Vol. 45, No. 2 (2023) 294-301, DOI: 10.24874/ti.1490.03.23.06

Tribology in Industry

www.tribology.rs

RESEARCH

Effect of Graphene Oxide and Plasma Treatment on Tribological Characteristics of Ultra-High Molecular Weight Polyethylene

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Keywords:

Graphene oxide
UHMWPE
Low-pressure plasma
Total hip replacement (THR)
Total knee replacement (TKR)
Wear resistance
Coefficient of friction

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Received: 11 March 2023
Revised: 12 April 2023
Accepted: 7 June2023

A B S T R A C T

A technology has been developed for preparing a suspension and deposition of a coating to the surface of ultra-high molecular weight polyethylene (UHMWPE) samples. After deposition of a graphene oxide layer onto the sample surface, the sample was treated in helium plasma at low pressure to stabilize and crosslink the deposited layer. It has been experimentally shown that the deposition of a graphene oxide coating on the surface followed by UHMWPE plasma treatment reduces the dynamic coefficient of sliding friction by more than three times (from 0.092 to 0.027), but no significant increase in adhesion of graphene oxide layer due to plasma treatment was observed.

1. INTRODUCTION

One of the most commonly used total hip (THR) and total knee (TKR) replacements is an endoprosthesis with a metal-UHMWPE or ceramic-UHMWPE friction pair (Figure 1). UHMWPE shows good performance properties, such as biocompatibility, high hardness and durability, good chemical resistance, abrasion resistance, impact resistance, manufacturability, low friction coefficient, and polymer nonpolarity [1–5]. In addition, the endoprosthesis with UHMWPE is budget-friendly, and the ceramic-UHMWPE pair has the lowest dynamic coefficient of sliding friction (COF) [6].Since UHMWPE is subject to wear, its particles released during wear activate osteolysis and thus cause aseptic loosening of the implant, which leads to THR inefficiency and therefore the service life of joints with UHMWPE are often limited to 15–20 years [7].In recent decades, various attempts have been made to improve the wear resistance and performance of the material. In particular, the tribological properties of the polymer can be improved by crosslinking UHMWPE under gamma irradiation [8] or by reinforcing the polymer structure with various nanofillers, such as carbon nanotubes (CNT) [9, 10] or graphene oxide (GO) [11, 12] under dry friction conditions.

(a) (b) (c)

Fig. 1. Friction pairs in total hip (a) and knee (c) replacements (THR, TKR) with a liner made of UHMWPE: (b) elements of THR friction pairs, where the liner is in the middle.

However, gamma irradiation leads to partial oxidation and destruction of the polymer, and the introduction of various fillers into the UHMWPE composition, along with the improvement of surface tribological characteristics, is accompanied by a modification of its bulk mechanical properties, which does not always meet the requirements for the mechanical properties of an orthopedic material. Another way to improve the tribological properties of UHMWPE is to create a gradient polymer structure by strengthening its bearing surface without significantly changing its bulk properties. This can be achieved either by crosslinking the surface layer of UHMWPE in an inert gas plasma [13] or by depositing a coating on the surface with enhanced tribological characteristics [14, 15]. In particular, it was shown in [14] that the deposition of a graphene layer on UHMWPE leads to an improvement in its tribological characteristics.

In [16], the UHMWPE surface was treated with low-pressure plasma in an inert helium gas with different exposure times, as a result of which the surface hardness increased with the acquisition of a gradient structure, which was confirmed experimentally by its nanoindentation. As a result of modeling, the authors showed that the volumetric wear decreases up to 4 times after treatment in low-pressure helium plasma. The aim of this work is to study the possibility of improving the tribological characteristics of UHMWPE by deposition a GO layer and cross-linking of GO layer with a substrate by treatment in low-pressure helium plasma.

2. MATERIALS AND METHODS

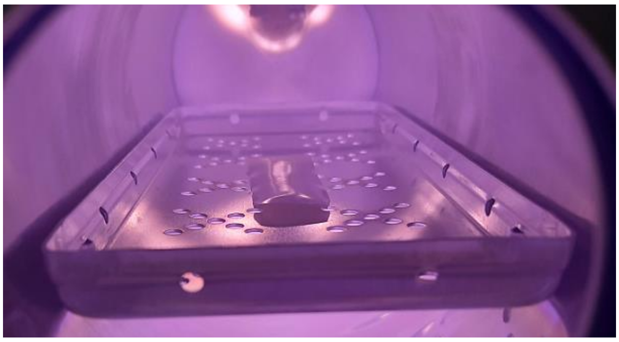
2.1 Material and depositing the GO layer

