Anomalous Wear Behavior of UHMWPE During Sliding Against CoCrMo Under Varying Cross-Shear and Contact Pressure

Michael J. Dreyer1,2 · William R. Taylor2 · Kilian Wasmer3 · Thomas Imwinkelried4 · Roman Heuberger4 · Bernhard Weisse1 · Rowena Crockett1

Received: 26 July 2022 / Accepted: 28 September 2022 / Published online: 21 October 2022 © The Author(s) 2022

Abstract
Wear of ultra-high-molecular weight polyethylene (UHMWPE) in joint implant applications has been shown to increase with cross-shear (CS, i.e., multidirectional sliding) but decrease with higher contact pressure (CP). Moreover, structural changes, resulting in protrusions, are known to occur to the surface of the pin following multidirectional sliding. However, these phenomena are not yet fully understood. In this study, we simultaneously varied CP and CS to derive an empirical formula for the wear factor as a function of these parameters. The wear factor increased when going from unidirectional sliding to multidirectional sliding but decreased with increasing CP, as has been previously observed. Following these tests, the protrusions on the pin surface were chemically and mechanically characterized to gain insights into both their origin and influence on wear behavior. Micro-FT-IR confirmed that the structures consist of polyethylene, rather than adsorbed, denatured proteins. It also allowed the crystallinity of both the protrusions and unaffected UHMWPE to be estimated, showing a strong positive correlation with the hardness of these different areas on the surface. Time-of-flight secondary-ion mass spectrometry was used to probe the chemistry of the surface and near-surface region and indicated the presence of contamination from the test fluid within the structure. This suggests that the protrusions are formed by the folding of UHMWPE following plastic deformation. It is also suggested that the higher hardness of the protrusions affords some protection of the surface, leading to the observed anomalous behavior, whereby wear increases with decreasing CP.

Rowena Crockett
rowena.crockett@empa.ch

1 Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland
2 Institute for Biomechanics, ETH Zurich, Leopold-Ruzicka-Weg 4, 8093 Zurich, Switzerland
3 Empa, Swiss Federal Laboratories for Materials Science and Technology, 3602 Thun, Switzerland
4 RMS Foundation, Bischmattstrasse 12, 2544 Bettlach, Switzerland
1 Introduction

Wear of ultra-high molecular weight polyethylene (UHMWPE) joint replacement is a common cause of implant failure [1] as the debris can cause adverse effects such as osteolysis and implant loosening [2]. Therefore, the wear behavior of UHMWPE continues to be of interest as new processing procedures and additives are examined in an effort to further develop the material and improve clinical outcomes.

UHMWPE wear is a highly complex phenomenon with unidirectional sliding leading to far lower wear rates than those observed for multidirectional sliding tests [3–6]. It has been proposed that unidirectional sliding causes strain hardening by orientating the polymer chains at the surface [4]. In multidirectional pin-on-disk (POD) testing, the path of motion can be represented by a rectangle. The cross-shear ratio (CS) can be defined as the ratio $A/(A+B)$, where $A$ is the smaller and $B$ the larger side of the rectangle ($0 \leq \text{CS} \leq 0.5$) [7].

Early theoretical models predicted wear to continuously increase up to a maximum at a CS of 0.5. Only few studies have experimentally examined the effect of varying CS on wear across the whole range of CS. Turell et al. found that when untreated UHMWPE was subjected to sliding, the wear increased at lower CS up to around 0.3, but then decreased slightly at higher values [7]. Similar behavior was later reported by Korduba and Wang [8], and incorporated into an updated theoretical model [9]. Following comparisons of experimental measurements of wear with theoretical studies, it has been concluded that orientation can occur in both directions of the multidirectional sliding and that asymmetry of the motion path, i.e., an intermediate amount of CS is needed to introduce orientation softening [10, 11]. Crosslinked UHMWPE, on the other hand, showed an overall lower wear rate and no clear wear peak at intermediate values of CS [6, 8]. This supports the proposal that wear is strongly influenced by orientation of the polymer chains, which is constrained by crosslinking [8, 12].

There have also been investigations into the role that contact area and pressure play with regard to UHMWPE wear. The classical Archard’s law calculates the wear volume $V$ by the formula $V = k \cdot F \cdot S$, where $k$ is an experimentally determined wear factor, $F$ is the normal force, and $S$ is the total sliding distance. For UHMWPE, however, $k$ is not a constant but rather a function of contact pressure (CP) and CS, as outlined above.

