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Composite Materials Based on Ultra High Molecular Polyethylene: Properties, Application Prospects

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Abstract

Results are presented concerning the obtaining and properties of ultra high molecular weight polyethylene (UHMWPE) as the material withstanding severe operation conditions, unlike usual polymer modifications. It was demonstrated that modifying UHMWPE *via* introducing ultra fine particles of inorganic materials promotes an increase in operational performance of ware made of UHMWPE. The results of research in the field of developing the technologies for obtaining ware made of composite materials based on modified UHMWPE are generalized. Novel rubber/polymeric materials were obtained based on modified UHMWPE, butadiene-nitrile, *cis*-isoprene and divinyl rubbers. Owing to record breaking low abrasability and due to increased operation resource under extreme service conditions concerning the ware made of the materials developed, the composite materials obtained could find wide application in various areas of engineering.

Key words: ultra high molecular weight polyethylene, composite materials, nanomodifying additives, rubber-modified polymeric materials

INTRODUCTION

Constructional materials based on synthetic polymers are notorious by the fact that the level of their properties and scale of operations became one of the factors determining the world technological progress. In all the branches of the industry, there is a tendency to replacing metal ware by elements, units and coatings made of polymers. This is caused, first of all, by the progress in the chemistry and technology of polymers, resulted in the creation of synthetic materials those not only are ranking over metals in strength, but also exhibit to a considerable extent lower density and higher corrosion resistance, high heat-insulating and dielectric parameters, the simplicity of processing into ware.

Polyethylene (PE) is the most large-scale produced polymer: its production volume amounts to about 100 million t per year. A great

number of PE types and grades are known: linear and branched PE, polyethylene with various molecular mass and various molecular mass distribution, copolymers of ethylene and olefins with different content of olefin as well as with different character of chemical and compositional distribution of olefin within the macromolecule *etc.* However, only separate PE grades those exhibit special physicomechanical properties, could be considered belonging to constructional polymers.

Ultra high molecular weight polyethylene (UHMWPE) represents one of the most prospective polymeric constructional materials belonging to a new generation of polymers. This material exhibits a unique complex of physicomechanical properties, it is demanded for various application areas due to a high wear resistance and stability in corrosive media, due to a low friction coefficient, a high impact elas-

ticity, in record breaking low brittle temperature (down to $-200\text{ }^{\circ}\text{C}$), which allows making ware based on this material for the operation under extreme conditions. Besides, UHMWPE belongs to the most available and cheap polymeric materials. Ultra high molecular weight polyethylene represents polyethylene with the molecular mass higher than 1 million g/mol.

UHMWPE parameters are presented below:

Density, g/cm^3	0.92–0.94
Tensile strength, MPa	48
Relative elongation at break, %	350
Modulus of elasticity, GPa	
at temperature values, $^{\circ}\text{C}$:	
23	0.69
–269	2.97
Coefficient of friction against steel:	
under dry friction	0.1–0.2
in aqueous medium	0.05–0.1
in oil medium	0.01–0.08
Transition temperature	
into plastic state, $^{\circ}\text{C}$	138–142
Shore A hardness	
Coefficient of linear expansion,	
$10^{-4}/\text{K}$, at temperature values, $^{\circ}\text{C}$:	
–200... –100	0.5
20–100	2
Electrical resistivity, Ohm/cm	$>5 \times 10^4$
Dielectric strength, kV/cm	900
Operating temperature, $^{\circ}\text{C}$	≤ 100

Figure 1 demonstrates data concerning the relative abrasability of different materials [1]. One can see that the abrasability of UHMWPE is more than five times lower than the abrasability of Teflon.

The ability the absorb the percussion energy belongs to one of remarkable UHMWPE proper-

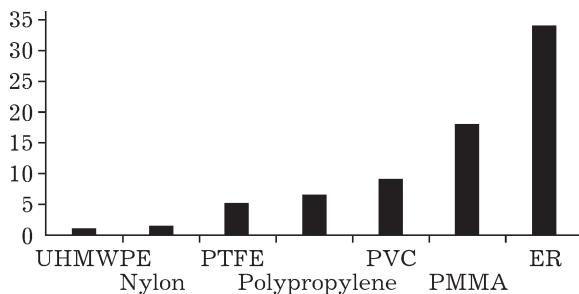


Fig. 1. Relative abrasability of different materials: UHMWPE – ultra high molecular weight polyethylene, PTFE – polytetrafluoroethylene (Teflon), PVC – polyvinylchloride, PMMA – polymethylmethacrylate, ER – epoxide resin [1].

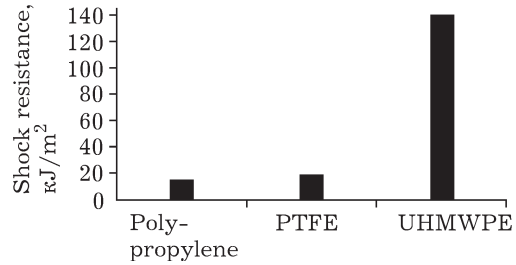


Fig. 2. Comparative shock resistance for different materials [1]. Design. see Fig. 1.

ties, which causes its use in the systems of individual and collective protection, the protection of orbiting space stations against meteorites and space garbage. Owing to this quality, along with a high resistance with respect to abrasion and a low coefficient of friction, the UHMWPE also finds wide application as the basis in the manufacture of plastic skis, snowboards.

Figure 2 presents data concerning comparative impact strength for various materials. One can see that the UHMWPE approximately seven times surpasses Teflon in resistance against applied shock at normal temperature values.

With temperature lowering $< 0\text{ }^{\circ}\text{C}$ the resistance against applied shock weakens, however this UHMWPE property does not disappear even at the temperature values near the absolute zero. Thus, ware made of UHMWPE can be successfully applied for the cryogenic engineering, liquid hydrogen pumps at $-253\text{ }^{\circ}\text{C}$.

