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Effect of Nano-CuO and 2-Mercaptobenzothiazole on the Tribological Properties of Ultra-High Molecular Weight Polyethylene

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Abstract: In this study, the tribological properties of nanocomposites based on ultra-high molecular weight polyethylene (UHMWPE) filled with nano-CuO and 2-mercaptobenzothiazole (CuO/MBT) in mass ratios of 1:1 and 2:1 were investigated. In the supramolecular structure of UHMWPE nanocomposites, spherulites of several hundred micrometers in size are formed. The density of UHMWPE nanocomposites slightly increases relative to the pure polymer, reaching a maximum at 2 wt.% CuO/MBT in both ratios. The Shore D hardness and compressive stress of the UHMWPE nanocomposites showed an improvement of 5–6% and 23–35%, respectively. The wear resistance and coefficient of friction of UHMWPE nanocomposites were tested using a pin-on-disk configuration under dry friction conditions on #45 steel and on P320 sandpaper. It was shown that the wear rate of UHMWPE nanocomposites filled with 2 wt.% CuO/MBT decreased by ~3.2 times compared to the pure polymer, and the coefficient of friction remained at the level of the polymer matrix. Abrasive wear showed an improvement in UHMWPE nanocomposites filled with 1 wt.% CuO/MBT compared to the polymer matrix and other samples. The worn surfaces of the polymer composites after dry friction were examined by scanning electron microscopy and IR spectroscopy. The formation of secondary structures in the form of tribofilms that protect the material from wear was demonstrated. Due to this, the wear mechanism of UHMWPE nanocomposites is transformed from adhesive to fatigue wear. The developed materials, due to improved mechanical and tribological properties, can be used as parts in friction units of machines and equipment.

Keywords: ultra-high molecular weight polyethylene; nano-CuO; 2-mercaptobenzothiazole; polymer composite materials



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1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a type of engineering thermoplastic that has been widely used as a self-lubricating polymer in friction units due to its superior tribological properties such as low coefficient of friction, wear resistance, high impact toughness, corrosion resistance, water absorption, and biocompatibility [1,2]. However, UHMWPE also has disadvantages such as low surface hardness, poor abrasion resistance and flexural strength, and poor creep resistance [3,4]. Therefore, to introduce UHMWPE more broadly into engineering and its application in the harsh conditions of modern industry, it is necessary to modify its mechanical and tribological properties. The most common way to improve the mechanical and tribological properties of UHMWPE is the introduction of dispersed and fiber fillers [5,6].

In polymers, fillers are responsible for the formation of performance characteristics and for providing the material with various desired properties (e.g., mechanical strength, thermal conductivity, or wear resistance). In the work of Selim Gürgen et al. [7], it was

shown that in SiC/UHMWPE composites, excessive loading of fillers into the polymer matrix leads to a loss of anti-wear properties. Also, the properties are strongly influenced by the surface modification of the filler when introduced into the polymer, as demonstrated in [8]. Thus, the main factors determining the properties of polymer composites are the types of fillers, their content and the compatibility between fillers, and the polymer matrix [9,10]. In many cases, both physicochemical and mechanical bonding work simultaneously to increase the degree of compatibility between fillers and the polymer matrix [11–15]. In addition, to obtain polymer composites with an improved complex of performance properties, it is necessary to select components that have a complex effect on the polymer matrix [16,17].

Recently, a new class of composite materials based on polymer matrix and nanoscale particles has been widely used due to their superior mechanical and physical properties compared to the pure polymers at low mass content [18]. Among the multifunctional nanoscale particles, copper oxide is particularly noteworthy. Copper oxide (CuO) has a number of significant advantages. CuO can be easily synthesized and its nanoparticles have more superior properties in terms of wear resistance and reduction in the coefficient of friction than other nanoparticles such as aluminum, zirconium, iron, and cobalt oxide [19,20]. However, the literature review showed that there are not many papers where nanoscale copper oxide is used as a modifier in the development of UHMWPE-based composites [21–25]. Ushakov A.V. et al. demonstrated that the properties of UHMWPE-based composites depend on the concentration of nanoscale fillers and are in the range of 1–2 wt.% CuO [25]. Cao Z. et al. showed that copper oxide nanoparticles were filled with UHMWPE in situ to inhibit possible agglomeration during preparation by mechanical mixing [24]. It is shown that the average sliding friction coefficient of UHMWPE decreased to 34% after filling with CuO nanoparticles, and the wear mechanism changed from adhesive wear to fatigue wear. 2-mercaptobenzothiazole (MBT) is a bicyclic heteroatomic molecule that is used as a rubber vulcanization accelerator and is widely used in the production of tires, rubber shoes, and other rubber products [26]. We have previously investigated the effect of wollastonite and 2-mercaptobenzothiazole on the mechanical and tribological properties of UHMWPE [27].

In this work, 2-mercaptobenzothiazole and nano-CuO are proposed to prepare wear-resistant UHMWPE nanocomposites. One of the drawbacks of UHMWPE is its low resistance to abrasive wear. However, few works are devoted to studying the abrasive wear of UHMWPE-based composites. In this context, it is of interest to evaluate the tribological properties of friction on steel #45 and abrasive paper under dry friction conditions. Therefore, the aim of the present work is to study the tribological properties of UHMWPE nanocomposites with copper oxide and 2-mercaptobenzothiazole.

2. Materials and Methods

Commercial ultra-high molecular weight polyethylene (UHMWPE, grade GUR-4130) powder with an average molecular weight of 6.8×10^6 g/mol and density of 0.93 g/cm³ was supplied by Celanese (Nanjing, China). Nanoscale copper oxide (CuO, purity > 99.8%) with an average particle size of 50 nm and specific surface area of 15–20 m²/g was supplied by LLC “PPT” (Tomsk, Russia). 2-Mercaptobenzothiazole (C₇H₅NS₂)—light yellow powder colors were manufactured according to the Russian standard GOST 739-74 [28].

In this work, fillers were prepared by mixing the components CuO and MBT, and this was carried out in the planetary mill Activator-2S (Activator, Russia) at 600 rpm for 10 min. The obtained were mixed in the mass ratio of CuO:MBT—1:1 further 1CuO/1MBT and CuO:MBT—2:1 further 2CuO/1MBT. Then, UHMWPE powders and CuO/MBT were mixed in a high-speed blade mixer in dry form with stirring device rotation speed of 1200 rpm for 2 min. The mass content of CuO/MBT in the polymer matrix was 0.5, 1, and 2 wt.%. The prepared materials of UHMWPE composites were carried out by hot pressing at a temperature of 175 ± 5 °C, pressure of 10 ± 0.5 MPa, and a holding time of 20 min followed by cooling to 80 °C.

Determination of compressive properties of specimens was carried out in accordance with ISO 604:2002 at a fixed speed of 1 mm/min. The density of specimens was determined by hydrostatic weighing method according to the Russian standard GOST 15139-69. Hardness of UHMWPE nanocomposites was measured by hardness tester TBP-D (Vostok-7, Moscow, Russia) on Shore hardness scale type D according to ISO 868-2003. A CETR UMT-3 tribometer (CETR, Mountain View, CA, USA) was utilized to evaluate the tribological properties of the UHMWPE nanocomposites under dry conditions on the scheme of friction “pin-on-disk”. The counterpart was #45 steel disk with hardness 45–50 HRC, roughness $R_a = 0.06\text{--}0.08\ \mu\text{m}$. The normal load was fixed at 150 N. The sliding velocity is 0.42 m/s with a sliding distance of 4522 m. Prior to the tribological test, the surfaces of the specimens were cleaned and weighed on an analytical scale (0.00001 g). The specific wear rate ($\text{mm}^3/\text{N}\cdot\text{m}$) was estimated as follows in Equation (1):

$$k = \frac{\Delta m}{\rho \cdot F_N \cdot d} \quad (1)$$

where F_N —normal force, N; d —sliding distance, m; Δm —mass lost during sliding, g; ρ —density of specimens, g/cm^3 .

