Polymer composite materials based on ultra-high molecular weight polyethylene

A A Okhlopkova¹, S N Danilova¹, A A Dyakonov¹,², A P Vasilev¹, A N Ivanov¹ and S A Sleptsova¹

¹North-Eastern Federal University, 46 Kulakovskogo St., Yakutsk, 677013, Russia
²Institute of the Physical-Technical Problems of the North, Siberian Branch of the RAS, 1 Oktyabrskaya St., Yakutsk, 677980, Russia

E-mail: okhlopkova@yandex.ru, dsn.sakhayana@mail.ru

Abstract. Ultra-high molecular weight polyethylene (UHMWPE) has a number of unique properties: low friction coefficient, high strength and toughness, frost resistance, and resistance to aggressive media. This determines the use of UHMWPE as a polymer matrix for the manufacture of high-strength technical products. The use of nanoparticles as polymer fillers, which has emerged over the last two decades, has made it possible to significantly improve the characteristics of nanocomposites while reducing their degree of filling, achieving an improvement in properties that could not be achieved using traditional fillers and modifiers. Due to the high specific surface area, nanofillers have high activity for structuring the polymer matrix. However, this becomes a problem in the development of polymeric materials with nanofillers, due to the processes of agglomeration, as well as the difficulty to distribute them uniformly in the volume of the polymer matrix. We have demonstrated an efficient mixing process for UHMWPE and nanofillers, consisting of mechanical activation in a planetary mill and the technology of liquid-phase compounding under the continuous action of ultrasonic vibrations. Despite the large number of studies aimed at enhancing the interfacial interaction between UHMWPE and inorganic fillers, the problem of the weak interaction between the polymer matrix and the inorganic filler remains unsolved. Thus, the research work is aimed at obtaining new composite materials based on UHMWPE strengthened with organically modified montmorillonite and compounds containing 2-mercaptobenzothiazole, ZnO and sulfur.

1. Introduction

Issues of developing durable and wear-resistant polymer composite materials (PCM) pertain to highly prospective and intensively developing areas of modern material engineering, which are determined by the necessity of replacing traditional and costly materials [1]. One of the prospective polymer matrixes for creating high-strength technical items is an ultra-high molecular weight polyethylene (UHMWPE). UHMWPE possesses a whole range of advantages such as a low friction ratio, increased mechanical strength, self-lubrication properties, chemical resistance to acids and bases, and durability in terms of cracking and wear [2]. In spite of its unique properties UHMWPE is characterized by low values of hardness, Young’s modulus, and susceptibility to constant load tensile creep. In order to improve the complete set of performance properties, various fillers of micro- and nanoscale sizes, such
as fibres (glass, basalt, carbonic, aramid, etc.), as well as dispersed matters (silicon dioxide, quartz, wood powder, metal oxides, metal powders, etc.), are introduced into UHMWPE [3, 4]. Using various matters as fillers we can intentionally alter the performance characteristics of materials.

Interfacial interaction between the filler and the polymer matrix plays and important role in determining qualities and properties of created composite materials. Weak adhesion between the PCM components brings about defects, which reduces the physical and mechanical, as well as tribological properties of materials. The process of combining PCM components is still a complex technological issue today [5]. At present, various approaches and modification methods are used in order to increase the interfacial interaction and facilitate an even dispersion of filler in a polymer. Methods of ultrasonic processing, mechanic activation, high-speed mixing of components of a composite material and other methods are used to upgrade the properties of PCMs [6-8]. Besides, various specific methods of preparing and modifying fillers, mixtures of fillers and polymers in different thinners, as well as adding surface active agents [9-11]. And CVD method modification for fillers – that is a chemical vapor deposition [12]. Also, utilization of functionalized fillers and other methods are used, too [13, 14].

Therefore, the given work contains a comparison of montmorillonite (MMT) without modifications to one with organo-modification. Such organo-modified clay (organoclay) shows good dispersion in the polymeric matrix and enhances interaction with polymer macromolecules compared to plain clay [15]. Besides, the work suggests an original technology of modifying UHMWPE in order to adjust the interfacial interaction between the components of PCM. A distinctive peculiarity of this technology lies in utilizing reactive compounds (2-mercaptopenthothiazole), which forms free radicals during processing the PCM, thus influencing the interaction of polymers with solid fillers.