Figure 3 demonstrates changing the UHMWPE impact strength (according to the cut technique) depending on temperature. One can see that UHMWPE possesses the best impact strength under normal conditions. At the temperature above $100\text{ }^{\circ}\text{C}$, UHMWPE loses its remarkable properties; therefore the UHMWPE operation at high temperature values is undesirable.

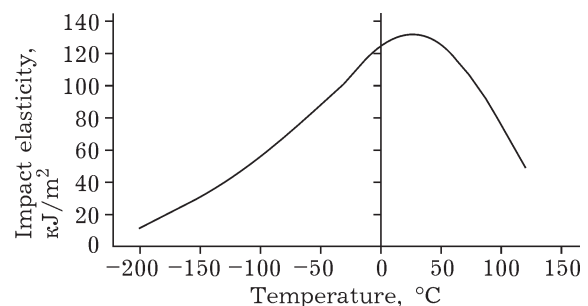


Fig. 3. Impact elasticity of UHMWPE depending on temperature [1].

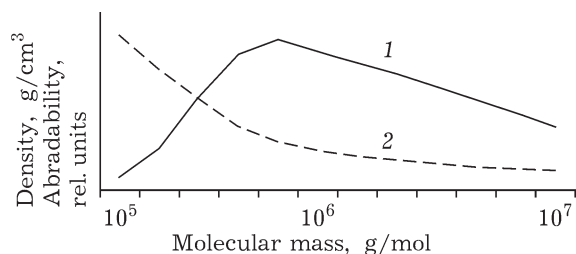


Fig. 4. polyethylene density (1) and abrasability (2) depending on the molecular mass.

It is known that polyethylene consists of crystalline and amorphous phase [2]. The ratio between them is close to unit being determined by the parameters of the material obtaining process. However, recently researchers have succeeded in establishing the existence of an order in the amorphous component. According to [3] UHMWPE consists of three phases: completely crystalline phase, completely amorphous phase and an intermediate phase. After irradiation, the latter is partially or completely transformed into the crystalline phase; this phase represents an interfacial one; the basic structural reorganization processes occur within this phase.

The molecular mass is one of the major parameters determining rheological and physico-mechanical properties of polyethylene. Figure 4 demonstrates simplified curves for some macro-properties of polyethylene depending on the molecular mass [2].

One can see that with increasing the molecular mass from above $1 \cdot 10^6$ g/mol, an implicitly expressed density extremum is observed as well as a considerable improvement of the abrasability parameter is registered. As the authors of [1] demonstrated, the increase in the molecular mass from $3 \cdot 10^6$ to $6 \cdot 10^6$ mol/g results in an approximately 30 % improvement of the abrasion resistance, whereas the shock strength decreases as much.

UHMWPE SCOPE

Ultra high molecular weight polyethylene finds application as:

1. Guiding rails and covering for bunkers, bodies for career dump-body trucks, cars and various mechanisms in mining industry, excluding sticking and ice freezing-on, loose and clay materials.

2. The elements of constructions subject to shock loading and abrasion in mechanical engineering, textile and pulp and paper industry: rolls, toothed gearings, bearing sleeves, etc. Metallic shaft can freely rotate in sleeves made of UHMWPE, despite any misalignment or the presence of sand, dust and other kinds of pollution. Pipes made of UHMWPE are resistant against temperature drops and ground shearing. Coal, ore, oil products and other materials can be transported in a water pulp through such pipelines. Pipeline wear in such a main would be minimal, whereas any sticking is excluded.

3. Separators for automobile accumulators those are remarkable for favourable strength against shocks.

4. Tapes and plates for manufacturing sliding surfaces for sports equipment (ski, snowboards, etc.)

5. Cold-resistant and resistant to wear composite materials for rubber products.

6. Implants. Sliding element in artificial joints are made of high-purity UHMWPE.

7. Filters. The pore size of UHMWPE filters is determined by technological parameters under obtaining, at the same time from the same material one could to obtain filters with different pore size.

8. Ware and special purpose equipment, including case elements of arms and military equipment, constructional materials for aerospace production, the means for individual and collective armoring, etc.

9. Shipbuilding, motor industry, reinforcing pipes and cables, manufacturing super-strong rope products.

Now the worldwide production of UHMWPE powder amounts to approximately 200 thousand tons per year and exhibits a steady tendency to grow. The main manufacturers of UHMWPE are presented by Germany, Holland, Japan. In 2009, Ticona Co. (Germany) launched a factory for manufacturing UHMWPE powder in China, 20 thousand tons per year in productivity.

OBTAINING UHMPE POWDER

Ultra high molecular weight polyethylene is made by the method of suspension ethylene polymerization in the environment of a hydro-

carbon solvent with the use of the modern supported catalysts of Ziegler–Natta type [4]. The end-product of the polymerization process represents is UHMWPE powder with mean particle size ranging within 50–200 μm . Depending on the application field of this polymer and the ways of its processing into final products it is necessary to produce various grades of UHMWPE powders those are different in the molecular mass, powder particle morphology (powder particle size and bulk density) as well as supramolecular structure.

It is known that the properties of UHMWPE depend on the composition of catalyst and on ethylene polymerization conditions on these catalysts. A wide set of highly efficient supported titanium-magnesium catalysts (TMC) were developed by now at the Boreskov Institute of Catalysis, SB RAS (Novosibirsk) for UHMWPE manufacture, those are different in dispersity, morphology and ability with respect to adjusting the molecular mass [5, 6]. Together with Katalizator OJSC (Novosibirsk), a pilot-line production plant of these catalysts was developed; a pilot unit was created in Tomsk (Tomskneftekhim Ltd.) for manufacturing UHMWPE *via* the suspension method up to 100 t per year in capacity [7], whereby the technology for obtaining UHMWPE powder was worked through.