Abrasive wear characteristics were evaluated using the friction scheme “pin-on-disk” on abrasive paper P320 (aluminum oxide, grain size $\sim 50\ \mu\text{m}$), the friction track was—200 m, load—10 N, at a constant sliding velocity—0.2 m/s. After each experiment, the abrasive paper was changed, and the sample was cleaned and weighed on an analytical scale (0.00001 g). The wear was measured by the weight difference before and after the experiment, and the volume loss wear was calculated.

The supramolecular structure and worn surfaces of the polymer matrix and nanocomposites were observed by scanning electron microscopy (SEM) Jeol JSM-7800F (JEOL, Tokyo, Japan). The samples were taken in the secondary electron mode at an accelerating voltage of 1–2 kV. The Fourier transform infrared spectroscopy (Varian 7000 FT-IR, Palo Alto, CA, Varian, USA) was scanned from 550 to $4000\ \text{cm}^{-1}$. The surface roughness (R_a , in μm) of UHMWPE nanocomposites was measured using a contact mode surface profilometer TR220 Surface Roughness Tester (TIME Group, Beijing, China).

3. Results and Discussion

It is known that the parts of friction units require high indices of mechanical properties; in particular, the compressive stress determines the bearing capacity and plays an important role in changing the parameters of the friction surface [2,29]. Table 1 shows the results of compressive stress at a specified relative strain of 10%, Shore D hardness, and density of the pure UHMWPE and UHMWPE nanocomposites as a function of the content and mass ratio of components.

Table 1. Results of compressive stress at a specified relative strain 10%, Shore D hardness, and density of UHMWPE nanocomposites.

Sample	Compressive Stress, MPa	Shore D Hardness	Density, g/cm^3
Initial UHMWPE	17 ± 1	62 ± 1	0.93
UHMWPE + 0.5 wt.% 1CuO/1MBT	21 ± 1	65 ± 1	0.94
UHMWPE + 1 wt.% 1CuO/1MBT	22 ± 1	66 ± 1	0.94
UHMWPE + 2 wt.% 1CuO/1MBT	22 ± 1	65 ± 1	0.95
UHMWPE + 0.5 wt.% 2CuO/1MBT	21 ± 1	66 ± 1	0.93
UHMWPE + 1 wt.% 2CuO/1MBT	22 ± 1	66 ± 1	0.94
UHMWPE + 2 wt.% 2CuO/1MBT	23 ± 1	65 ± 1	0.95

As can be seen from Table 1, the value of compressive stress at a specified relative strain of 10% UHMWPE nanocomposites increased in all composites by 23–35% and Shore D hardness by 5–6% compared to the initial polymer. It can be seen that for UHMWPE

nanocomposites, there is practically no difference between compressive stress and hardness depending on the content and ratio CuO/MBT. This may be due to the fact that CuO and MBT were used, which strengthen the polymer matrix to the same extent. In addition, it is known that with a low filler content in UHMWPE, the mechanical properties remain approximately at the same level, as has been shown in other works [30–32]. The improvement in compressive stress when CuO/MBT is added to the polymer may be due to the fact that the fillers are well dispersed in the bulk UHMWPE. Another effect may be the excellent compatibility of the polymer matrix with CuO/MBT so that the load transfer mechanism is efficient [33,34]. In the case of increasing Shore D hardness, in addition to the above effects, it is also the case that CuO is a hard metal oxide, which can prevent the indenter from penetrating into the polymer matrix. Thus, the addition of CuO/MBT to UHMWPE confirmed their reinforcing effect. The density of UHMWPE nanocomposites slightly increases relative to the pure polymer, reaching a maximum at 2 wt.% CuO/MBT in both ratios. It is likely that such a change in the density of the samples is associated with a higher density of copper oxide, as well as increased interfacial binding due to the organic filler MBT. Similar results of changes in the density of UHMWPE with the addition of nanoparticles have been published in the works of other authors [24,35].

Figure 1 shows the results of the investigation of the initial UHMWPE by SEM. The supramolecular structure of pure UHMWPE is a lamellar crystal structure, which has been well studied [36].

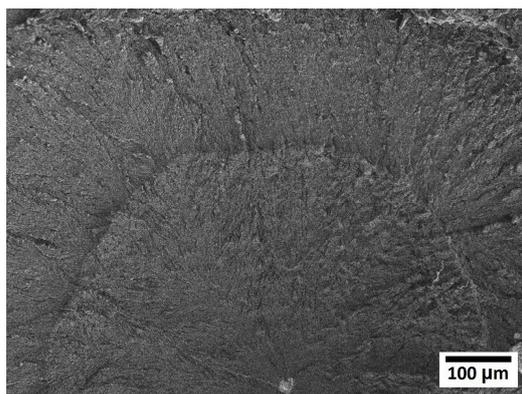


Figure 1. SEM image of the initial UHMWPE.

Modification of UHMWPE by the introduction of CuO/MBT fillers leads to changes in the supramolecular structure. The results of the SEM study on the supramolecular structure of UHMWPE nanocomposites depending on the filler content and the ratio of CuO/MBT are shown in Figure 2.

As can be seen from Figure 2a,d, the supramolecular structure of UHMWPE nanocomposites with 0.5 wt.% CuO/MBT loading shows they form spherulites with a homogeneous structure and a size of several hundred micrometers (some are indicated by yellow arrows). The UHMWPE nanocomposites containing 1 wt.% of CuO/MBT show a change in the supramolecular structure with the formation of a large number of smaller spherulites (Figure 2b,e). When the filler content is increased up to 2 wt.% in UHMWPE, a heterogeneous and defective spherulite-like structure is formed (Figure 2c,f). The formation of a disordered structure is probably due to the high filler content, which prevents the formation of more organized spherulites. It is worth noting that a marked difference in the supramolecular structure can be seen when comparing UHMWPE nanocomposites containing 1 wt.% fillers with each other, depending on the filler ratio CuO/MBT. This can be explained by the fact that nanocomposites with a mass ratio of 2:1 contain a larger amount of nanoscale filler CuO, other conditions being equal.