2. Materials and Methods

For the research we used UHMWPE GUR 4022 (obtained from Celanese Corporation, Germany). The salient characteristics of UHMWPE are presented in table 1.

| Table 1. Characteristic of the UHMWPE GUR-4022. |
|-------------------------------------------------|
| Properties                                      | Data            |
| Molecular weight, g/mol                         | 5.3×10^6        |
| Average particle size, μm                       | 145             |
| Density, g/cm^3                                | 0.93            |

And as a filler we used MMT of MONAMET 1H1 brand without modifications and MONAMET 1P3 brand (“Metaclay”, Russia) the surface of particles in which was modified with resorcinol resin with presence of a surfactant containing aliphatic radicals ranging from 14 to 18 methylene groups. Combinations of fillers such as zinc oxide, sulphur powder and 2-mercaptopenthothiazole (MBT).

Samples for research were obtained by hot pressing at a temperature of 175 °C and a pressure of 10 MPa holding for 20 minutes, followed by cooling to room temperature. The hardness (H) of the samples was measured by pressing the ball Russian standard ISO 2039/1-87 on the UMT-3 universal testing tribometer. Testing parameters of the hardness PCM shown in table 2.

The mechanical properties of UHMWPE and PCM were studied using the Autograph AGS-J tensile testing machine (Shimadzu, Japan). The tensile strength, elongation at break and Young’s modulus were tested according to ASTM D3039/D3039M-14 at the moving gripper speed of 50 mm/min, the number of samples was 6. The tribological characteristics of UHMWPE and PCM were determined according to ASTM G99–17 using a universal testing machine UMT-3 (CETR, USA). The pin-on-disc testing method was used for tribological characterization.

Table 3 illustrates the testing parameters of the tribological properties of the PCM. The counterbody was made of tempered unalloyed carbon steel AISI 1045.
Supramolecular structure of PCM was characterized by scanning electron microscopy (SEM) JSM-7800F (JEOL, Japan) with the X-MAX-20 attachment (Oxford Instruments plc, UK) in the secondary electrons mode at an accelerating voltage of 1–1.5kV.

**Table 2. Data of the testing hardness.**

| Characteristics                              | Data         |
|----------------------------------------------|--------------|
| Diameter of the steel ball indenter, mm      | 5.0±0.05     |
| Accuracy of indentation depth measurement, mm| ±0.005       |
| Indentation time, s                          | 0.1          |
| Sample size, mm                              | 30×30        |
| Thickness of the sample, mm                  | 4.0±0.1      |

**Table 3. Data of the tribological testing.**

| Parameters                              | Data         |
|-----------------------------------------|--------------|
| Diameter of the sample, mm              | 10.00±0.02   |
| Height of the sample, mm                | 20.0±0.2     |
| Hardness of the counter-body, HRC       | 56–58        |
| Roughness of the counter-body, μm       | 0.06–0.08    |
| Load, MPa                               | 1.9          |
| Linear slipping velocity, m/s           | 0.5          |
| Test time of each sample, h             | 3            |

3. **Results**

3.1. *Comparison influence with and without organically modified MMT on the mechanical and tribological properties of the PCM*

Using of organo-modified filler greatly simplifies the technological process of creating PCMs and solves the problem of combining the hydrophilic surface of the filler with non-polar or low-polarity polymer matrix [16]. The mechanical and tribological properties of a PCM filled with MMT with and without the organo-modification are presented at figure 1. A polymer filled with MMT without the modification leads the increased by 20 % tensile strength compared to those of initial UHMWPE. In the cases of polymer containing a modified MMT, there was registered an increase of the yield strength by 26 %. Nonetheless, the coefficient of friction of the PCM with low amount of MMT remains unchanged from that of the original UHMWPE. The further increase of filler content up to 5 wt.% is followed by some decrease of strength PCM, which is related to the formation of defect areas initiating material failure from external stresses [17].