The catalysts and polymerization technology developed provide obtaining UHMWPE powder within a wide range of molecular mass values (from $1 \cdot 10^6$ to $8 \cdot 10^6$ g/mol) with optimum and adjustable morphology. In particular, powders with an average particle size ranging from 60 to 250 μm were obtained with a narrow size distribution. Figure 5 demonstrates electron microscopy images of catalyst and UHMWPE polymer particles obtained using this catalyst. UHMWPE powders obtained exhibit a high bulk density of 380–480 g/L (the bulk density value is controlled). The ash level of the polymer does not exceed 0.02 mass %. High catalyst activity provides the yield of polymer amounting to 20–50 kg per 1 g of the catalyst.

Thus, by now a modern domestic technology for UHMWPE powder production is developed, which allows obtaining a wide-grade assortment of this polymer. Experimental batches of UHMWPE were made those successfully passed testing by various consumers. The re-

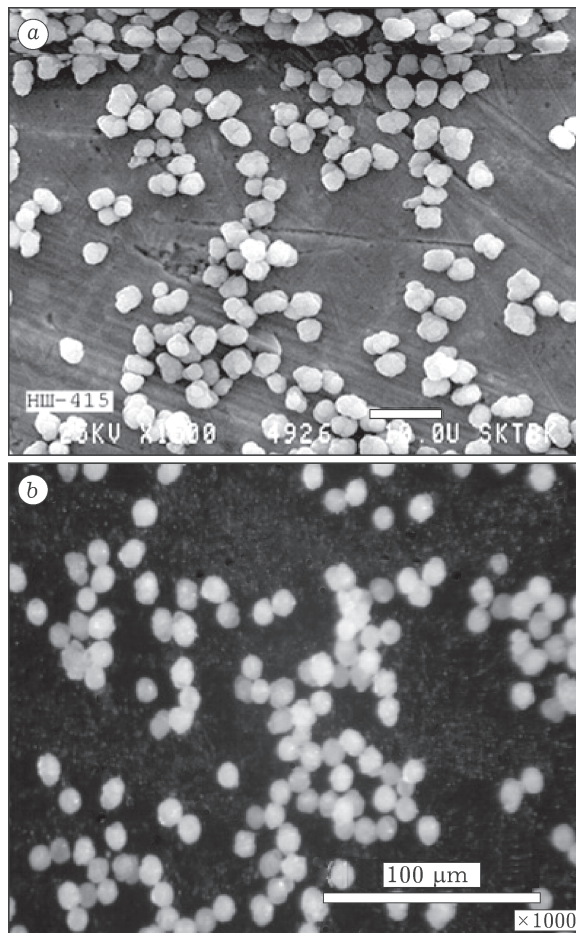


Fig. 5. Morphology of TMC-PE catalyst (a) and of UHMWPE particles obtained (b).

sults obtained make a basis for developing a commercial UHMWPE manufacture and for a wide implementation of this new constructional polymer to the Russian market.

UHMWPE POWDER PROCESSING INTO PRODUCTS

Ultra high molecular weight polyethylene as a perspective constructional material is known for a long time [8, 9], but its manufacture and promotion to the market has been limited, first of all, by serious difficulties arising with its processing into ware. High-efficiency processing methods and equipment traditional for polyethylene (extrusion, casting under pressure, *etc.*) are not suitable for processing this polymer. However, for the last years, in the course of development the technology for obtaining UHMWPE and the methods for its processing, the manufacture and application of this ma-

terial to a considerable extent increases. The research devoted to UHMWPE in Russia and abroad, are directed mainly on the development and perfection of technologies for its processing, taking into account the difficulties caused by a high molecular mass of this polymer. As the result of these developments on industrial scale, such methods of UHMWPE processing as hot pressing, sintering, ram extrusion, spraying (hot flame, electrostatic), as well as gel formation (for fibre obtaining) were mastered.

One of the features of UHMWPE consists in a high viscosity of liquid melt. At normal pressure with the increase in temperature the powder of UHMWPE does not exhibit any transition into the plastic state up to the decomposition. This fact causes the feature of the technology for processing UHMWPE powder into bulk products (plates, pipes, seals, etc.).

Basing on UHMWPE powder, one can obtain also high-strength threads using the method of gel formation and orientation superdrawing. This technology determines the progress of many branches of modern engineering. The industrial release of such threads is mastered now by such companies as DSM (Holland), Honeywell (USA) and Mitsui (Japan). Rather extensively, these works is being performed in China [10]. The production of high strength UHMWPE threads all over the world amounts to about 4000 t/year. UHMWPE threads favourably differ from other kinds of high strength reinforced (aramid, carbon) fibres by the level of specific mechanical parameters, the ability with respect to the absorption and dispersion of high-speed dynamic shock, the immunity with respect to the action of moisture, absolute radio transparency, low density ($<1 \text{ g/cm}^3$).

UHMWPE films can be used for metal surface protection in food and pharmaceutical industries. For the formation of a surface film from UHMWPE on a prepared metal surface one may use the method of applying UHMWPE powder in electrostatic field. The technique for preparing the surface, applying the coating and testing is close to that presented in [11]. We established that unlike the technique presented in [11], for obtaining continuous UHMWPE film on the surface of a metal the warming temperature should be higher than $220 \text{ }^\circ\text{C}$. In this case, a smooth homogeneous coating is

formed, $30\text{--}50 \text{ }\mu\text{m}$ thick. For increasing the thickness of the coating it is necessary to repeat applying and heating operations several times. The coating obtained is characterized by a high shock strength and high bending elasticity. The coating-to-metal adhesion determining by the method of exfoliation of net-like cuts according to the State Standard GOST 15140-78 is considered the best technique. The coating is continuous and impenetrable for chloride ion being efficient for protection against fungi, metal surface corrosion in the rooms connected with cooking, ventilation boxes.