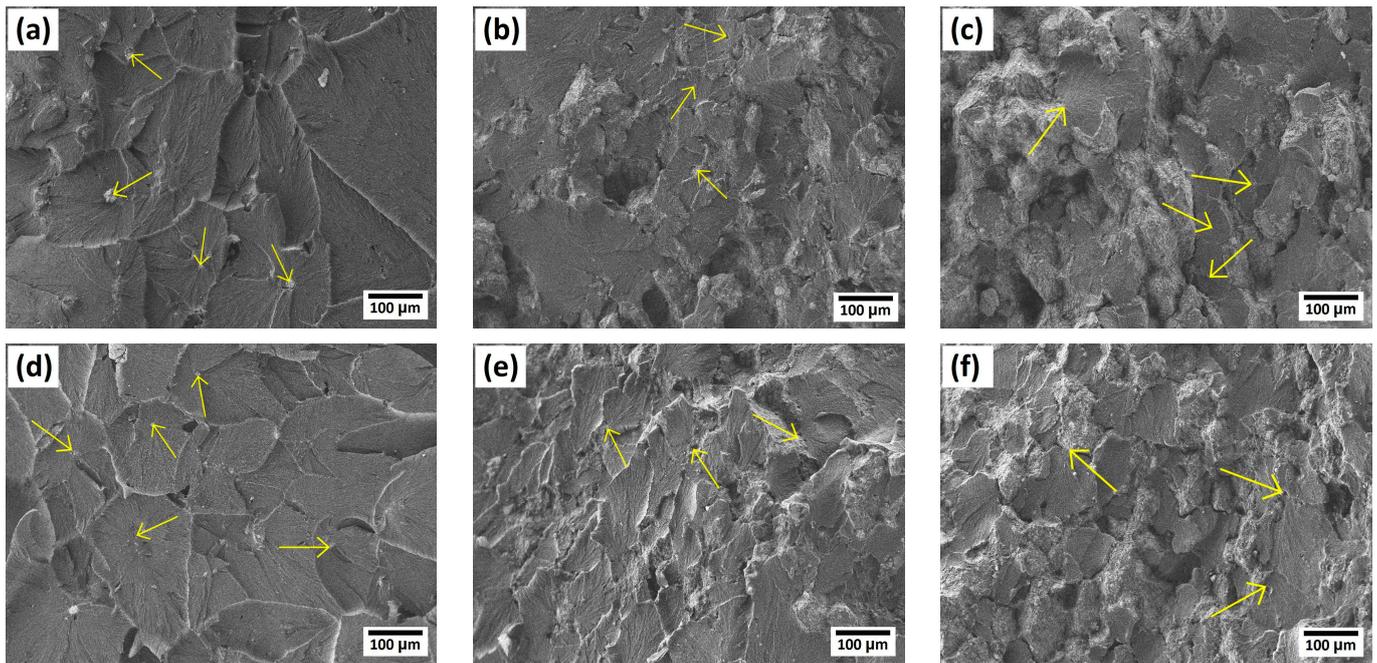


Figure 2. SEM images of supramolecular structure of UHMWPE nanocomposites: (a) UHMWPE + 0.5 wt.% 1CuO/1MBT; (b) UHMWPE + 1 wt.% 1CuO/1MBT; (c) UHMWPE + 2 wt.% 1CuO/1MBT; (d) UHMWPE + 0.5 wt.% 2CuO/1MBT; (e) UHMWPE + 1 wt.% 2CuO/1MBT; (f) UHMWPE + 2 wt.% 2CuO/1MBT.

In order to determine the possible use of the obtained materials in friction units of machines and equipment, studies were carried out to evaluate the tribological properties under conditions of dry sliding friction at room temperature on #45 steel and P320 sandpaper. The tribological properties of UHMWPE nanocomposites under conditions of dry sliding friction at room temperature against #45 steel are depicted in Figure 3.

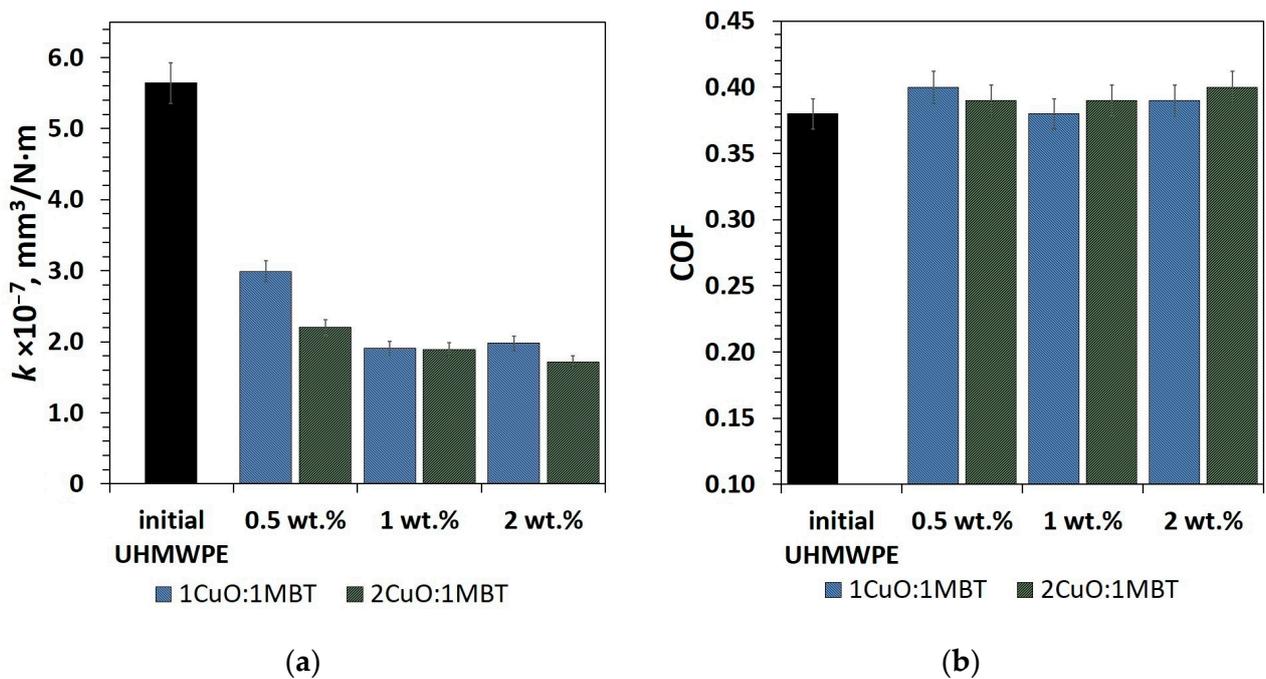


Figure 3. Tribological properties of UHMWPE nanocomposites: (a) specific wear rate; (b) coefficient of friction.

From Figure 3a, it can be seen that the wear resistance of the UHMWPE nanocomposites increases in all specimens compared to the pure polymer. As the CuO/MBT content in UHMWPE increases, the wear resistance reaches a maximum at a content of 2 wt.% with a component ratio of 2:1. It has been found that the smallest reduction in the specific wear rate of UHMWPE nanocomposites in a 1:1 ratio is achieved at a content of 1 wt.%, which is 2.9 times lower relative to the polymer matrix. In the case of UHMWPE nanocomposites at a mass ratio of 2:1, the decrease in the specific wear rate occurs at 2 wt.%, which is 3.2 times lower compared to pure polymer. The specific wear rate of UHMWPE nanocomposites with 0.5 wt.% 1CuO/1MBT is 23% higher compared to UHMWPE + 0.5 wt.% 2CuO/1MBT. The value of the specific wear rate in the remaining UHMWPE nanocomposites at 1 and 2 wt.% contents is approximately the same. The coefficient of friction of UHMWPE nanocomposites in all samples is in the range of 0.39–0.41 (Figure 3b). Thus, the UHMWPE nanocomposites retain a relatively low value of the coefficient of friction corresponding to values of the initial polymer.

The surface roughness results of the UHMWPE nanocomposites before and after the friction test are summarized in Table 2. The introduction of CuO/MBT fillers into UHMWPE leads to an increase in the roughness values— R_a . As the filler content increases from 0.5 to 2 wt.%, R_a increases by about ~25 to 31%; i.e., the surfaces become rougher. Similar results for the introduction of fillers into UHMWPE were obtained in [7]. After friction tests of UHMWPE nanocomposites, their surface roughness decreases. The higher the CuO/MBT filler content in UHMWPE, the greater the reduction in surface roughness. Depending on the filler content in the polymer, similar results are observed, which do not depend on the mass ratio of the filler components.

Table 2. Results of surface roughness of UHMWPE nanocomposites before and after friction test.

Sample	R_a , μm before Friction Test	R_a , μm after Friction Test
Initial UHMWPE	0.33	0.29
UHMWPE + 0.5 wt.% 1CuO/1MBT	0.35	0.31
UHMWPE + 1 wt.% 1CuO/1MBT	0.39	0.34
UHMWPE + 2 wt.% 1CuO/1MBT	0.46	0.35
UHMWPE + 0.5 wt.% 2CuO/1MBT	0.36	0.31
UHMWPE + 1 wt.% 2CuO/1MBT	0.38	0.32
UHMWPE + 2 wt.% 2CuO/1MBT	0.45	0.34

Figure 4 shows SEM images of the worn surface of the initial UHMWPE, which is characterized by grooves along the friction direction (indicated by yellow arrows). The formation of such grooves is due to the plowing effect and a micro-cutting process by the surface of a steel counterpart, which increases the loss of material. This type of worn surface is typical of this polymer [37,38].