Tribological investigation of PCM revealed that the addition of 5 wt.% of organo-modified MMT decreases the wear rate by 17 times and reduced the friction coefficient by 18 % compared with the initial polymer. These are results of the increase in wear resistance of a PCM due to the participation of the organo-modifier in the intensification of tribo-chemical reactions. The organic component takes part in forming labile structures on the friction surfaces of the composite material which bring about the localization of shear deformations and facilitate the surface sliding processes of the steel counter-body. The use of an MMT without a modifier results in some decrease of weight wear rate by 16 %, for filler quantities of 1 wt.% and 2 wt.. The coefficient of friction is reduced by 10 % for an MMT filling quantity of 0.5 wt.% and it is unchanged by the increase of a filler content to the level of the
original UHMWPE. Hence, MMT without modifications fails to bring about a significant change in the friction coefficient.

![Graphs showing mechanical and tribological properties of PCM on filler content](image)

**Figure 1.** Dependence of mechanical and tribological properties of PCM on the content of fillers

The composite with organo-modified MMT shows better mechanical and tribological properties compared with those of the composites/MMT without modifier. The observed results can be explained by the strengthening effect of the polymer matrix due to its interaction with the modified surface of the organoclay.

In order to explain the acquired mechanical results microstructures of composites were studied. Besides, to compare the interfacial interaction between the polymer matrix and MMT samples filled with non-modified and organo-modified clay were drawn for comparison (figure 2). It is obvious that the supramolecular structure of UHMWPE transforms lamellar to spherulitic at the introduction of the fillers. Along with this, the composite with an organo-modified MMT is distinctive for its formation of a dense microcrystalline packing with a uniform supramolecular structure which confirms the enhancement of strength properties of PCM. Such a phenomenon can be explained by structural lability of small spherulites having enough time to get reorganized at the outside stretching action while the large-sized spherulitic structure starts to disintegrate [18]. As observed in figure 2, PCM containing non-modified clay is notable for containing large agglomerates and defects as well as for the uneven mixing with the clay (“a structural fragmentation” of the system in whole). Besides, when filling unmodified clay into the polymer, the resulting composition contains interlayer nano-spaces. For the case that the PCM is filled with organoclay agglomerates of filler this is not observed.
Figure 2. Micrographs of the supramolecular structure of: (a) UHMWPE, (b-c) PCM filled with unmodified MMT, and (d-e) organo-modified MMT

3.2. Investigation of the effect sulphur, zinc oxide and 2-mercaptobenzothiazole on the characteristic of PCM

Further studies concerned the use of combined filler in the system of ZnO/S/MBT. The advantage of using combined fillers for enhancing the properties of PCM consists in the fact that each of the fillers introduced there had different influences on the polymer matrix. For example, it was shown in work [19] that a combined filler represented by carbon fiber and vermiculite greatly enhanced the mechanical properties and wear resistance of the PCM based on polytetrafluoroethylene. Thus, combined use of fillers having different nature allows for achieving the necessary performance properties of PCM.

Figure 3 shows the results of studies of mechanical properties of PCM filled with sulphur, 2-mercaptobenzothiazole and zinc oxide depending on their content. The analysis of the acquired data in the studies of the physical and mechanical properties of PCM showed that the fillers added to it in the proportion of 1 wt.% ZnO / 1 wt.% S / 1 wt.% MBT to the polymer brings about a substantial increase in the tensile strength by 44 % and Young’s modulus by 70 % as compared to the original UHMWPE.

Similar results were obtained in work [20], in which the authors greatly enhanced the polymer properties using sulphur as a filler. It was shown that the mechanical characteristics of the developed materials exceed those of characteristics of UHMWPE filled with nanosized particles of CuO, AlN, SiO₂, as well as those of basalt and carbon fibers [21-23]. Figure 3 shows that the hardness of the
composite containing 5 wt.% ZnO / 5 wt.% S / 5 wt.% MBT increased by 13 % compared to UHMWPE. The registered enhancement of mechanical properties of PCM can be explained by changes in the supramolecular structure of UHMWPE at the addition of complex fillers together with the formation of clearly expressed spherulitic structures without defect areas (figure 5).