It has commonly been observed in POD studies of UHMWPE sliding against cobalt–chromium–molybdenum
(CoCrMo) that with increasing CP the wear factor $k$, and thus, the wear rate, follows a downward parabolic trend [13–17]. This has been observed in studies on the influence of changing contact area under constant load and changing load under constant contact area [15, 18]. Some POD studies have also found the wear factor $k$ to increase up to a critical CP between 2 and 3 MPa and only then decrease with increasing CP [18, 19]. Above this threshold, protrusions on the surface have been reported [15]. Similar protrusions have been observed following hip-simulator tests on artificial joints [20]. In this study, we investigated the combined influence of CP and CS on the wear behavior of a gamma-sterilized UHMWPE in POD tests to obtain data for future numerical modeling studies of implanted joint prostheses. The surfaces of the pins used in these experiments were examined to determine a range of chemical and mechanical properties. This allowed a clearer insight into the changes that occur at the surface during multidirectional sliding to be achieved. In particular, the previously observed protrusions were examined with the aim of better understanding the influence of CS and CP on their formation [15].

### 2 Materials and Methods

#### 2.1 Wear Tests

Gravimetric wear tests on UHMWPE pins were performed on an OrthoPOD (AMTI, Watertown, MA, USA, OrthoPOD), a six-station multidirectional POD tester. To increase the number of combinations of CP and CS, two sets of three pins each were tested simultaneously, where each set of pins had a different tip diameter. While the applied normal force and CS was the same for all six stations, this enabled two different CPs to be imposed simultaneously. In total, eight tests were performed for a total of 16 CS–CP combinations (Table 1). The rectangular motion path, with length $A$ and $B$, was varied to give

$$\text{CS} = \frac{A}{A + B} \quad (1)$$

between 0.00 and 0.26, the physiologically relevant range for the knee [14]. Constant loads of 110–250 N were applied to pins with diameters of 3.1–13.8 mm. This resulted in nominal CPs between 1.5 and 30 MPa shown in Table 1, again representing the relevant range in the knee [13, 14, 21]. Each test was run for four intervals of one week at 1 Hz, up to 2,280,000 total cycles, including a running-in period of 1 week.

The UHMWPE pins were manufactured from stock Sulene-PE and gamma-sterilized with an irradiation dose of 25–40 kGy under nitrogen atmosphere (Zimmer Biomet, Winterthur, Switzerland). The base of the pin, used to hold it in the POD rig, had a diameter of 9.5 mm and the tip, which was in contact with the counter-surface, had varying diameters (Table 1). The surface roughness (Ra) was 46 ± 16 µm.

The CoCrMo disks were polished to a mirror finish with a roughness below Ra < 5 nm. The test lubricant was bovine calf serum BCS (Hyclone™ Calf Serum Lot#AF29165348, GE Healthcare Lifesciences, USA) diluted to a protein concentration of 20 g/L, the concentration commonly assumed for the knee according to ISO 14243-1 [22]. Then, 7.44 g/L ethylenediaminetetraacetic acid disodium salt dihydrate (Sigma Aldrich, USA) and 2.4 g/L sodium azide (Sigma Aldrich, USA) were added as per ASTM F732-17 to minimize bacterial growth and precipitation of calcium phosphate onto the bearing surfaces [23]. Finally, the lubricant was passed through a 0.7 µm filter.

The pins were pre-soaked in BCS for at least one week before each test. During the test, the pins were submerged in approximately 20 mL of BCS at 37 °C, which was replaced weekly. Gravimetric wear was measured according to ASTM F732-17. For each test condition, one control pin was soaked in lubricant to allow a weight correction for liquid absorption.

#### 2.2 Wear Model Fitting

As the pin’s tip experiences creep deformation and widens under the static load, the tip diameter at the end of each test was measured using calipers (Futuro, BRW, Switzerland). The actual applied force $F_{\text{actual}}$ at each station was measured using a 250 N load cell (Mecmesin AFTI, UK). These measured values were used to calculate the actual contact pressure $CP_{\text{actual}}$. The value of the rectangular sliding path length $l_{\text{actual}}$ and of $CS_{\text{actual}}$ was measured for each test from a drawing of the pin’s motion made with a pencil.

For each pin, the wear factor $k$ ($\text{mm}^3 \text{ N}^{-1} \text{ m}^{-1}$) was calculated as follows:

$$k = \frac{\dot{W}}{CP_{\text{actual}} \cdot CS_{\text{actual}} \cdot F_{\text{avg}} \cdot \rho} \quad (2)$$

where \(\dot{W}\) is the gravimetric wear rate calculated as the slope of the linear regression of wear over number of cycles from 570,000 to 2,280,000 cycles, \(\rho\) is the assumed material density of 935 kg/m$^3$ [15], and $F_{\text{avg}}$ is the average value of the applied force $F_{\text{actual}}$ throughout the test.