Using the method extrusion one can obtain bricks, pipes, plates. In this case one frequently use softeners or UHMWPE powder with the minimum viscosity of liquid melt [12]. The pressure in an extruder is determined by the molecular mass of the powder and the viscosity of the liquid melt. In this case, a partial ordering is observed in the amorphous component of the polymer, there is an anisotropy appearing in the direction of the liquid melt movement [13]. The seamless pipes obtained are used as slurry pipelines, guiding rails for loading and unloading coal, cement, concrete, building mortar. These pipes are not stuck with seaweed, shrimps, they possess high resistance in sea water whereby they can find wide application in oil and gas branch in developing the territories of the North, coastal shelf. The work concerning the creation of UHMWPE pipe manufacture is performed in Russia in St. Petersburg and Krasnoyarsk.

The method of UHMWPE powder processing into bulk ware and billets by the technique of hot pressing [14, 15] is the most widespread one. Hot pressing is carried out in special compression moulds. The first (cold) pressing occurs at rather low temperature values ($<100 \text{ }^\circ\text{C}$) during 5-10 min at a pressure up to 10 MPa. In the course of this cycle, air should be removed; particles should fill all the volume as much as possible. The cycle of hot pressing is carried out at the temperature of $180\text{--}230 \text{ }^\circ\text{C}$. The duration of the pressing procedure is determined by the thickness of the product obtained; in this case it is important that all the volume was melt. In the case when air particles are baked within polymeric matrix, to remove them is extremely difficult. The cooling process should be carried out under the pressure close to

10 MPa. After cooling, UHMWPE shrinkage amounts to 4–8 %. Depending on filling materials introduced, the shrinkage value, as well as the time of hot pressing, is different to a considerable extent. This, first of all, could be caused by changing the heat conductivity and the character of interaction between the particles of polymer and filling material. One can make ware products with a much more complicated shape using the obtained workpieces at the temperature of 160–180 °C.

Thin belts and sheets those provide the sliding surface of sports equipment, are obtained via chipping heated blocks. Further they are again heated up to the temperature of about 150 °C to clamp between plates up to complete cooling [15].

The UV light influence could result in cracks to appear within a year. In order to reduce negative UV effect on the material, one uses to add UV protecting stabilizers [15]. For manufacturing UHMWPE ware with antistatic properties, the powder should be added with as much as about 6 % of soot which allows operate with UHMWPE products during the period not less than 5 years under the influence of solar energy.

COMPOSITE MATERIALS BASED ON UHMWPE

Composite materials based on UHMWPE can exhibit to considerable extent better operational properties as compared to pure UHMWPE, rubbers and plastic, especially at negative temperature values.

One of the reserves for improving the quality of polymeric materials consists in using nanotechnological approaches. So, owing to modifying initial polymers by nanodisperse additives it can be possible to control the structure and properties of materials within a wide range due to nucleation and orientation effects, changing the conformation of macromolecules, their chemical binding with the surface of nanosized particles and “healing” structural defects. Adding any ultra fine nanosized inorganic particles such as aerosil, talc, alumina – is accompanied by improving the physicomachanical properties of the polymer [16–18]. In this case the resistance parameters with respect to abrasion, to cracking increases, a number of other parameters changes.

For example, with introducing as much as 15 mass % of short-cut carbon fibre into pure UHMWPE results in improving either parameters and deterioration of others [19, 20] observed. In particular, the modulus of elasticity increases whereas the creep level decreases, however, the growth rate of destruction cracks in this case increases. The authors of [21, 22] concluded that there is a multiple increase in UHMWPE wear resistance due to its modification *via* introducing the particles of inorganic materials using the method of mechanochemistry. With the introduction of ultra fine particles of activated copper spinel with the size of about 100 nm, a decrease of the friction coefficient with simultaneous increase in wear resistance is observed [23]. The composites obtained exhibit increased impact strength [24, 25]. A considerable growth of wear resistance was observed also with entering multilayer carbon nanotubes into UHMWPE [26]. Introducing aerosil as a nanomodifier is accompanied by increasing the crystallinity and hardness of UHMWPE, wear decrease under rubbing against a steel shaft [27].

The composite material based on UHMWPE and hydroxyapatite is distinguished by improved technical characteristics and meets the requirements for prosthetics materials [28].

With the use of UHMWPE as a material for slider bearings at a speed of 1 km/s, it was experimentally established that for pure UHMWPE the maximum load under dry friction amounts to 0.2–0.3 MPa, and in an aqueous environment this parameter amounts up to 1 MPa. Filling the UHMWPE with graphite (up to 40 mass %) results in *pv* factor increase (*p* is pressure, *v* is speed) amounting up to 3–4 MP · m/s as well as an order of magnitude decreasing the polymeric composite wear process [29]. By no means to a lesser extent, the rate of wear process is affected by the nature of the surface under contact [30]. Similar laws in changing the properties and technical characteristics were obtained with filling fluoroplastic by particles of different nature and size [31–34]. Ware made of UHMWPE can successfully replace ware made of Teflon in many branches.

A technology for obtaining composite materials based on UHMWPE with adding the powders of inorganic materials with various dis-

persity levels using the method of hot pressing [35–40] was developed at the ICCT, SB RAS (Krasnoyarsk).

With this purpose, a cycle of studies concerning modifying UHMWPE powder was performed. In this case, different methods were used for modifying: mechanochemical activation, plasma processing, introducing organometallic compounds with the decomposition temperature close to the temperature of hot pressing, introducing the particles of inorganic materials with different nature and size. As the result of application of all the listed methods there is an increase of wear resistance observed for the materials obtained. The strength parameters depend on the method of modifying, the type of particles introduced, on their size and concentration.

It was demonstrated that particles introduced should be much less in size than the particles of UHMWPE [36]. With small sizes of particles introduced and the concentration lower than 1 % one can observe an increase in breaking strength parameter value. The further increase in the size and concentration of entered particles is accompanied by breaking strength decrease and lowering the shock strength. The results obtained could be explained attracting the model of hardening thermoplastics those contain ultra fine inorganic filling materials proposed in [41] (Fig. 6).