Figure 3. The dependence of the mechanical characteristics of PCM on the ratio of fillers:
1 – initial UHMWPE;
2 – UHMWPE/ 0.5 wt.% ZnO/ 0.5 wt.% S/ 0.5 wt.% MBT;
3 – UHMWPE/ 1 wt.% ZnO/ 1 wt.% S/ 1 wt.% MBT;
4 – UHMWPE/ 2 wt.% ZnO/ 2 wt.% S/ 2 wt.% MBT;
5 – UHMWPE/ 2 wt.% ZnO/ 5 wt.% S/ 2 wt.% MBT;
6 – UHMWPE/ 2 wt.% ZnO/ 5 wt.% S/ 5 wt.% MBT;
7 – UHMWPE/ 5 wt.% ZnO/ 5 wt.% S/ 5 wt.% MBT

It was observed in the tensile tests for PCM that the stress characteristics of the modified (1 wt.% ZnO / 1 wt.% S / 1 wt.% MBT) UHMWPE are 1.75 higher compared to those of the original polymer (figure 4). Having analyzed the curves a) and b) it was found out that the stress-strain curve possesses two values of Yield stress point, and it is probably connected with the rearrangement of macromolecules UHMWPE during the deformation. Such character of the curve demonstrates resistance to tensile strength with a structure that is different from the original.

In order to define the mechanism of the interaction between the UHMWPE and the used additions structural research for PCM was conducted using the SEM method. Figure 5 shows microphotographs of supramolecular structure of UHMWPE and PCM. As is shown in figure 5, the supramolecular structure of the composite with combined fillers is characterized by the formation of spherulites. It was also registered that particles of zinc oxide initiate the crystallization growth. The further increase of the filler content in UHMWPE brings about fragmentation of the supramolecular structure which explains the reduction of the mechanical characteristics of PCM. According to works [24-27], the
spherulite structure of PCM increases the rigidity and bearing capacity of the material. A decrease in the size of the structural components of the composite helps to reduce the proportion of defective areas and pores, as well as stress concentrations.

![Stress-strain curve](image)

**Figure 4.** Stress-strain curve a) of the initial UHMWPE and b) PCM filled with S, ZnO and MBT

![Micrographs](image)

**Figure 5.** Micrographs of the supramolecular structure of the PCM at x500 magnification:
(a) - initial UHMWPE; (b) - UHMWPE + 0.5% ZnO + 0.5% S + 0.5% MBT;
(c) - UHMWPE + 1% ZnO + 1% S + 1% MBT

4. Discussion

4.1. Mechanical and tribological properties of PCM filled by MMT
As you know, powdered MMT is usually represented by agglomerates, each of which contains up to several tens of silicate plates of the clay mineral. To ensure the dispersion of the clay, MMT powders
are treated with a surfactant. Quaternary ammonium salts (QAS) are usually used as surfactants for the treatment of clays. Positively charged \( \text{NH}_4^+ \) interact with the negatively charged surface of the aluminosilicate, displacing the interlayer cations of alkali and alkaline earth metals, and thereby increasing the distance between the silicate plates, facilitating the intercalation of polymer macromolecules or their fragments into the interlayer space (figure 6) [28]. The main disadvantage of using QAC is their low thermal stability - when processing UHMWPE (about 200 °C), the destruction of surfactants begins. Therefore, along with the modification of the QAC, the clays are additionally treated with heat stabilizers. For this, a resorcinol resin is used, which is an aromatic ether that contains polar bridging ether groups (figure 7) [29].

![Figure 6. The reaction of ion exchange between Na\(^+\) MMT and a cationic surfactant to obtain "organoclay" [28]](image)

![Figure 7. Resorcinol bis(diphenyl phosphate) (rdp) [29]](image)

The increase in the mechanical properties of PCM may be explained in the wettability of the MMT surface by non-polar UHMWPE. Also, due to the intercalation of surfactant particles into the interlayer space of the MMT plates, the dispersion of agglomerates is ensured. Structural studies in figure 2 shows that the presence of agglomerated filler particles was not recorded in the supramolecular PCM containing organo-modified MMT. It is shown in [30] that organo-modified MMT “Cloisite C15A” promotes better delamination of layered clay components, which leads to a decrease in the wear rate by 41 % and the friction coefficient by 38 % compared to unfilled UHMWPE. The research results are confirmed by structural studies of the SEM friction surface. It is shown that the formation of a smooth transfer film on the conjugated counter-body is observed on the friction surface of such a composite. Based on these studies, it can be assumed that a secondary structure is formed on the friction surface of the composites from the tribo-degradation products of UHMWPE and organo-modified MMT. Such a layer during frictional contact protects the material from wear.