$CP_{\text{actual}}$, $CS_{\text{actual}}$, and $k$ were used as input to a nonlinear least-squares optimization to find an expression for $f(CS, CP)$ performed in MATLAB (Mathworks, Inc., USA). Analogous to previously published models, we assumed that the function for the wear factor was of the form $k(CS, CP) = f(CS) \cdot g(CP)$ [14, 17, 18]. Contrary to those
studies, we enforced that \( f(CS) > 0 \) for \( CS = 0 \) because wear does still occur during unidirectional sliding.

### 2.3 Topography

3D profiles of the surfaces were measured with a Dektak Stylus Profilometer with a stylus of 2 \( \mu \)m diameter (Bruker, Germany). 2D profiles were taken from the 3D images. A piece of rubber was placed around the contact area to allow the whole pin to be measured with the contact profilometer. This has been removed from the images shown to improve clarity.

### 2.4 Infrared Spectroscopy

All infrared spectra were measured using a Hyperion 1000 FT-IR Spectrometer (Bruker, Germany). Micro-FT-IR was measured with a germanium crystal with a tip diameter of 100 \( \mu \)m, which was applied to the relevant features of the surface with a load of 0.8 N. ATR-IR spectra were measured on the same instrument on a germanium crystal. The software IGOR from Wavemetrics (OR, USA) was used to fit the peaks around 1460 cm\(^{-1}\) to obtain the crystallinity [24].

### 2.5 Mechanical Properties

The mechanical properties of the pins were determined using a ZHN Nanoindenter (Zwick Roell, Germany) with a Berkovitch indenter. The QCSM module (quasi-continuous stiffness mode) was used to determine the indentation hardness at varying depths using a maximum of 50 mN load [25].

### 2.6 Time-of-Flight-Secondary Ion Mass Spectrometry (ToF-SIMS)

The surfaces of the pins were examined with a ToF-SIMS 5 (Iontof, Germany). The ions in the analysis beam were Bi\( _3^+ \) with an energy of 25 keV and a cycle time of 100 \( \mu \)s. Depth profiling was carried out with a cesium sputter gun with an energy of 1 keV. An area of 500 \( \times \)500 \( \mu \)m was sputtered and an area of 50 \( \times \)50 \( \mu \)m was imaged.

### 3 Results

#### 3.1 Wear Tests

The wear tests (Table 1) were interrupted after intervals of 570,000 cycles to assess the wear behavior over time. Within a standard error of \(< 1 \times 10^{-7} \text{ mm}^3/\text{Nm}\), the wear factor remained constant during the test.

As evident from Fig. 1a, the dependency of \( k \) on \( CP \) followed a negative power-law decay (\( CP^{-\frac{a}{ \alpha}} > 0 \)). The wear factor \( k \) was lowest for unidirectional sliding (\( CS = 0 \)) and increased when going to multidirectional sliding. Comparing tests 1 and 2, where \( CS_{\text{actual}} = 0.22 \) and 0, respectively, the wear factor was more than ten times higher for the high
CS at 0.22 for both the large and small pin compared to unidirectional sliding (see data points in Fig. 1b). Within the range of non-zero CS values investigated here, there was no simple correlation with the wear factor (Fig. 1b).

3.2 Wear Model Fitting

Wear factors were small at CS = 0 and then quickly increased (Fig. 1b), but did not show an obvious trend. Therefore, a curve \( f(CS) \) with a positive intercept at CS = 0 was chosen that rises to a horizontal asymptote so that there is no extrapolation to unrealistic values for values of CS larger than the upper limit investigated here [14]:

\[
f(CS) = a_1 + a_2 \cdot (1 - \exp(-a_3 \cdot CS)).
\]  

(3)

Following the observed trend in Fig. 1a, \( g(CP) = CP^{-a_4} \) was chosen to model the contact-pressure dependence [14, 18]. All factors \( a_i > 0 \). The curve-fitting procedure yielded the following formula, which may be used as input to numerical models (Fig. 1c):

\[
k(CS, CP) = 10^{-6} \cdot (0.0202 + 0.888 \cdot (1 - \exp(-50.9 \cdot CS))) \cdot CP^{-0.640}.
\]  

(4)

The \( R^2 \) value was 0.56.

3.3 3D Profiles

The surfaces of the pins were assessed with a profilometer after the end of the POD wear tests. Figure 2 shows the 3D profile of a pin after unidirectional sliding, along with a
profile across the diameter of the pin at a right angle to the direction of sliding.