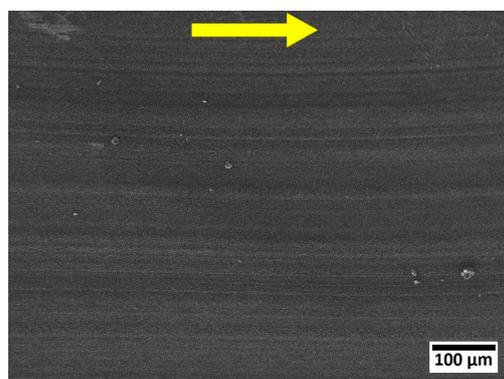


Figure 4. SEM image of the worn surface of the initial UHMWPE.

Further, Figure 5 shows SEM images of the worn surface of UHMWPE nanocomposites depending on mass ratio and content of CuO/MBT.

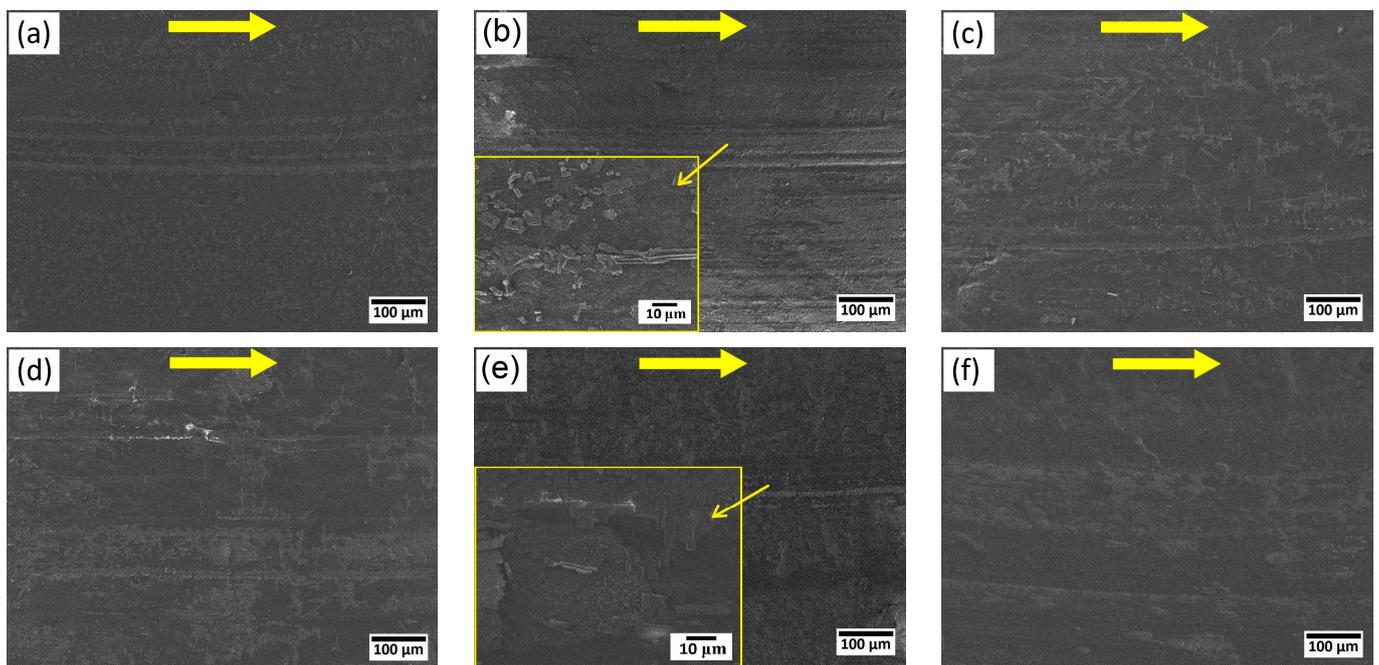


Figure 5. SEM images of worn surface of UHMWPE nanocomposites: (a) UHMWPE + 0.5 wt.% 1CuO/1MBT; (b) UHMWPE + 1 wt.% 1CuO/1MBT; (c) UHMWPE + 2 wt.% 1CuO/1MBT; (d) UHMWPE + 0.5 wt.% 2CuO/1MBT; (e) UHMWPE + 1 wt.% 2CuO/1MBT; (f) UHMWPE + 2 wt.% 2CuO/1MBT.

As can be seen from Figure 5, the worn surfaces of the UHMWPE nanocomposites show small structural formations along the sliding direction (indicated by yellow arrows) that are not characteristic of the initial polymer. At higher magnification, the formation of new structural elements on the worn surface of the composites can be seen in Figure 5b,e. These structures are identified as secondary structures (tribofilms) consisting of filler particles and polymer. The formation of tribofilms improves the wear resistance of UHMWPE nanocomposites compared to the polymer matrix. It can be seen that tribofilms on the friction surface form a protective layer in the form of contact spots, where frictional stresses between the contacting surfaces are localized. As a result, plastic deformation and adhesive wear of the material surface are reduced, thus increasing the resistance of the material to wear. The formation of secondary structures in the form of tribofilms on the worn surface of polymer composites is one of the key mechanisms for adaptation of polymer composites during friction [39]. This also changes the wear mechanism of polymer composites from adhesive to fatigue wear. Thus, the friction of UHMWPE nanocomposites results in the localization of frictional loads on separate contact spots (tribofilms), which are more resistant to wear, i.e., reduce wear of the material.

Figure 6 shows the results of IR spectroscopy of the surface of polymer nanocomposites before and after the friction test. IR spectra of UHMWPE nanocomposites revealed strong peaks in the surfaces before the friction test in the region of 2915, 2847, 1465, and ~ 719 cm^{-1} , which are attributed to the polymer matrix [37,40]. These main absorption bands of the UHMWPE are still present in all the nanocomposite specimens investigated after the friction test.

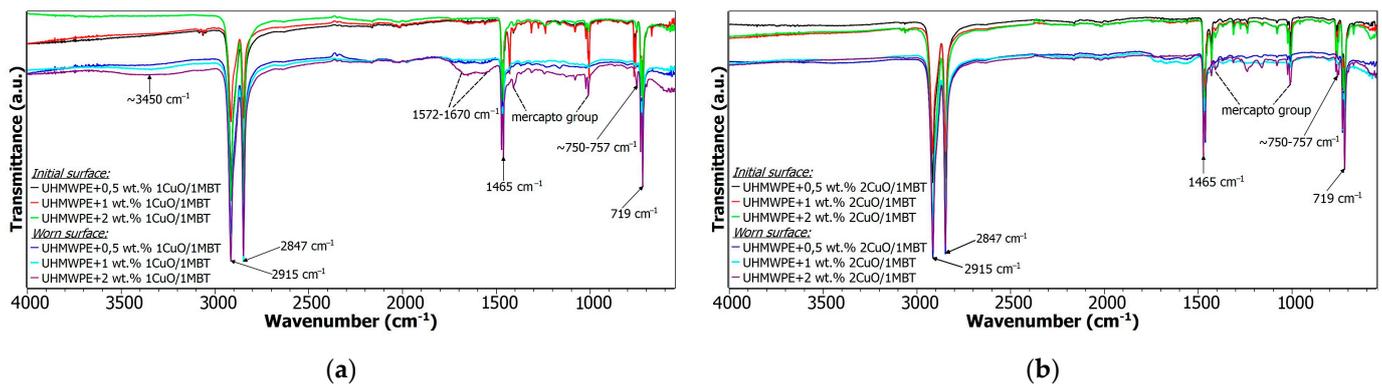


Figure 6. IR spectra of UHMWPE nanocomposites: (a) 1:1 ratio; (b) 2:1 ratio.