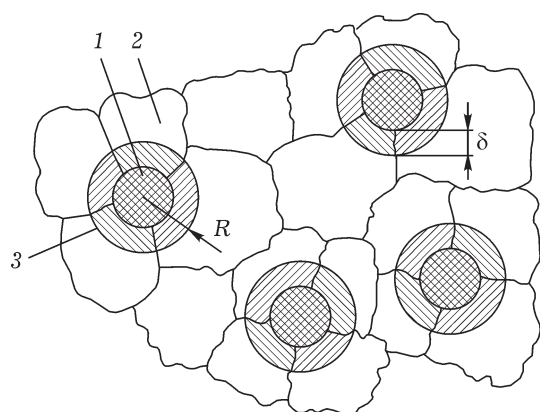


Fig. 6. Scheme of polymer structure formation under filling the polymer by modifying ceramic particles: 1 – modifier particle; 2 – polymer particle; 3 – polymer surface layer at the interface with a modifying particle; R is the radius of action for particle polarization charge field; δ is the surface layer thickness.

In this work using the method of heat induced depolarization we revealed the presence of spontaneous polarization charge in filled thermoplastics. It was demonstrated that the polarizing field resulting from the particles of a filling material causes induced dipole moments within the polymer, which provides an increase in strength due to the occurrence of additional electrostatic interactions. An increase in strength, changing in the crystallinity and melting temperature for the thermoplastic in this layer were registered.

Studies concerning the methods for obtaining UHMWPE with different modifiers

The shape of UHMWPE particles is close to spherical one. Obtaining the product using the method of hot pressing one should impose a load effort that could deform UHMWPE particles, to result in a complete removal of air from free space. In this case the binding energy between particles is determined by hydrogen bonds between hydrocarbon chains belonging to adjacent molecules as well as by the level of mutual penetration of chains belonging to the amorphous part of particles. The contact area in this case is minimal. Thereof the ware made of UHMWPE, obtained by a simple pressing of powder, do not exhibit required strength parameters.

One could increase the energy of interaction between particles *via* perturbation of UHMWPE particles, *via* increasing the effective surface of UHMWPE particles, *via* changing supramolecular UHMWPE polymeric structure. In the first case, one additionally introduces different size particles of inorganic materials into the structure of powder under pressing. Depending on the chemical activity and size the particles introduced could interact with UHMWPE molecules increasing the effective dipole moment of a particle, could take penetrate into the structure of UHMWPE to change the ratio between crystalline and amorphous phases, as well as the character of intermolecular interaction under melting with the subsequent crystallization.

The molecular structure of UHMWPE could be changed without breaking intramolecular bonds using the method of mechanical activation [35–37]. Owing to a high UHMWPE plas-

ticity, the value of specific energy under mechanical activation is insufficient for breaking C–C bonds, but this value could be sufficient for partial changing supramolecular polymer structure [23]. The requirements mentioned above are satisfied by AGO-2 mechanical activator that allows at developing specific power up to 100 W/g the acceleration of balls up to 60g. In this case, owing to water-cooling, the temperature in drums does not exceed 60 °C.

Introducing ultra fine particles of solid crystalline materials into the polymer structure influences the internal structure of the polymer. For this purpose, the particles of following inorganic materials with the different nature and dispersity were entered into UHMWPE powder:

1. Carbosil with the average particle size amounting to 3500 nm.
2. Tungsten (VI) oxide with particle size less than 100 nm.
3. Silicon carbide with particle size less than 100 nm.
4. Carbon nanotubes (10–100 nm).
5. Aluminium silicates of obtained from man-caused wastes, with particle sizes up to 500 nm.
6. Microspheres with the average size of particles of about 20 μm .
7. Heterometallic vinylidene complexes in the size of 5–10 nm.

The introduction of ultra fine powders was carried out *via* joint activation of the mixture of UHMWPE powders and inorganic powders using AGO-2 mechanical activator at the frequency of drum rotation amounting to 1290, 1820, 2220 min^{-1} . Preliminary, the powders were thoroughly mixed and then sifted through a 2 mm mesh sieve. The mass fraction of inorganic powders was varied within the range of 1–15 %. The duration of joint activation ranged from 1 to 10 min.

With introducing vinylidene complexes the latter were preliminarily dissolved in an organic solvent, then UHMWPE powder was impregnated with the solution and dried in an exhaust hood at the temperature of 20–25 °C up to complete drying.

The introduction of nanosized particles (titanium oxide, tungsten (VI) oxide, fullerenes) into UHMPE was carried out with the use of low vacuum low frequency and high frequency plasma of [42].

Studying the effect of activation on the structure and shape of UHMWPE particles

The samples of modified UHMWPE powders obtained were investigated using the method of small angle X-ray scattering (from 1'–3') with the use of KRM-1 chamber, the wavelength $\lambda = 1.520 \text{ \AA}$, synchrotron radiation.

The differential thermal analysis (DTA) was performed using a Q-1000 derivatograph. A weighed portion amounting to 0.2 g was heated with the rate of 10 K/min up to 1273 K.

Vibration spectra were recorded on a Bruker Vector 22 and Tensor 27 FT-IR spectrometers (Germany). The processing of the spectral information was performed with the use of OPUS software package, version 5.0. Samples for registering IR spectra were prepared in the form of tablets in KBr matrix. The conditions of sample preparation were identical. The concentration of the substance in all the experiments amounted to 3 mg/1000 mg KBr.

The measurements of temperature and melting heat were performed in aluminium crucibles with the heating rate of 10 °C/min using a Netzsch DSC 204F1 differential scanning calorimeter. According to ASTM D3418-82 and ASTM D3417-83 standard procedures, the reproducibility with respect to temperature amounts to $\pm 1.5 \text{ K}$, the difference in temperature between the results of parallel measurements should be less than 0.2 K and less than 1 % in measuring the enthalpy value.