In all cases where multidirectional sliding was implemented, protrusions were observed on the surfaces. The smaller pins showed generally larger protrusions distributed over the whole surface (Fig. 3). Protrusions were not observed on pins following unidirectional sliding (Fig. 2).

The topographies of the three pins within each set of measurements, that is the same CP and CS ratio, were similar (not shown). However, pins of the same size sliding under different conditions showed differing coverage of protrusions but with similar heights (Fig. 4).

The 3D profiles of the larger pins showed that the protrusions were generally found towards the center. At the outer edge of the larger pins, a border is visible with a low roughness (Fig. 5).

### 3.4 Mechanical Properties and Crystallinity

For the determination of micro-hardness, each measurement point was repeated at least seven times on different areas of the samples. As some of the protrusions covered small areas, many of the repetitions were carried out on different protrusions on the same pin. This might explain the larger deviation seen for the protrusions on the pins (Fig. 6) than for unused pins or areas without protrusions. The QCSM module was used to measure load–displacement curves to allow the calculation of hardness at varying indentation depths (Fig. 6) [26, 27].

An FT-IR microscope was used to determine the chemistry on two of the protrusions on pin no. 22 with 5.1 mm diameter and pin no. 7 with 13.8 mm diameter, and on a relatively flat area of the pin no. 7. The low load of 0.8 N was applied to the relatively large FT-IR probe with a diameter of 100 µm to ensure that the measurements were carried out at the surface rather than probing the bulk. The indentation left by the micro-FT-IR tip is shown in Fig. 7 and has a depth of approximately 0.5 µm. The penetration depth of the infrared light for UHMWPE is 0.1 µm at a wavelength of 1500 cm⁻¹ and 1.8 µm at 750 cm⁻¹ [28]. All three spectra were dominated by peaks assigned to polyethylene, as opposed to for example proteins from the fluid used in the wear measurements. A contamination of the surface is evident in the spectra in the region 1500 to 1800 cm⁻¹ and is compared to the
residue of the testing fluid following drying under vacuum in Fig. 8a. The surfaces were cleaned carefully according to ASTM F732-17 after use [23].

The three FT-IR spectra are not identical, as can be seen from a comparison of the peaks assigned to CH$_2$ scissoring at around 1460 cm$^{-1}$ and CH$_2$ rocking at around 712 cm$^{-1}$ (Fig. 8).

These peaks were fitted using the peak-fitting function in IGOR (Wavemetrics). A fit of the absorbance at around 712 cm$^{-1}$ could not be achieved satisfactorily with only the 3 peaks that have been assigned to crystalline and amorphous polyethylene [24, 30–34]. Therefore, the peaks at around 1460 cm$^{-1}$ were used. The equation given in [24] was used together with the value of 1.2 for the intrinsic relationship between the intensities of the peaks assigned to crystalline and amorphous polyethylene (Eq. 5).

$$X_c = I(1464 + 1472)/(1.2 \times 1450),$$

where $X_c$ is the crystallinity and $I$ is the intensity of the peaks at 1472, 1464, and 1450 cm$^{-1}$.

Three of the fits are shown in Fig. 9.

The calculated crystallinities were 0.49 ± 0.003 for the area without protrusions (Fig. 9a), and 0.59 ± 0.005 (no. 22) and 0.59 ± 0.01 (no. 7) for protrusions both of the pins (Fig. 9b, c). The difference between the fits and the fitted peaks (residuals) are shown in Fig. 9.

### 3.5 Time-of Flight Secondary Ion Mass Spectrometry

The chemistry of the protrusions on the surface of pin 7 was also probed using ToF-SIMS with depth profiling (Fig. 10). An area of 500×500 μm was sputtered with Cs$^+$ ions while an area of 50×50 μm was measured using Bi$_3^+$ ions. The sputtered area is shown in Fig. 10a. The surface within the 500×500 μm is sputtered at the same rate regardless of height, thus the shape of the protrusion is still visible in the crater at the end of the measurement. Sufficient depth was measured to ensure that the chemistry through the whole height of the protrusion could be probed.
Fig. 8 a ATR-IR spectra of a sample of the dried test fluid, and unused UHMWPE in the region 1500 to 1800 cm$^{-1}$ in comparison to the micro-IR spectrum measured on a protrusion on UHMWPE following sliding: dashed lines an area on the used pin 7 (13.8 mm diameter) with no protrusions; dotted lines a protrusion on a pin with diameter 5.3 mm (pin 22); continuous lines a protrusion on a pin with a diameter of 13.8 mm (pin 7). The spectrum of dried test fluid has been scaled down on the y-axis to allow a comparison with the UHMWPE surface. Infrared spectra of the surfaces of UHMWPE following sliding, peaks assigned to b CH$_2$ scissoring and c CH$_2$ rocking for the three samples described in detail for each sample in Fig. 9. A detailed description of the crystal splitting of peaks in the IR of polyethylene can be found in [29].