As can be seen from Figure 6, new peaks appear on the worn surfaces of polymer nanocomposites in the region of ~ 750 to 757 and ~ 1006 to 1590 cm^{-1} , which are due to the presence of MBT filler content and belong to the mercapto group [41,42]. At the same time, no peaks were detected in relation to CuO. From the bands of IR spectra of UHMWPE nanocomposites, it can be seen that the intensity of peaks belonging to the MBT group decreases after friction. This may be due to the fact that after friction on the worn surface, MBT particles are discretely distributed, which was evident from the SEM results. In the IR spectra of the UHMWPE + 2 wt.% 1CuO/1MBT composite after the friction test, the presence of absorption bands in the region of ~ 3450 and ~ 1596 to 1651 cm^{-1} was registered related to oxygen-containing groups [43,44]. The identified absorption bands in the indicated regions are caused by the oxidation of UHMWPE in the process of wear during friction testing, and indicate the occurrence of tribo-oxidative processes [45]. At the same time, in other composites, these absorption bands in the IR spectra are rather weak in intensity, which is due to insignificant oxidative reactions during the wear process, indicating the inhibition of oxidative reactions. Thus, the appearance of new absorption bands on the UHMWPE nanocomposite surface generally agrees with the results of the analysis of the worn surface by SEM, where structural formations in the form of tribofilms consisting of fillers and polymer matrix were revealed.

Figure 7 shows the results of volume loss and the coefficient of friction of UHMWPE nanocomposites after the friction test against P320 sandpaper under dry friction conditions.

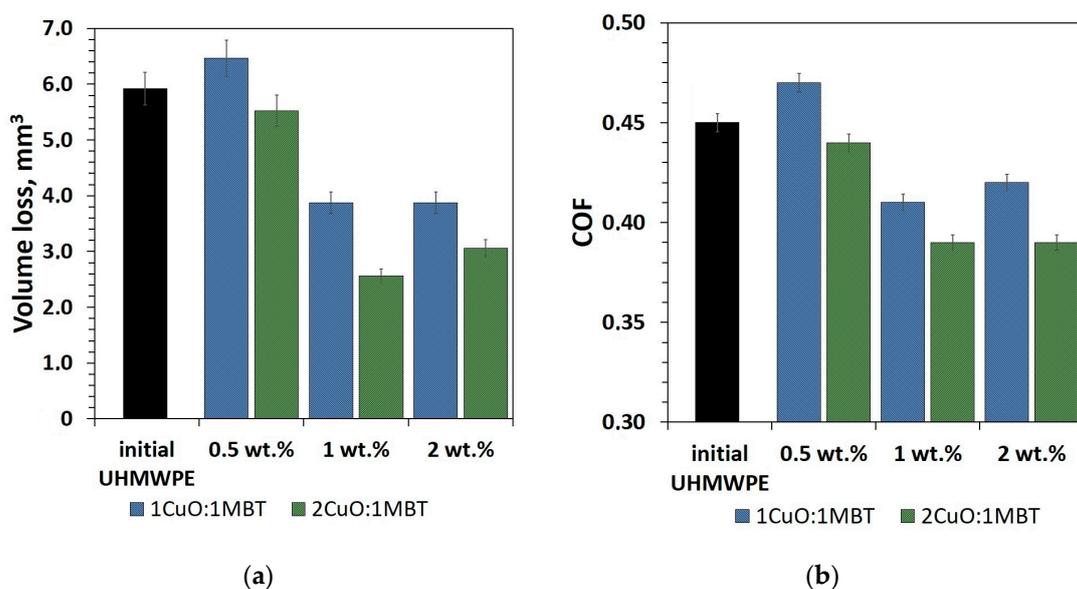


Figure 7. Abrasive wear results of the UHMWPE nanocomposites: (a) volume loss; (b) coefficient of friction.

As seen from Figure 7a, the abrasive wear resistance of UHMWPE with 0.5 wt.% of fillers is at the level of the polymer matrix, as well as the coefficient of friction. The relatively low abrasion resistance at 0.5 wt.% CuO/MBT content in UHMWPE in both ratios is probably due to plastic deformation of the polymer and composites, thus relatively high values of the coefficient of friction are observed. It can be seen that at the content of 1 wt.% of CuO/MBT in UHMWPE, there is a 34–57% decrease in volume loss, and at the content of 2 wt.%, by 34–48% relative to the polymer matrix. The coefficient of friction of the UHMWPE nanocomposites is reduced by 9–13% at 1 wt.% content and by 7–13% at 2 wt.% content (Figure 7b). This is possibly due to the fact that CuO/MBT can accumulate on the worn surface and form a lubricating film. Similar results of a reduction in the coefficient of friction of UHMWPE nanocomposites due to the effect of interlayer sliding have been described in [38]. It can be seen that, as a result of abrasive wear, the volume loss value passes through a minimum as the CuO/MBT content in the polymer increases. The volume loss value of UHMWPE + 1 wt.% 2CuO/1MBT is 34% lower than that of UHMWPE + 1 wt.% 1CuO/1MBT. In the case of UHMWPE + 2 wt.% 2CuO/1MBT, it is 21% lower compared to the UHMWPE + 2 wt.% 1CuO/1MBT. It was also observed that a higher nano-CuO content (2:1 ratio) in UHMWPE was more effective than a 1:1 ratio for the same loading in the matrix.

Figure 8 shows SEM images of the abrasive wear surface of pure UHMWPE. It can be seen that on the worn surface of pure UHMWPE, an abrasive wear mechanism is observed with the formation of deep grooves in the direction of friction (indicated by yellow arrows), caused by hard abrasive particles of sandpaper. In addition, the formation of elongated ribbon-like outgrowths causing an adhesive wear mechanism due to detachment from the substrate under strong shear action is observed [46].

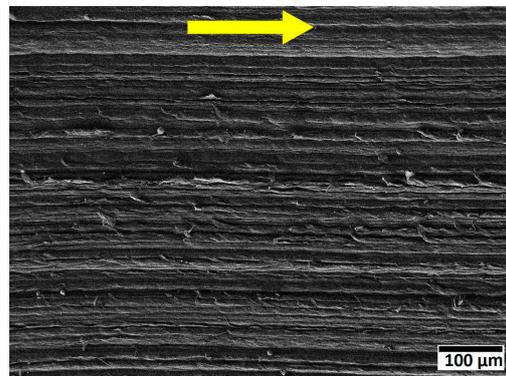


Figure 8. SEM images of the abrasive wear surface of the initial UHMWPE.

SEM images of the abrasive wear surface of UHMWPE nanocomposites as a function of their ratio and content of CuO/MBT fillers are shown in Figure 9.

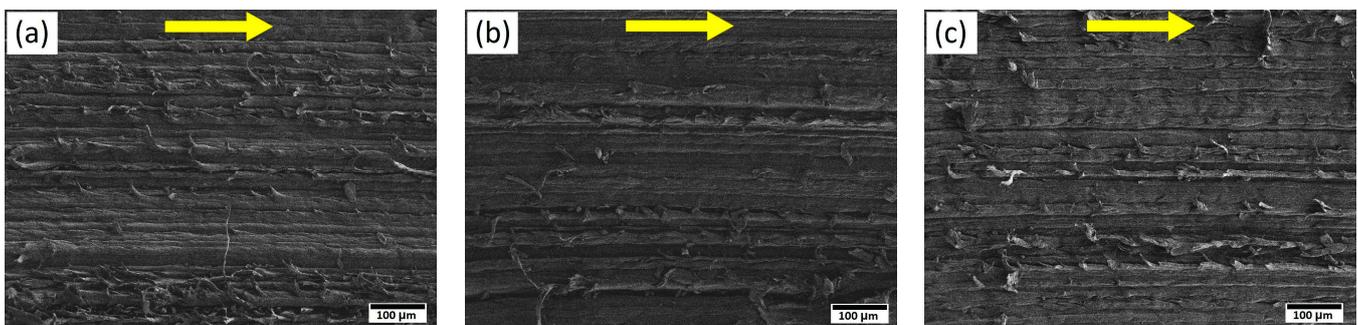


Figure 9. Cont.