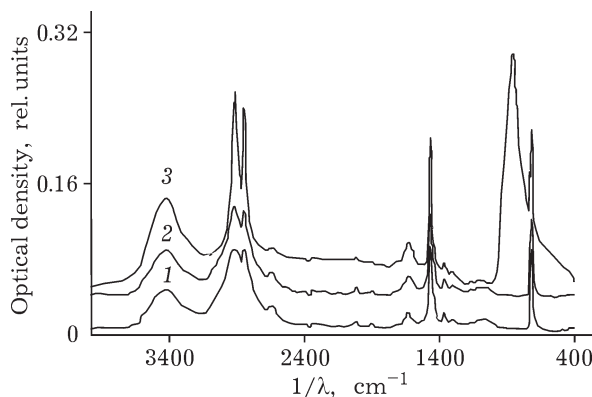


Fig. 7. IR spectra of UHMWPE powders: 1 – initial, 2 – powder activated during 10 min, 3 – the same with 14 % SiC; the frequency of drum rotation was equal to 1820 min^{-1} .

TABLE 1

Spectral parameters of valence vibrations for CH₂ groups

UHMWPE samples	Peak intensity	Half-width of absorption band, cm ⁻¹
Initial	0.125	195
Activated (10 min)	0.141	177
The same with adding 14 % SiC	0.227	98

The electron photomicrographs of initial and the activated samples were obtained using a Carl Zeiss Stemi 2000-C stereomicroscope.

According to IR spectroscopy, after the mechanical activation, there are narrowing CH₂ vibration bands and growing of peak intensity observed (Fig. 7 and Table 1). However, under joint mechanical activation of UHMWPE powders and inorganic ultra fine particles, the growth of CH₂ vibration band (2851, 1432, 712 cm⁻¹) intensity was to a considerable extent higher. This tendency is observed for UHMWPE powders having different molecular mass obtained using various catalysts. Figure 7 demonstrates the IR spectra of UHMWPE powders before and after mechanical activation and activated one with a filling material (14 % SiC).

A similar dependence of CH₂ vibration peak intensity is observed for all the types of UHMWPE, irrespective of the molecular mass and the type of the catalyst used. The increase in the intensity of CH₂ vibration band is observed under activation of UHMWPE powder without any filling material, too (see Table 1). In this case, there is any deformation of UHMWPE powder particles observed. Changing the arrangement of hydrocarbon chains occurs in the amorphous part which determines strength characteristics. The bands experience narrowing with the increase in the energy of activation (drum rotation frequency). However, much more considerable changes are observed under the joint activation of UHMWPE powder with nanomodifiers (Fig. 7, curve 3, Table 1). The growth of the peak intensity of bands is almost adequate to the content a nanomodifier introduced.

According to optical microscopy data, the mechanical activation results in the plastic deformation of UHMWPE particles. From the images of initial UHMWPE activated with no modifier and together with SiC modifier (Fig. 8) one can see that the mechanical activation re-

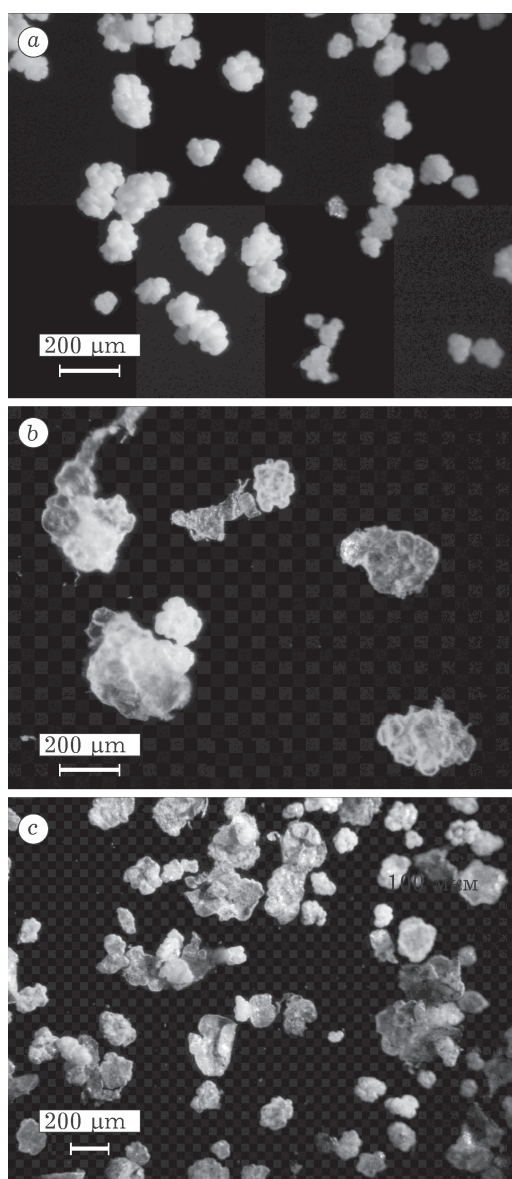


Fig. 8. Photomicrographs of UHMWPE particle samples: a - initial; b - activated (10 min/5 g, 2220 min⁻¹), c - the same with SiC as a modifier.

TABLE 2

Comparative DSC characteristics for activated UHMWPE

UHMWPE samples	Melting point*, °C		Crystallinity level, %	
	T_1	T_2	X_1	X_2
Initial	146.1	135.1	76.8	54.9
	145.8	134.9	78.3	54.9
Activated	146.8	136.9	70.3	56.7
	146.9	137.1	69.7	57.3
UHMWPE + 7 % SiC, activated	146.1	136.2	66.3	51.7
	145.7	135.3	68.3	51.2

*Peak maximum on melting curves.

sults in the lamination of almost spherical UHMWPE particles to give translucent flat flakes 50–200 μm in size. Besides, the particles are much darker due to the introduction of ultra fine SiC particles.