UHMWPE samples 20 mm x 60 mm in size, 1 mm thick were made from commercially available orthopedic polymers PE 1000 (Tetra, Russia) or Chirulen GUR 1020 (POLY HI SOLIDUR, Germany) by hot pressing (at 135°C). The surface of the prepared UHMWPE samples was coated with a GO layer from a water-alcohol suspension according to the developed method. To prepare the suspension, we used GO (Graphene oxide, powder, 15–20 sheets, 4–10% edge-oxidized, Sigma-Aldrich (USA)), 40 mg of which was weighed in a glass bottle on an AND HR-100AG analytical balance (Japan). Then, an appropriate volume of deionized water (Macron, ChromAR HPLC, CAS: 7732-18-5) was added to the weighing bottles with GO. The resulting mixture with a graphene oxide concentration of 4 mg/ml was sonicated in an Elmasonic S10H ultrasonic bath (Germany) with a power of 90W and a frequency of 50/60 Hz for 90 minutes to obtain a stable suspension. After preparing the suspension, it was diluted with ethyl alcohol in a water/alcohol ratio of 1/1. To apply the resulting suspension, each UHMWPE sample underwent preliminary standard preparation, which consisted in successive washing in ethyl alcohol in an Elmasonic S10H ultrasonic bath for 15 minutes, subsequent drying at room temperature, repeated washing of the sample in acetone, and another drying at room temperature. Then, studies were carried out on the following three types of fabricated samples, five of each type with five measurements of friction coefficient on each sample using a Labthink MXD-02 device (China).

1. Initial sample washed according to the standard procedure.

2. Washed sample subjected to treatment in a vacuum plasma cleaning system on an EV-PlasmaCleaner-2.0L unit (Russia) under conditions of air supply at a flow rate of 50 ml/min for 900 seconds at a discharge power of 100 W in order to increase the adhesion of the UHMWPE surface to GO (see Figure 2). The UHMWPE sample treated in air plasma was then transferred to a setup for sputtering the previously prepared GO suspension, which consisted of a thermometer, a Lumme LU-3625 heating tile (China) connected to a TRM500 temperature controller (Russia), and a fan used to cool the sample.

(a)



(b)

Fig. 2. Plasma treatment unit: (a) general view; (b) view inside the vacuum chamber during sample processing.

The UHMWPE sample was placed on a special copper substrate located on the surface of the tile, to which the thermocouple of the temperature controller and the thermometer were attached. After heating the sample for 5 minutes at a temperature of 75.0 ± 0.5°C, a suspension of GO was sprayed onto it from a distance of 10-15 cm evenly over the entire sample using a Jas 1146 airbrush (China), which is connected to a Jas 1202 compressor (China) with automatic pressure regulator. The spraying was carried out with a suspension volume of 2 ml, 4 ml, 6 ml and 8 ml, 5 samples in each case, with its layer-by-layer application with a volume of approximately equal to 0.2 ml. Between the deposition of each layer, the sample was allowed time (approximately 30-50 seconds) to dry completely (Figure 3).

As a result of such layer-by-layer deposition, a more uniform deposition of the obtained suspension on the UHMWPE sample was achieved. After spraying, the samples were dried on a tile at a temperature of 75°C for 30-50 seconds with further COF measurement.

(a)

(b)

(c)

(d)

Fig. 3. Instrument base for the graphene oxide deposition process onto a UHMWPE sample: a) thermometer (TL-32), heating tile (Lumme LU-3625) and fan (Aceline UWTF-4); b) thermostat TRM500; c) airbrush Jas 1146 and compressor Jas 1202; d) 2 ml airbrush funnel.

As a result of such layer-by-layer deposition, a more uniform deposition of the obtained suspension on the UHMWPE sample was achieved. After spraying, the samples were dried on a tile at a temperature of 75°C for 30-50 seconds with further COF measurement.

3. To stabilize and crosslink the deposited layer with the substrate, the sample was subsequently treated in helium plasma at a reduced pressure of 0.133 mbar, a gas flow of 5 cm^3/min, and a discharge power of 50 W for 360 seconds. Then, after measuring the coefficient of friction, a similar treatment with helium plasma was repeated for another 360 seconds, followed again by measurement of the coefficient of friction.