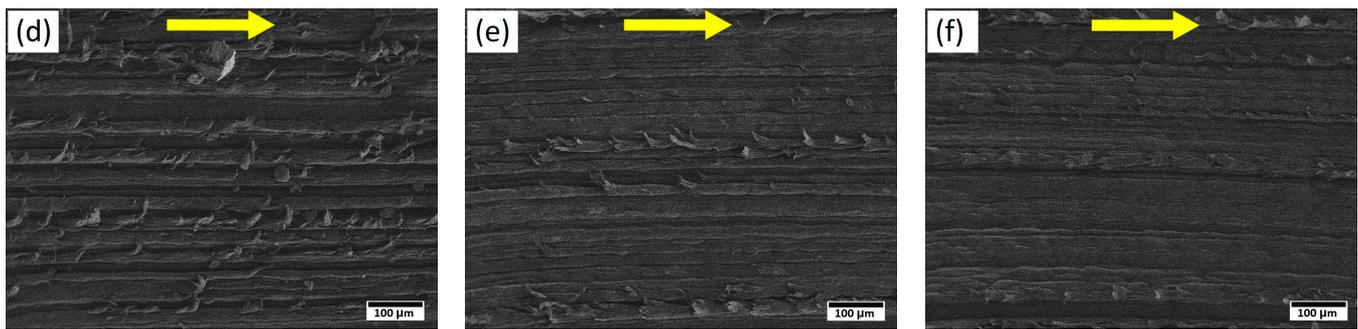


Figure 9. SEM images of abrasive wear surface of UHMWPE nanocomposites: (a) UHMWPE + 0.5 wt.% 1CuO/1MBT; (b) UHMWPE + 1 wt.% 1CuO/1MBT; (c) UHMWPE + 2 wt.% 1CuO/1MBT; (d) UHMWPE + 0.5 wt.% 2CuO/1MBT; (e) UHMWPE + 1 wt.% 2CuO/1MBT; (f) UHMWPE + 2 wt.% 2CuO/1MBT.

Figure 9 shows that on the worn surface of the UHMWPE nanocomposites, as well as in the polymer matrix, grooves along the friction direction and elongated ribbon-like chips can be seen. This is due to the high plasticity of the matrix due to micro-cutting and micro-ploughing actions, which are the main causes of abrasive wear [46,47]. However, the surfaces of the UHMWPE nanocomposites after abrasive wear are different from each other, depending on the mass content of the fillers. It is observed that as the filler content increases from 0.5 to 2 wt.% in UHMWPE, the wear reduces, and the groove depth and the number of elongated ribbons on the worn surface decreases. This tendency is especially evident in composites at a ratio of 2:1. The surfaces of UHMWPE + 1 wt.% 2CuO/1MBT and UHMWPE + 1 wt.% 2CuO/1MBT composites are the smoothest, contributing to their minimal abrasive wear.

Figure 10 shows high-magnification SEM images of UHMWPE nanocomposites at 1 wt.% filler loading.

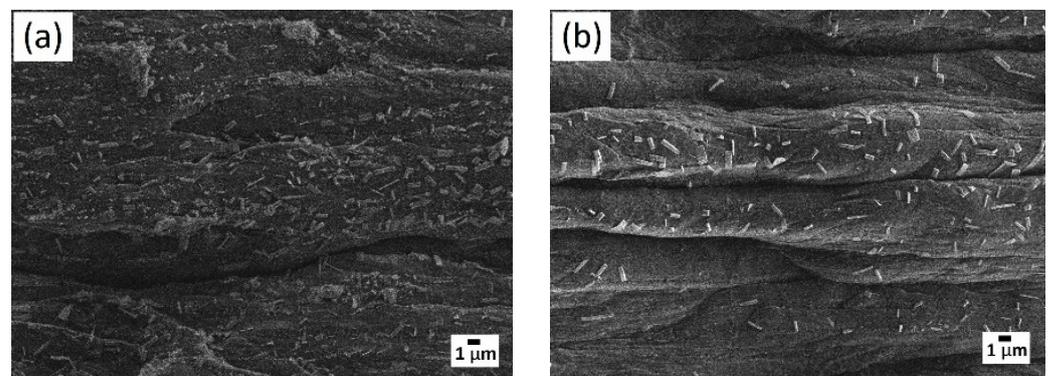


Figure 10. SEM image of the abrasive wear surface at high magnification: (a) UHMWPE + 1 wt.% 1CuO/1MBT; (b) UHMWPE + 1 wt.% 2CuO/1MBT.

Figure 10 shows that in the nanocomposite at a ratio of 1:1, a larger amount of MBT fillers is observed on the worn surface compared to at a ratio of 2:1. At the same time, nano-CuO particles cannot be seen on worn surfaces. The coefficient of friction of pure UHMWPE was lower than that of composites for abrasive wear in papers [46,47]. In this work, the coefficient of friction value of the initial polymer is higher in abrasive wear compared to UHMWPE nanocomposites with 1–2 wt.% CuO/MBT loading. The fillers accumulate on the worn surface and produce a solid lubricant effect. Consequently, they demonstrate the formation of a lubricating film on the friction surface, which reduces the coefficient of friction and abrasive wear. Thus, the optimal amount of CuO/MBT is 1 wt.% at a ratio of 2:1, and less or more CuO/MBT does not promote the formation of a protective

surface film and, at the same time, increases the plastic deformation of UHMWPE, thereby increasing the coefficient of friction.

4. Conclusions

The tribological properties of UHMWPE nanocomposites with CuO/MBT fillers at different ratios of 1:1 and 2:1 were investigated. The studies showed that the compressive stress of UHMWPE nanocomposites increased by 23–35% and the Shore D hardness increased by 5–6%. Structural studies using SEM showed that when CuO/MBT is added to UHMWPE, spherulites are formed in the supramolecular structure. Tribological tests showed improved wear resistance in all nanocomposites compared to the polymer matrix. The best results were obtained in the UHMWPE nanocomposite with 1 wt.% 1CuO/1MBT and 2 wt.% 2CuO/1MBT, which is 2.9–3.2 times higher than the pure polymer. The results for abrasive wear show that the best results are obtained with 1 wt.% CuO/MBT in UHMWPE. When comparing the composites relative to each other, it was found that the resistance to abrasive wear is higher in UHMWPE nanocomposites with a CuO/MBT ratio of 2:1. Thus, UHMWPE + 1 wt.% 2CuO/1MBT is characterized by high resistance to abrasive wear, which is 34% lower than that of UHMWPE + 1 wt.% 1CuO/1MBT. It is revealed that the surface roughness of UHMWPE nanocomposites increases with increasing filler content and decreases in composites after friction tests. Studies of the worn surfaces of UHMWPE nanocomposites have shown the formation of secondary structures in the form of tribofilms consisting of filler particles and polymer. Such tribofilms on the friction surface increase the wear resistance of the material by localizing the frictional loads on themselves. Thus, from the above studies, UHMWPE + 2CuO/1MBT with a filler content of 1–2 wt.% has the best tribological properties. The developed materials, due to improved mechanical and tribological properties, can be used as parts in friction units of machines and equipment, as well as protective coatings and linings.

