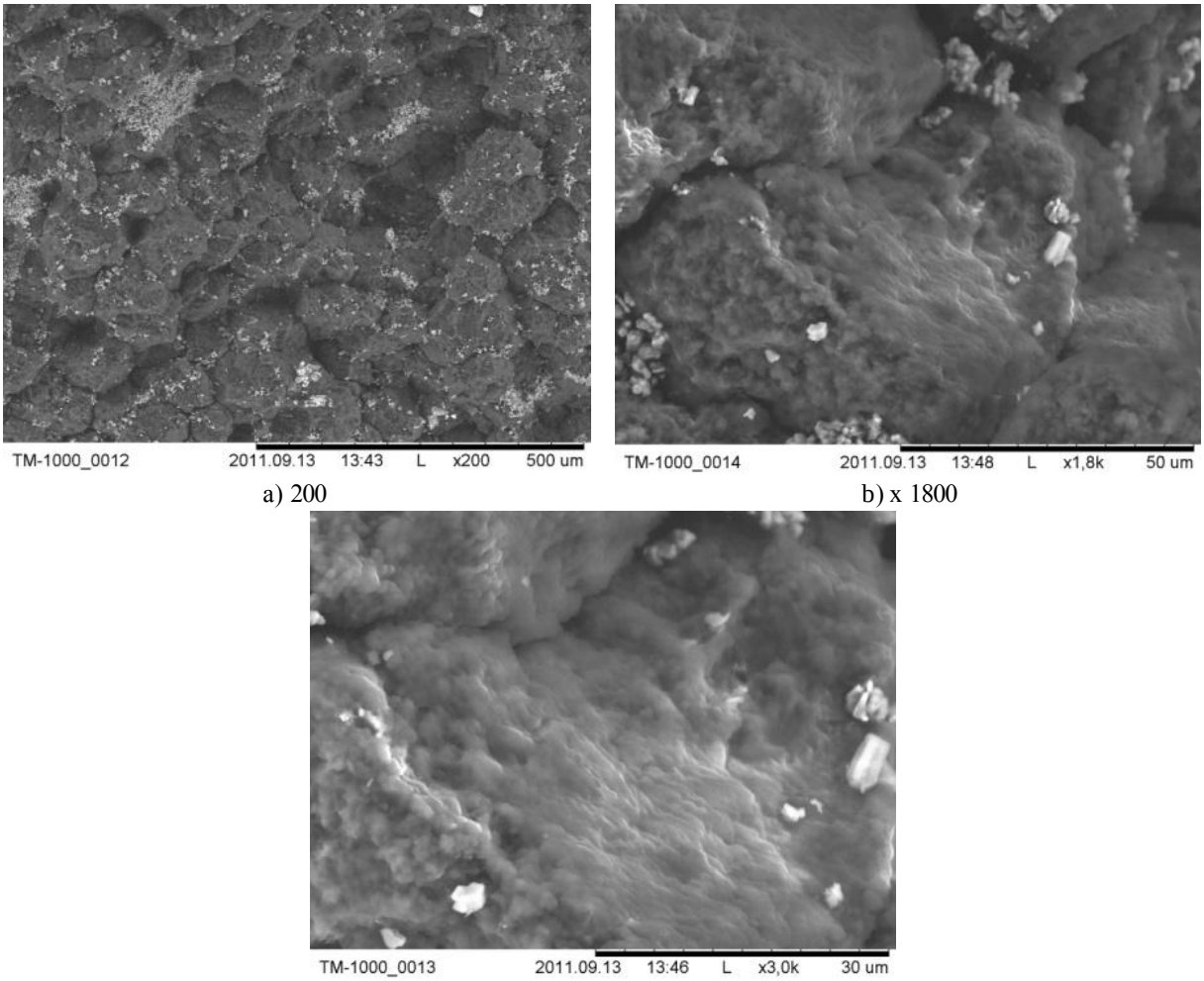
**Figure 10** Effect of agents on the hardness of aluminum oxide (HB) and the relative amount of wear PKM

The results of investigating the physical and mechanical characteristics of the samples of composite materials (UHMWPE- $Al_2O_3$ * clad) are shown in the graphs in Fig. 9, 10.

The measurement results show that increase of the content of modifying agent $Al_2O_3$ (granular), mixed with UHMWPE contributes to the increase of the density of the compact which corresponds to calculations in the proposed geometric model. The highest density values are provided (as predicted in accordance with the geometric model) in agents of about 20% $Al_2O_3$. However, the study of hardness (HB) and the relative wear (J) (Fig. 10) shows nonmonotonic, extreme nature of the changes in these parameters with increasing the concentration of the ceramic component of PTP.

The optimum concentration is about 10 % mass. of $Al_2O_3$. The extreme nature of the changes in hardness and wear (with increase in additives over 20% the properties are worse) can be certainly explained by increase in "contact" of the particles of ceramic high-temperature (refractory) phase, by a violation of the integrity of the matrix binding phase of UHMWPE powders, and as a result by embrittlement of the material.

PCM samples received on the proposed scheme in the mode of stepwise heating with the additional compaction at the temperature of the 90°C have satisfactory parameters for the microstructure and density (Fig. 11), there are no large pores and aggregates inclusions of $Al_2O_3$ over then 10 microns, the hardening phase $Al_2O_3$ is sufficient uniformly distributed over the volume of the matrix UHMWPE (Fig. 11). Physical and mechanical properties of PCM obtained from optimized modes are shown in Table 1.




a) 200 b) x 1800

c) x 3000

**Figure 11.** The nature of the fracture surface of the sample containing 90% UHMWPE-10% $Al_2O_3$

| Composite material | Density, g/cm $^3$ | Brinell hardness, HB | The relative wear, g/m |
|---|---|---|---|
| UHMWPE | 0.96 | 360 | 0.0092 |
| UHMWPE+5 mass % $Al_2O_3$ | 0.99 | 362 | 0.0055 |
| UHMWPE+10mass % $Al_2O_3$ | 1.03 | 365 | 0.0037 |
| UHMWPE+15mass % $Al_2O_3$ | 1.08 | 358 | 0.0074 |
| UHMWPE+20mass % $Al_2O_3$ | 1.11 | 355 | 0.0074 |

**Table 1**. Physical and mechanical properties of PCM based on UHMWPE

## Conclusion

The possibility of improving the physical and mechanical characteristics of UHMWPE by adding in their structure modifying agents of $Al_2O_3$ ceramic particles are substantiated and experimentally confirmed. Using the proposed method of manufacture allows to obtain polymeric materials of UHMW PE and compositions on its basis, using aluminum oxide with durability in 1.5-2.5 times higher than that of the original ultra-high molecular polyethylene, this allows its use in the engineering industry in the manufacture of wear-resistant lining elements for the protection of the bunkers, bodies of vehicles, transporters.