2.2 Helium plasma treatment setup

To treat the surface of the samples with low-temperature He plasma, a standard unit for plasma cleaning EV Plasma Cleaner 2.0L (Russia) was used (Figure 2) and the scheme of the experimental setup for the low-pressure plasma processing system is shown in Figure 4. A discharge was ignited in a helium gas flow from a high-voltage generator with a frequency of 40 kHz at a power of 50 W, at a pressure of 0.133 mbar, and a gas flow of 5 cm^3/min. The UHMWPE sample was treated, respectively, for 360 seconds and then again for another 360 seconds.

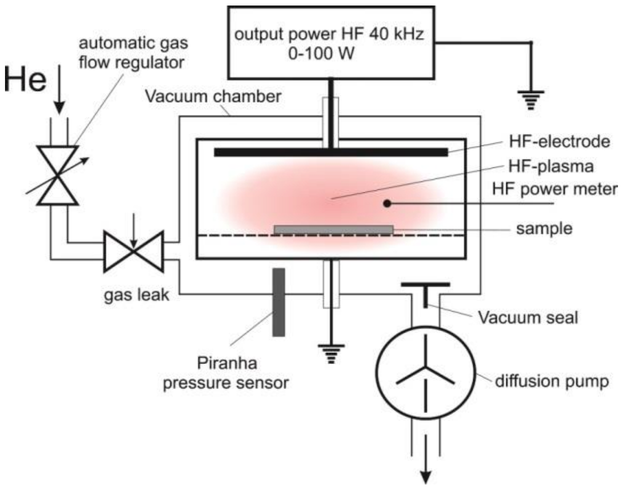


Fig. 4. Scheme of the experimental setup for the low-pressure plasma processing system [16].

2.3 FTIR Spectroscopy

Fourier transform IR spectroscopy was used to study UHMWPE surface chemical composition (see Figure 5) of the initial sample (curve 1), UHMWPE sample treated with air plasma (curve 2) and UHMWPE sample after a GO layer deposition with further treatment with helium gas plasma at low pressure (curve 3). The IR spectra were recorded using a Perkin Elmer 1720X Fourier IR spectrometer with an Attenuated Total Reflectance (ATR) attachment on a ZnSe 45° crystal (USA) and a FT-801 Fourier IR spectrometer (Russia) with ZnSe ATR attachment.

3. RESULTS AND DISCUSSION

3.1. Quantitative performances of the deposited GO layer

To take into account the effect of the deposited GO layer on the dimensional performances of the orthopaedic UHMWPE material design, for example, a liner in a THR, we measured and calculated the weight and size characteristics of the GO layer, such as mass, thickness of its layer, and volume. Depending on the volume of the used GO suspension (2, 4, 6 and 8 ml), the average values of the indicated characteristics of its layer were measured (mass) and calculated (thickness and volume), which are given in Table 1. From the analysis of the Table 1 results, we can conclude that the effect of deposition of a GO layer on the structural dimensions, for example, of an UHMWPE liner in a THR, can be neglected, since the radial clearance in its head-on--liner conjunction, as a rule, lies within 150 μm [17}.

Table 1. Weight and size of the GO layer.

Suspension volume, ml	2	4	6	8
Mass, mg	0.965	1.78	2.35	7.05
Thickness, μm	0.447	0.824	1.088	3.264
Volume, mm^3	0.536	0.989	1.306	3.916

3.2. FTIR Spectroscopy of UHMWPE

Figure 5 shows the IR spectra of the UHMWPE surface for the initial samples (curve 1), samples processed in air plasma (curve 2), and samples with further deposition of a GO layer on them and subsequent treatment with helium gas plasma at low pressure for 360 seconds (curve 3). In spectrum 1, the absorption bands with maxima at 2915 and 2847 cm^{-1} correspond to the stretching vibrations of the C–H bond, and the bands at 1472 and 1462 cm^{-1} correspond to the bending vibrations of the C–H bond. After treatment in air plasma (curve 2), new absorption bands appear with maxima at 1713 and 965 cm^{-1}, corresponding to the formation of polar oxygen-containing C=O groups and double trans-vinylene bonds -C=C-, respectively.

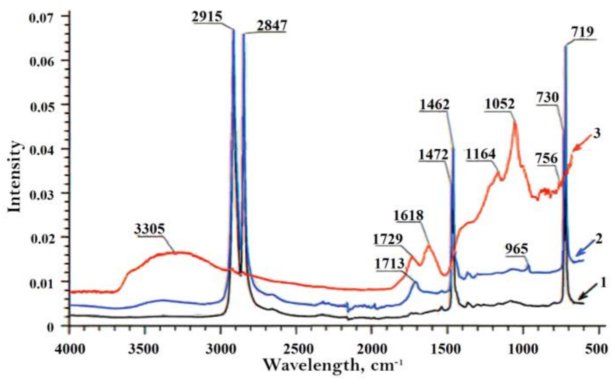


Fig. 5. ATR IR spectra of the original UHMWPE (1); UHMWPE processed in air plasma (2); UHMWPE coated with a GO layer and treated in helium plasma at low pressure for 360 seconds (discharge power 50 W, helium flow 5 cm^3/min) (3).