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References

1. Cao, X.; Li, Y.; He, G. Fabrication of Self-Lubricating Porous UHMWPE with Excellent Mechanical Properties and Friction Performance via Rotary Sintering. *Polymers* **2020**, *12*, 1335. [[CrossRef](#)]
2. Abdul Samad, M. Recent Advances in UHMWPE/UHMWPE Nanocomposite/UHMWPE Hybrid Nanocomposite Polymer Coatings for Tribological Applications: A Comprehensive Review. *Polymers* **2021**, *13*, 608. [[CrossRef](#)]
3. Tian, Y.; Guo, L. Adhesion Performance of UHMWPE Fiber Treated with Polyethylene Wax Grafted Methyl Methacrylate Alone or in Conjunction with Silane Coupling Agent. *J. Adhes. Sci. Technol.* **2021**, *35*, 1219–1235. [[CrossRef](#)]
4. Zec, J.; Tomić, N.Z.; Zrilić, M.; Lević, S.; Marinković, A.; Heinemann, R.J. Optimization of Al₂O₃ Particle Modification and UHMWPE Fiber Oxidation of EVA Based Hybrid Composites: Compatibility, Morphological and Mechanical Properties. *Compos. Part B Eng.* **2018**, *153*, 36–48. [[CrossRef](#)]
5. Danilova, S.N.; Ivanov, A.N.; Spiridonov, A.M.; Abakunova, E.V.; Okhlopkova, A.A. Polymer-Silicate Composites Based on Ultra-High Molecular Weight Polyethylene and Organo-Modified Montmorillonite. *Mater. Today Commun.* **2023**, *37*, 107408. [[CrossRef](#)]
6. Shelly, D.; Lee, S.-Y.; Park, S.-J. Compatibilization of Ultra-High Molecular Weight Polyethylene (UHMWPE) Fibers and Their Composites for Superior Mechanical Performance: A Concise Review. *Compos. Part B Eng.* **2024**, *275*, 111294. [[CrossRef](#)]
7. Gürgen, S.; Sert, A.; Kuşhan, M.C. An Investigation on Wear Behavior of UHMWPE /Carbide Composites at Elevated Temperatures. *J. Appl. Polym. Sci* **2021**, *138*, 50245. [[CrossRef](#)]

8. Ramesh, M.; Deepa, C.; Rajeshkumar, L.; Tamil Selvan, M.; Balaji, D. Influence of Fiber Surface Treatment on the Tribological Properties of *Calotropis gigantea* Plant Fiber Reinforced Polymer Composites. *Polym. Compos.* **2021**, *42*, 4308–4317. [[CrossRef](#)]
9. Karger-Kocsis, J.; Mahmood, H.; Pegoretti, A. Recent Advances in Fiber/Matrix Interphase Engineering for Polymer Composites. *Prog. Mater. Sci.* **2015**, *73*, 1–43. [[CrossRef](#)]
10. Feng, J.; Venna, S.R.; Hopkinson, D.P. Interactions at the Interface of Polymer Matrix-Filler Particle Composites. *Polymer* **2016**, *103*, 189–195. [[CrossRef](#)]
11. Wang, S.; Ma, J.; Feng, X.; Cheng, J.; Ma, X.; Zhao, Y.; Chen, L. An Effective Surface Modification of UHMWPE Fiber for Improving the Interfacial Adhesion of Epoxy Resin Composites. *Polym. Compos.* **2020**, *41*, 1614–1623. [[CrossRef](#)]
12. Borisova, R.V.; Nikiforov, L.A.; Spiridonov, A.M.; Okhlopko, T.A.; Okhlopko, A.A.; Koryakina, N.S. The Influence of Brominated UHMWPE on the Tribological Characteristics and Wear of Polymeric Nanocomposites Based on UHMWPE and Nanoparticles. *J. Frict. Wear* **2019**, *40*, 27–32. [[CrossRef](#)]
13. Panin, S.V.; Kornienko, L.A.; Huang, Q.; Buslovich, D.G.; Bochkareva, S.A.; Alexenko, V.O.; Panov, I.L.; Berto, F. Effect of Adhesion on Mechanical and Tribological Properties of Glass Fiber Composites, Based on Ultra-High Molecular Weight Polyethylene Powders with Various Initial Particle Sizes. *Materials* **2020**, *13*, 1602. [[CrossRef](#)]
14. Bhusari, S.A.; Sharma, V.; Bose, S.; Basu, B. HDPE/UHMWPE Hybrid Nanocomposites with Surface Functionalized Graphene Oxide towards Improved Strength and Cytocompatibility. *J. R. Soc. Interface* **2019**, *16*, 20180273. [[CrossRef](#)]
15. Azam, M.U.; Samad, M.A. UHMWPE Hybrid Nanocomposite Coating Reinforced with Nanoclay and Carbon Nanotubes for Tribological Applications under Water with/without Abrasives. *Tribol. Int.* **2018**, *124*, 145–155. [[CrossRef](#)]
16. Aparna, A.; Sethulekshmi, A.S.; Jayan, J.S.; Saritha, A.; Joseph, K. Recent Advances in Boron Nitride Based Hybrid Polymer Nanocomposites. *Macromol. Mater. Eng.* **2021**, *306*, 2100429. [[CrossRef](#)]
17. Praveenkumara, J.; Madhu, P.; Yashas Gowda, T.G.; Sanjay, M.R.; Siengchin, S. A Comprehensive Review on the Effect of Synthetic Filler Materials on Fiber-Reinforced Hybrid Polymer Composites. *J. Text. Inst.* **2022**, *113*, 1231–1239. [[CrossRef](#)]
18. Cazan, C.; Enesca, A.; Andronic, L. Synergic Effect of TiO₂ Filler on the Mechanical Properties of Polymer Nanocomposites. *Polymers* **2021**, *13*, 2017. [[CrossRef](#)]
19. Asnida, M.; Hisham, S.; Awang, N.W.; Amirruddin, A.K.; Noor, M.M.; Kadirgama, K.; Ramasamy, D.; Najafi, G.; Tarlochan, F. Copper (II) Oxide Nanoparticles as Additive in Engine Oil to Increase the Durability of Piston-Liner Contact. *Fuel* **2018**, *212*, 656–667. [[CrossRef](#)]
20. Jatti, V.S.; Singh, T.P. Copper Oxide Nano-Particles as Friction-Reduction and Anti-Wear Additives in Lubricating Oil. *J. Mech. Sci. Technol.* **2015**, *29*, 793–798. [[CrossRef](#)]
21. Wang, Z.; Ma, Y.; Guo, L.; Tong, J. Influence of Polyphenyl Ester and Nanosized Copper Filler on the Tribological Properties of Carbon Fibre-Reinforced Ultra-High-Molecular-Weight Polyethylene Composites. *J. Thermoplast. Compos. Mater.* **2018**, *31*, 1483–1496. [[CrossRef](#)]
22. Li, W.; Feng, M.; Liu, X.; Yang, J. Improvement of Copper Oxides-Coated Ultra-High Molecular Weight Polyethylene Fibers Reinforced Rigid Polyurethane Composites in Strength and Toughness. *Fibers Polym.* **2021**, *22*, 1883–1888. [[CrossRef](#)]
23. Shiv, J.K.; Kumar, K.; Jayapalan, S. Recent Advances in Polymer Using Metal Oxides Nanocomposite and Its Hybrid Fillers for Tribological Application. *Adv. Mater. Process. Technol.* **2023**, 1–12. [[CrossRef](#)]
24. Cao, Z.; Shi, G.; Yan, X.; Wang, Q. *In Situ* Fabrication of CuO/UHMWPE Nanocomposites and Their Tribological Performance. *J. Appl. Polym. Sci.* **2019**, *136*, 47925. [[CrossRef](#)]
25. Ushakov, A.V.; Karpov, I.V.; Fedorov, L.U.; Lepeshev, A.A. Mechanical and Tribological Properties of Complex-Modified Material Based on Ultra High Molecular Weight Polyethylene and CuO. *J. Frict. Wear* **2014**, *35*, 7–11. [[CrossRef](#)]
26. Skotnicka, A.; Kabatc-Borcz, J. Design, Synthesis, and Spectral Properties of Novel 2-Mercaptobenzothiazole Derivatives. *Materials* **2024**, *17*, 246. [[CrossRef](#)] [[PubMed](#)]
27. Danilova, S.N.; Okhlopko, A.A.; Yarusova, S.B.; Dyakonov, A.A.; Gordienko, P.S.; Papynov, E.K.; Shichalin, O.O.; Buravlev, I.Y.; Vasilev, A.P.; Zhevtun, I.G.; et al. Study on the Impact of a Combination of Synthetic Wollastonite and 2-Mercaptobenzothiazole-Based Fillers on UHMWPE Polymeric Matrix. *J. Compos. Sci.* **2023**, *7*, 431. [[CrossRef](#)]
28. GOST 739-74; 2-Mercaptobenzothiazole. Specifications, Standards Publishing House: Moscow, Russia, 2000; 11p.
29. Li, J.; Guo, Z.; Hua, M.; Qin, X.; Wen, S. Tribological Characteristics of UHMWPE Composite and Relationship with Its Compressive Behavior. *SCI CHINA SER G* **2004**, *47*, 79–87. [[CrossRef](#)]
30. Padhan, M.; Marathe, U.; Bijwe, J. A Comparative Assessment of Nano and Microparticles of Carbides for Performance Augmentation of UHMWPE in Abrasive and Erosive Wear Modes. *Wear* **2023**, *514–515*, 204568. [[CrossRef](#)]
31. Reddy, S.K.; Kumar, S.; Varadarajan, K.M.; Marpu, P.R.; Gupta, T.K.; Choosri, M. Strain and Damage-Sensing Performance of Biocompatible Smart CNT/UHMWPE Nanocomposites. *Mater. Sci. Eng. C* **2018**, *92*, 957–968. [[CrossRef](#)]
32. Diabb Zavala, J.M.; Leija Gutiérrez, H.M.; Segura-Cárdenas, E.; Mamidi, N.; Morales-Avalos, R.; Villela-Castrejón, J.; Elías-Zúñiga, A. Manufacture and Mechanical Properties of Knee Implants Using SWCNTs/UHMWPE Composites. *J. Mech. Behav. Biomed. Mater.* **2021**, *120*, 104554. [[CrossRef](#)]
33. Ni, Z.; Pang, W.; Chen, G.; Lu, P.; Qian, S. The Influence of Irradiation on Thermal and Mechanical Properties of UHMWPE/GO Nanocomposites. *Russ. J. Appl. Chem.* **2017**, *90*, 1876–1882. [[CrossRef](#)]
34. Mirsalehi, S.A.; Khavandi, A.; Mirdamadi, S.; Naimi-Jamal, M.R.; Roshanfar, S.; Fatehi-Peykani, H. Synthesis of Nano-HA and the Effects on the Mechanical Properties of HA/UHMWPE Nanocomposites. *Adv. Mater. Process. Technol.* **2016**, *2*, 209–219. [[CrossRef](#)]