The analysis of differential scanning calorimetry (DSC) data indicate that the crystallinity level under mechanical activation decreases (Table 2), especially in the case of the mechanical activation of UHMWPE powder together with modifying particles. After the first melting, the crystallinity level for activated UHMWPE increases, whereas this parameter decreases for the same UHMWPE activated with SiC.

The reduction of crystal phase amount in the initial polymer, according to XRD phase analysis and DSC, can be explained by the increase in the amount of a near-surface phase [36, 41]. The occurrence of wide high intensity absorption bands in Raman spectra of filled polymers is connected with polymer polarization due to modifier introduction. According to the results of small-angle synchrotron radiation scattering, introducing the particles of inorganic substances into a polymeric matrix is accompanied by decreasing the sizes of primary formations of filled UHMWPE as compared to the initial UHMWPE. In this case, this is observed only at a concentration value lower than a certain concentration of introduced particles. With the further increase in the amount of particles entered, the size of structural formations increases and the abrasability parameter becomes worse. A minimum abrasion level is observed for samples with smaller size of structural formations [43], which is in a good agreement with the conclu-

sions by the authors of [3, 41] concerning the presence of an intermediate phase.

Figure 9 demonstrates data concerning the relative abrasability of samples after plasma and mechanical activation procedures, the introduction of fullerenes or solid particles of different size measured according to the GOST 426–77 (method for determining the abrasion resistance under sliding against rigidly fixed abrasive particles).

One can see that the abrasability could be up to several hundred times different depending on the type of modifying procedure. The introduction of larger solid particles with simultaneous powder activation with a high level of energy results in a maximum growth of abrasion resistance (see Fig. 9, type of modification 8).

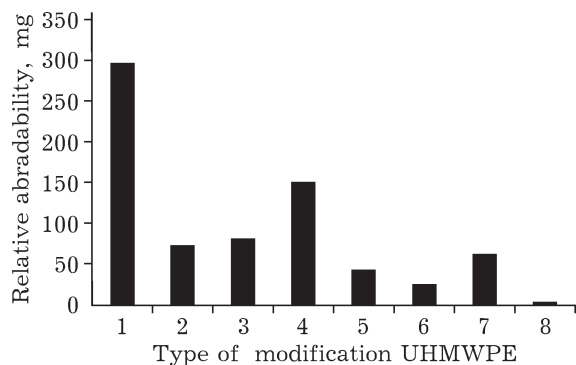


Fig. 9. Relative abrasability of UHMWPE samples (molecular mass equal to 5.0 million g/mol) with different type of modification: 1 – initial, 2 – mechanically activated (AGO-2 activator) during 10 min, 3 – with 1 % fullerene added, 4 – processed in a plasma discharge, 5–7 – with introduced ultra fine SiC particles with size ranging within 50–200 μm , in the amounts of 2, 7 and 30 %, respectively, 8 – with 5 % SiC introduced (particle size up to 1000 μm).

The studies performed allowed the researchers to develop composite materials based on modified UHMWPE with prescribed properties for particular service conditions [35]. Products made of them using the method of hot pressing were delivered for pre-production operation. According to the results of finished industrial tests, ware made of UHMWPE materials are an order of magnitude surpassing with respect to Teflon in resistance against abrasive wear (tested at Polus-Zoloto JSC), they are more than twice surpassing with respect to Caprolon under operation in the mode of periodic shock loading (Geophysical Service of the SB RAS), they are to a considerable extent surpassing in strength with respect to vacuum ceramics and Caprolon in the mode of hydraulic shock with a microsecond-duration impact and 40 MPa front, in a plasma chamber (Plasma Scientific Research Institute of Gas Discharge Devices, Ryazan).

Rubber polymeric UHMWPE composites

Two-layer ware based on UHMWPE and rubbers are known [44] for the protection of equipment against shock. The bottom rubber layer exhibits the required properties of plasticity, whereas the top layer made of UHMWPE possesses a low friction coefficient and high resistance with respect to abrasion. With introducing UHMWPE in the structure of a rubber sole, its resistance with respect to abrasion increases [45].

In the northern regions of Russia, as much as up to 30 % cases of mechanisms' failure during the winter period are caused by the working capacity loss of rubber seals due to their insufficient frost resistance and abrasion resistance. The elasticity parameters are connected with softener content, however the increase in its content does not solve to a considerable extent the problem of increasing the frost resistance of rubbers [46], since softener agents can be washed away by hydrocarbon environment. Owing to the fact that the UHMWPE does not become fragile and possesses record-breaking low abrasability even at cryogenic temperature values, its application as a part of rubbers should improve to a considerable extent their frost resistance and the resistance with respect to abrasion.

Indeed, the authors of [47] demonstrated that the introduction of UHMWPE powder into butadiene-nitrile rubber B-14 results in a considerable improvement of tribotechnical properties and oil resistance. Wear resistance increases by 25 % comparing to that for the base rubber B-14, the friction coefficient decreases by 40 %, the temperature decrease within the friction zone averaged about 10–15 °C, the mass wear in this case decreased by 35–65 % depending on the filling level. However, elasticity parameters in this case became worse.