In the spectrum of surface layer 3, the absorption band with a maximum at about 3000 cm^{-1} corresponds to the stretching vibrations of the O–H group bounded to the carbon atom in GO in different places. The absorption band at 1730 cm^{-1} can obviously be attributed to stretching vibrations of C=O in carbonyl groups and/or ketones, and the absorption band at 1620 cm^{-1} can be attributed to bending vibrations of adsorbed molecules. According to the literature data [18, 19], the absorption band at 1164 cm^{-1} can be associated with vibrations of the C–O–C epoxy group, and the absorption band at 1052 cm^{-1}, with phenylhydroxyl groups.

3.3. Dynamic coefficient of sliding friction

The UHMWPE samples dynamic coefficient of sliding friction was experimentally measured under dry friction conditions with reciprocating movements at the Labthink MXD-02 Coefficient of friction tester with a pressing force of 1.96 N (Figure 6).

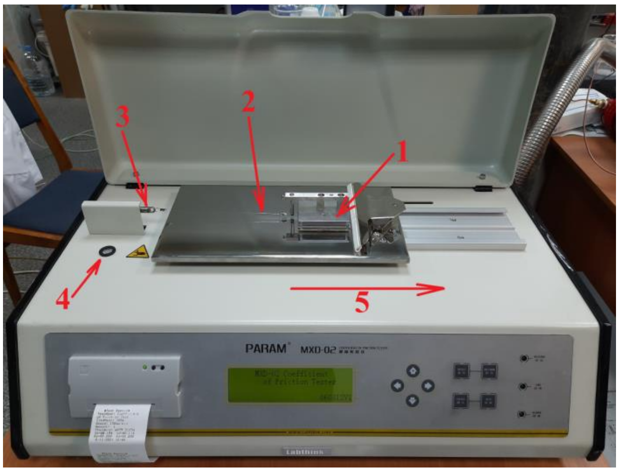


Fig. 6. Device for the coefficient of friction measurements: 1) a special load weighing 200 g with a sample fixed to it; 2) a special transparent polymer thread; 3) detector; 4) built-in level indicator; 5) the direction of metal platform movement under the fixed sample.

The measurements were carried out on the three types of fabricated samples listed above, five of each type with five measurements of friction coefficient on each sample, averaging over five measurement points. The results of measuring the coefficient of friction of the samples processed in air plasma with deposited suspension of GO and further processing in helium plasma for 360 seconds and followed by another treatment in helium plasma for 360 seconds are shown in Figure 7.

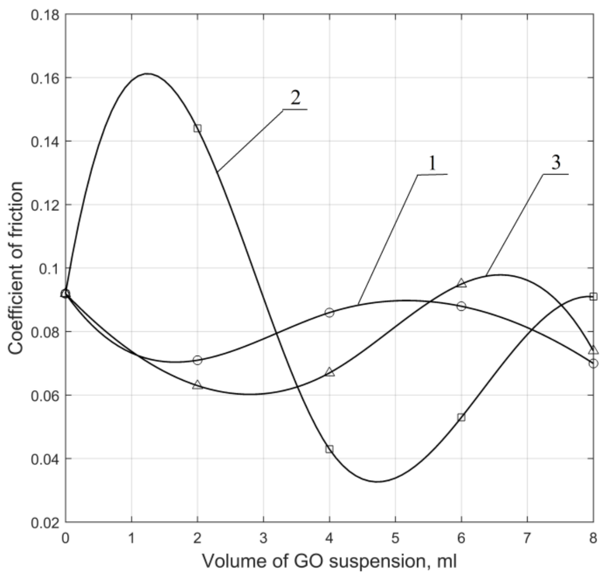


Fig. 7. The results of measuring the coefficient of friction of the samples: processed in air plasma with deposited suspension of GO (1); with further processing in helium plasma for 360 seconds (2); followed by another treatment in helium plasma for 360 seconds (3)

As follows from these data, the greatest decrease in the friction coefficient to a value of approximately 0.027 is observed in samples with an deposited volume of GO of slightly more than 4 ml and treated in helium plasma at low pressure for 360 seconds, which, compared with the initial untreated samples with a friction coefficient value of 0.092, shows its more than three times decrease. Unfortunately, the processing of the deposited layer in helium plasma at low pressure did not lead to a significant increase in the layer adhesion to the UHMWPE substrate, which manifested itself in partial peeling of the deposited layer under load during the COF measurement before and after plasma treatment.