35. Amurin, L.G.; Felisberto, M.D.; Ferreira, F.L.Q.; Soraes, P.H.V.; Oliveira, P.N.; Santos, B.F.; Valeriano, J.C.S.; De Miranda, D.C.; Silva, G.G. Multifunctionality in Ultra High Molecular Weight Polyethylene Nanocomposites with Reduced Graphene Oxide: Hardness, Impact and Tribological Properties. *Polymer* **2022**, *240*, 124475. [[CrossRef](#)]
36. Bucknall, C.; Altstädt, V.; Auhl, D.; Buckley, P.; Dijkstra, D.; Galeski, A.; Gögelein, C.; Handge, U.A.; He, J.; Liu, C.-Y.; et al. Structure, Processing and Performance of Ultra-High Molecular Weight Polyethylene (IUPAC Technical Report). Part 2: Crystallinity and Supra Molecular Structure. *Pure Appl. Chem.* **2020**, *92*, 1485–1501. [[CrossRef](#)]
37. Gürgen, S. Wear Behavior of UHMWPE Composites under Oxidative Effect. *Polym. Degrad. Stab.* **2022**, *199*, 109912. [[CrossRef](#)]
38. Shi, W.; Dong, H.; Bell, T. Tribological Behaviour and Microscopic Wear Mechanisms of UHMWPE Sliding against Thermal Oxidation-Treated Ti6Al4V. *Mater. Sci. Eng. A* **2000**, *291*, 27–36. [[CrossRef](#)]
39. Struchkova, T.S.; Vasilev, A.P.; Okhlopkova, A.A.; Danilova, S.N.; Alekseev, A.G. Mechanical and Tribological Properties of Polytetrafluoroethylene Composites Modified by Carbon Fibers and Zeolite. *Lubricants* **2021**, *10*, 4. [[CrossRef](#)]
40. Cai, T.; Zhan, S.; Yang, T.; Jia, D.; Tu, J.; Li, Y.; Li, J.; Duan, H. Influence Mechanism of Organic-Modified α -Zirconium Phosphate on Tribological Properties of UHMWPE. *Wear* **2023**, *512–513*, 204548. [[CrossRef](#)]
41. Rai, A.K.; Singh, R.; Singh, K.N.; Singh, V.B. FTIR, Raman Spectra and Ab Initio Calculations of 2-Mercaptobenzothiazole. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2006**, *63*, 483–490. [[CrossRef](#)]
42. Li, X.-H.; Tang, Z.-X.; Zhang, X.-Z. Molecular Structure, IR Spectra of 2-Mercaptobenzothiazole and 2-Mercaptobenzoxazole by Density Functional Theory and Ab Initio Hartree–Fock Calculations. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2009**, *74*, 168–173. [[CrossRef](#)] [[PubMed](#)]
43. Catauro, M.; Scolaro, C.; Dal Poggetto, G.; Pacifico, S.; Visco, A. Wear Resistant Nanocomposites Based on Biomedical Grade UHMWPE Paraffin Oil and Carbon Nano-Filler: Preliminary Biocompatibility and Antibacterial Activity Investigation. *Polymers* **2020**, *12*, 978. [[CrossRef](#)] [[PubMed](#)]
44. Lu, P.; Wu, M.; Ni, Z.; Huang, G. Oxidative Degradation Behavior of Irradiated GO/UHMWPE Nanocomposites Immersed in Simulated Body Fluid. *Polym. Bull.* **2021**, *78*, 5153–5164. [[CrossRef](#)]
45. Okhlopkova, A.A.; Danilova, S.N.; Dyakonov, A.A.; Vasilev, A.P.; Tuisov, A.G.; Kychkin, A.K. Tribological Properties of Composites Based on a UHMWPE Modified Borpolymer. *J. Frict. Wear* **2022**, *43*, 27–34. [[CrossRef](#)]
46. Kumar, A.; Bijwe, J.; Sharma, S. Hard Metal Nitrides: Role in Enhancing the Abrasive Wear Resistance of UHMWPE. *Wear* **2017**, *378–379*, 35–42. [[CrossRef](#)]
47. Sharma, S.; Bijwe, J.; Panier, S. Assessment of Potential of Nano and Micro-Sized Boron Carbide Particles to Enhance the Abrasive Wear Resistance of UHMWPE. *Compos. Part B Eng.* **2016**, *99*, 312–320. [[CrossRef](#)]

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