4.2. **Enhance mechanical properties of UHMWPE with combined fillers**

Improvement of the deformation and strength properties of PCM with combined fillers is associated with the plasticizing effect of 2-MBT and sulfur on UHMWPE. This facilitates the processes of a reorganization of UHMWPE macromolecules during stretching. At the same time, zinc oxide particles act as reinforcing elements of the composite material. It was revealed that 2-MBT interacts with UHMWPE macromolecules within the amorphous phase. Based on the results of investigations of the
IR spectra of PCM (figure 8), the appearance of new peaks related to oxygen-containing functional groups appeared. For example, in the 1595 cm\(^{-1}\) region, which corresponds to the stretching vibrations of –C=O of the carbonyl group. And in the area of 1180-1400 cm\(^{-1}\), corresponding to the vibrations of –C–O–C– groups [31]. The emergence of new active oxygen-containing functional groups indicates the occurrence of oxidative processes during the processing of UHMWPE composites, which suggests their participation in the formation of the polymer structure. The reactive formed groups from the polymer chain can interact with filler particles and/or decomposition products, thereby enhancing interfacial interaction [32-33]. As a result of these factors, there is an increase in the tensile strength of PCM by 44%, elongation at the break by 19%, and elastic modulus by 70%.

**Figure 8.** IR spectra of films of the initial UHMWPE and UHMWPE/2-MBT composite

5. **Conclusion**

As a result of this work, an enhancement of interfacial interaction between UHMWPE fillers added to it has been found, which has been proven by the increase of the whole set of mechanical characteristics of composites. The results of studies of the PCM microstructure have shown that the supramolecular structure of composites with organo-modified MMT has no defects, such as hollows and pores at the phase boundary. Besides, a uniform distribution of organoclay is also observed in the polymer matrix without the presence of agglomerated particles.

The prospective use of combined fillers in the future as functional additives into the UHMWPE has been proven. A substantial enhancement of the tensile strength characteristics of PCM by 44% of the relatively unfilled UHMWPE has been observed.

The studies of the structure revealed that adding fillers into UHMWPE is capable of bringing about the formation of a spherulitic structure of composites where particles of non-organic fillers serve as centers of crystallization. The energy of the destruction of such a spherulitic structure exceeds that of lamellar structure, which explains the increase in the strength and wear resistance of PCM compared to the original UHMWPE.

As a result, the optimal formula of PCM with a complex enhancement of performance properties has been worked out. The developed materials are intended for the manufacture of parts for friction units of machinery and equipment operated in extreme climatic conditions in regions with a cold climate. For structural materials where higher strength and hardness values are required, a combination of zinc oxide, sulfur and 2-mercaptobenzthiazole fillers is preferred. For example, as a lining material used for facing mining and processing and mining equipment.

**Acknowledgments**

The work was carried out with support of the Ministry of Science and Higher Education of the Russian Federation Scientific Research Work № FSRG-2020-0017
References