It was shown in [16] that with an increase in the time of plasma treatment, the surface roughness enhances, which correlates well with an increase in the friction coefficient. This is an indirect confirmation that enhance in the duration of treatment, in addition to an increase in the concentration of cross-links, contributes to enhance in surface roughness due to the possible heating of the treated surface. Therefore, in the indicated study, the optimal duration of treatment was determined, which made it possible to maximize the surface hardness of UHMWPE.

In our case, the surface roughness increases due to treatment in air plasma for 900 seconds (Figure 7, curve 2). A small amount of GO (about 1 ml) was then applied to the treated surface. Upon further treatment with helium plasma, an even greater increase in roughness occurred, which led to an increase in the friction coefficient to a value of 0.16. A further increase in the thickness of the applied GO layer with a suspension volume of more than 4 ml, using a similar processing technology, showed a significant decrease in COF due to smoothing the surface roughness with the GO layer. An increase in the volume of the applied GO suspension and subsequent treatment in helium plasma, however, did not lead to sufficient crosslinking the surface layer of the sample. Curve 1 was obtained in the absence of subsequent surface treatment with helium plasma, and COF in this case varies in a small range, differing little from the COF of the initial samples with a value of 0.092, shown at zero abscissa of the GO suspension volume. In curve 3, double treatment with helium plasma also leads to a slight change in COF. This is probably due to a slight increase in the surface roughness of UHMWPE due to the long duration of plasma treatment.

4. CONCLUSION

As a result of experimental studies on a qualitative study of the UHMWPE surface tribology in the form of measuring the coefficient of sliding friction, a correlation between the coefficient of sliding friction and the volume of graphene oxide suspension applied to the UHMWPE surface and with the technology of plasma surface treatment was found.

The results obtained showed that the deposition of a graphene oxide coating onto the surface of UHMWPE treated in air plasma, followed by treatment with helium plasma at low pressure for 360 seconds, reduces the dynamic coefficient of sliding friction by more than three times (from 0.092 to 0.027). At the same time, no significant increase in coating adhesion due to plasma treatment was observed. Further studies can be aimed at increasing coating adhesion by chemical functionalization of graphene, for example, with amines [20–22] in combination with plasma treatment of the UHMWPE surface.

In addition, earlier the authors of this study carried out a numerical simulation of the surface wear of UHMWPE films treated with low-pressure plasma in an inert helium gas with different exposure times, as a result of which the surface hardness increased with the acquisition of a gradient structure, which was confirmed experimentally by nanoindentation [16]. As a result, it was shown by simulating that the volumetric wear of the surface is reduced by up to 4 times. Currently, samples of UHMWPE liners for total hip replacement processed according to this method are being prepared with further tests on a wear simulator for total hip replacement, developed by the authors and manufactured at Sevastopol State University, for comparison with the results of numerical simulation. The general view of the simulator is shown in Figure 8.

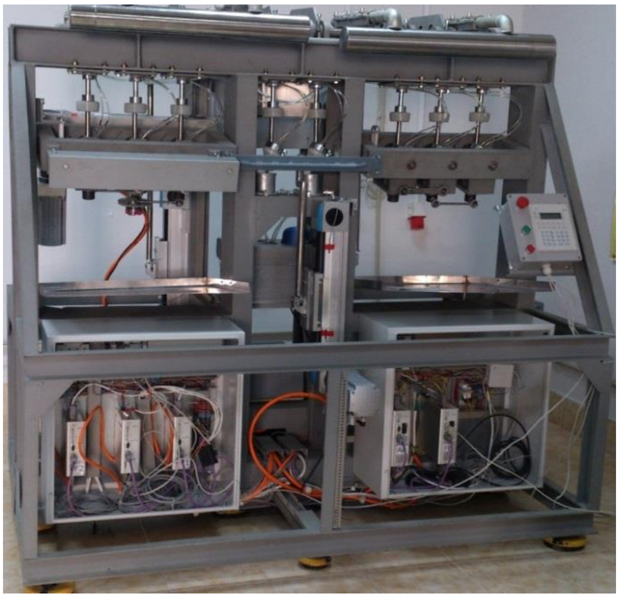


Fig. 8. The wear test simulator general view.

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