The elasticity reduction is caused by the differences in the nature of surface groups of rubbers and polyethylene. Two polymers dif-

TABLE 3

Results of testing rubber-modified polymeric materials based on butadiene-nitrile rubber and modified UHMWPE

Parameters	Mixture number						Rubber B-14		
	1	2	3	4	5	6			
Concentration of modified UHMWPE (mass parts)	10	10	15	15	20	20	–		
Brittle temperature, °C	–62	–61	–63	–62	–67	–66	–60		
Conventional tensile strength, MPa	11.2	10.9	11.7	12.4	10.1	9.6	11.3		
Relative elongation at break, %	153	168	146	199	62	46	156		
Abradability, cm ³ /(kW · h)	118	75	106	78	68	42	399		
Shore A hardness	72	68	73	74	85	90	70		
Mass change after the action of isooctane/toluene mixture (23 °C, 24 h), %			18.4	18.8	19.1	18.9	15.5	16.3	24.1
Relative residual deformation at constant compression level of 30 % (70 °C, 24 h), %	21.1	20.5	22.1	24.4	26.0	29.4	22.1		

ferent in nature do not interact between each other. The activation of UHMWPE powder *via* introducing ultra fine particles with the use of mechanical activation technique results in increasing the polarization charge [41]. Owing to its occurrence, as well as to the increase in the effective surface of UHMWPE particles after the mechanical activation, strengthening the interaction between rubber and UHMWPE particles could be possible. As a result, the elasticity parameters could, to all appearance, be improved due to the introduction of modified UHMWPE, with no worsening.

A cycle of research work was performed at the ICCT of the SB RAS, concerning the development of composite materials based on traditional rubbers and UHMWPE. Table 3 demonstrates the results of tests performed at the ICCT of the SB RAS concerning rubber polymeric materials based on butadiene-nitrile rubber and modified UHMWPE.

The modifying of UHMWPE was carried out using an AGO-2 planetary mill with the introduction of natural and synthetic materials. UHMWPE powders were used with the molecular mass of 5.0 million g/mol obtained with the application of catalysts from the Boreskov Institute of Catalysis, SB RAS. The mass fraction of UHMWPE introduced did not exceed 20%. Reference samples were prepared according to the GOST 30263–96. Testing for abrasability was carried out according to the GOST 426–77, the

conditional breaking strength, unit elongation, residual elongation after breaking, the change of the unit elongation after ageing in air were determined according to the GOST 270–75 and the GOST 9.024–74.

The Shore A hardness and hardness change after the action of the standard liquid for testing rubbers (SZhR-3) was determined according to the GOST 263–75 and GOST 9.024–74. The change in volume of standard samples after the action of isooctane/ toluene mixture (7 : 3) at 23 °C during 24 h was determined according to GOST 9.030–74. The fragility temperature of samples was determined according to GOST 7912–74.

The relative residual deformation in air at the compression value of 20–30 % at 100 °C during 24 h was determined according to GOST 9.029–74.

One can see that mixture No. 3 (15 mass parts with respect to the UHMWPE rubber modified with carbon nanoparticles) is characterized by increased strength and unit elongation. In all other cases, one can observe an insignificant improvement of strength or its worsening. The Shore A hardness increases with the increase in UHMWPE content. The abrasability parameters depend on the nature and particles entered into UHMWPE, however these values stably decrease in the course of increasing the UHMWPE content. In this case, the resistance against the action of organic solvents increases. The fragility temperature decreases by 1–7 °C.

TABLE 4

Testing results for rubber-polymeric materials based on the combination of *cis*-isoprene and *cis*-butadiene rubbers at a ratio of 85 : 15

Parameters	Mixture number						Base recipe of rubber IRP 1370*
	L-3	L-3-1	L-3-2	L-3-3	L-3-4	L-3-5	
Brittle temperature, °C	–58	–56	–60	–61	–63	–63	–56
Conventional tensile strength, MPa	23.5	22.7	23.0	22.4	23.9	23.7	26.9
Relative elongation at break, %	497	499	483	491	502	513	570
Abradability, cm ³ /(kW · h)	94.7	85.6	98.4	48.9	35.9	21.4	102.3
Shore A hardness	68	66	69	70	69	67	65
Changing the norm of relative elongation at break after ageing in air (100 °C, 24 h), %	–26.3	–23.7	–31.6	–26.4	–28.4	–28.2	–34.2

*According to the State Standard GOST 20–85.

Similar results were obtained for rubber polymeric materials obtained with use of the mixture of isoprene and divinyl rubbers and modified UHMWPE in the amount of 9 mass parts (Table 4).

One can see that the UHMWPE introduction into the composition of rubbers results in an increase in the material hardness, a 2–5-fold decrease of adorability, the temperature range of use extending down to -63°C , the elasticity parameters after ageing becoming more stable. In some cases, according to service conditions it is necessary to increase the hardness. For developing the materials working at a high pressure, we developed seals with high rigidity and skeleton properties with no use of fabric materials. This simplifies to a considerable extent the manufacturing technology. Such type of seals are much more cheap being characterized by an order of magnitude and more increased operating resource as compared to chevron materials earlier used as seals.

The materials proposed possess a wide range of technical characteristics; therefore they could be used in order to obtain ware with preset properties on their basis for particular service conditions. For different rubbers the efficiency of UHMWPE introduction is different.

Thus, with the introduction of modified UHMWPE in the composition of a rubber mixture and the correction of its base recipe, composite materials were obtained based on traditional rubbers and modified UHMWPE with a 2–6-fold increase in the abrasion resistance, improved resistance against organic solvents, with a 2–6 $^{\circ}\text{C}$ lowered fragility temperature, with the conservation of elasticity parameters.

CONCLUSION

In the course of developing composite materials based on UHMWPE, introducing various particles we obtained the materials whose properties to a considerable extent differ from the properties of the initial UHMWPE. A technology was developed for obtaining composite materials based on UHMWPE modified *via* the method of hot pressing. The materials obtained could successfully replace Teflon, Caprolon,

polyurethane, babbitt, bronze and others in a number of different fields.

Novel rubber/polymeric materials were proposed based on modified UHMWPE, butadiene-nitrile, *cis*-isoprene and divinyl rubbers. Rubber polymeric materials are used for obtaining sealants operating in the environment of oils, fuel, water and aqueous emulsion. The materials exhibit a high resistance with respect to abrasion and frost resistance. Formulas for obtaining rubber/polymeric materials with a wide set of properties were composed. Ware based on the materials developed are remarkable for 6–8 times increased abrasion resistance with the conservation of other parameters within the State Standard (GOST) requirements for the given kind of ware.

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