[1] Kurdi A and Chang L 2018 *Lubricants* 7(1) 2
[2] Kurtz S 2009 *UHMWPE biomaterials handbook: ultra-high molecular weight polyethylene in total joint replacement and medical devices* (Burlington: Academic Press)
[3] Šupová M, Martynková G S, Barabaszová K 2011 *Science of advanced materials* 3(1) 1-25
[4] Rajak D K, Pagar D D, Menezes P L, Linel E 2019 *Polymers* 11(10) 1667
[5] Bryk M T 1989 *Destruction of filled polymers* (Moscow: Chemistry) 192
[6] Okhlopkova A A, Borisova R V, Nikiforov L A, Spiridonov A M, Okhlopkova A A, Jeong D Y, Cho J H 2016 *Bulletin of the Korean Chemical Society* 37(4) 439-44
[7] Yin X, Li S, He G, Feng Y, Wen J 2018 *Ultrasonics sonochemistry.* 43 15-22
[8] Zhang H, Wang L, Chen Q, Li P, Zhou A, Cao X, Hu Q 2016 *Materials & Design* 92 682-9
[9] Zee J, Tomič N Z, Zrilić M, Lević S, Marinković A, Heinemann R J 2018 *Composites Part B: Engineering* 153 36-48
[10] Wang Y, Qiao X, Wan J, Xiao Y, Fan X 2016 *RSC Advances* 6(83) 80262-7
[11] Feng C P, Chen L, Wei F, Ni H Y, Chen J, Yang W 2016 *RSC Advances* 6(70) pp 65709-13
[12] Silva C R, Lago R M, Veloso H S, Patricio P S 2018 *Journal of the Brazilian Chemical Society* 29(2) 278-84.
[13] Chen R, Ye C, Xin Z, Zhao S, Xia J, Meng X 2018 *Journal of Polymer Research* 25(6) 135
[14] Yeh J, Wang C K, Tsai C C, Ren D H, Chiu S H 2016 *Textile Research Journal* 86(16) 1768-87.
[15] Mikitaev A K, Kaladzhyan A A, Lednev O B, Mikitaev M A 2004 *Investigated in Russia* 7 1365-90
[16] Demidyonok K V, Bahov F N, Chernikova U Yu, Solomkin I A, Novikov A I, Zlobin V B, Aleshinskaya S V, Hilazhdinov V V 2013 *Vestnik evrazijskoj nauki* 5(18)
[17] Danilova S N, Okhlopkova A A, Sleptsova S A, Ivanov A N, Grigoreva L A, Spiridonov A M 2019 *IOP Conf. Series: Earth and Environmental Science* 320 012059
[18] Sutyagin V M, Bondalevna L I 2003 *Chemistry and physics of polymers* (Tomsk: TPU Publishing) 208
[19] Vasilev A P, Struchkova T S, Nikiforov L A, Okhlopkova A A, Grakovitch P N, Shim E L, Cho J H 2019 *Molecules* 24(2) 224
[20] Jena K K and Alhassan S M 2016 *Journal of Applied Polymer Science* 133(9) 43060
[21] Okhlopkova T A, Borisova R V, Nikiforov L A, Spiridonov A M, Sharin P P, Okhlopkova A A 2016 *Russian Journal of Applied Chemistry* 89(9) 1469-76
[22] Panin S V, Alexenko V O, Kornienko L A, Buslovich D G 2018 *AIP Conference Proceedings:* *AIP Publishing* 2007(1) 040014
[23] Panin S V, Kornienko L A, Alexenko V O, Qiao Y, Ivanova L R 2016 *IOP Conference Series: Materials Science and Engineering:* *IOP Publishing* 156(1) 012026
[24] Panin S V, Shilko S V, Kornienko L A, Chernous D A, Alexsenko V O, Buslovich D G, Korchagin M A, Chikina M V 2017 *MOJ Applied Bionics and Biomechanic* 1(5) 192-9
[25] Khalil Y, Hopkinson N, Kowalski A, Fairclough J P A 2019 *Materials* 12(21) 3496
[26] Tanniru M, Yuan Q, Misra R D K 2006 *Polymer* 47(6) 2133-46
[27] Way J L, Atkinson J R, Nutting J 1974 *Journal of materials science* 9(2) 293-9
[28] Tratyakova V D, Bahov F N and Demidyonok K V 2011 *Vestnik evrazijskoj nauki* 4(9) 8
[29] Bahov F N 2013 *Vestnik evrazijskoj nauki* 3(16) 8
[30] Ali bin A, Mohammed A S, Merah N 2018 *Polymer composites* 39(7) 2224-31
[31] Tarasevich B N 2012 *The IR spectra of the major classes of organic compounds* (Moscow: MGU (Moscow State University) 54
[32] Xanthos M 2010 *Functional fillers for plastics* (John Wiley & Sons) 531
[33] Karaseva Yu S Bashkatova T V Cherezova Ye N Khusainov A D 2006 Bulletin of the Technological University 5 57-62