Fig. 9 FT-IR spectra (solid line) and fits (dotted line) using three peaks assigned to crystalline and amorphous polyethylene as well as the residual error in the fitting parameters: a an area on the used pin 7 (13.8 mm diameter) with no protrusions, b a protrusion on a pin with diameter 5.3 mm (pin 22), and c a protrusion on a pin with a diameter of 13.8 mm (pin 7). The peaks at 1472 and 1463 cm$^{-1}$ (both CH$_2$ scissoring) were assigned to the crystalline phase and the peak at 1450 cm$^{-1}$ was assigned to the amorphous phase (13).
The peaks dominating the spectrum were characteristic of polyethylene and could be assigned to C\textsubscript{x} followed by C\textsubscript{x}H\textsubscript{y}, for example, C\textsubscript{3}, C\textsubscript{3}H, C\textsubscript{3}H\textsubscript{2}, C\textsubscript{3}H\textsubscript{3}, etc. There were, however, weaker peaks on the surface that could be assigned to contamination from the test fluid, including those assigned to CN\textsuperscript{−}, S\textsuperscript{−}, and CHO\textsubscript{2}\textsuperscript{−}. These peaks were monitored during depth profiling and the resulting 3D images are shown in Fig. 11. The measurement of larger fragments is hampered by the Cs\textsuperscript{+} sputtering, which adds to the energy available and encourages fragmentation.

It can be seen from the images (Fig. 11) that the contamination from the test fluid was relatively low on the surface, consistent with the micro-FT-IR, but increased in concentration at some stage during sputtering, indicating a layer of contamination trapped within the protrusion. Above and below this layer, the spectra are dominated by polyethylene.

4 Discussion

Wear factors of or below 1.1 \times 10^{-6} \text{ mm}^3/\text{Nm} were measured in this study. For the same material pairing, Saikko et al. reported larger values of approximately 2 to 4 \times 10^{-6} \text{ mm}^3/\text{Nm} for multidirectional sliding at low pressures [15, 18, 35]. However, the results here still fall in the expected range for conventional irradiated UHMWPE reported by Baykal et al. [21].

The largest change in wear factor was observed on going from unidirectional to multidirectional sliding even at small values of CS, consistent with the previous studies [6, 14, 36]. The profiles of the pins used in unidirectional measurements showed only mild abrasive wear. A local maximum in wear at CS between 0.2 and 0.3 was not detected as the highest CS used was within this range [7, 8]. Moreover, the dependence of wear on CS in the multidirectional range was not trivial, and resulted in a low $R^2$ value of 0.56. However, the chosen shape of $f(\text{CS})$ was similar to functions reported in studies investigating similar ranges of CS [14, 17, 36].

The wear factor decreased with increasing CP, following a negative power law. Similar results were previously reported in other studies [15, 18, 33]. A change from increasing to decreasing wear factor at some critical CP in the range of 1–5 MPa was not observed. This may be because too few different values of CP were investigated in that range and the resolution was, therefore, not high enough.

Overall, both high pressure and low CS rate contributed to achieving lower wear factors. At high pressures, CS had little influence on the wear factor, while there was a trend to higher wear factors with increasing CS at low applied pressure, as observed in other studies [37, 38]. In line with these observations, the fitted function $k(\text{CS}, \text{CP})$ had smaller values than other published functions [14, 17, 18] for small CPs, but it exceeded them for values of CP larger than 3 to 10 MPa depending on the function.

Protrusions formed on the surfaces of all pins subjected to CS. Similar protrusions were not only observed in pin-on-disk wear tests [18, 39–41], but also in hip joint implant wear tests [20, 42]. While the protrusions, detected on all of the pins subjected to CS, were qualitatively similar on visual inspection, the profiles showed that their distribution was very different on the large and small pins (Fig. 12). Specifically, the protrusions were higher on the smaller pins.
These two regions, protrusions and background, were found to have differing mechanical properties and crystallinities. At lower indentation depths, differences were evident in what is known as the indentation size effect (ISE) region, believed to be caused by dislocation effects \[43\]. Following this region, at indentation depths of 4–6 µm, the correlation between the hardness and the crystallinity, as measured by FT-IR, is similar to that observed by Slouf et al. \[30\]. Higher values of 0.59 for crystallinity and a hardness of 0.065 GPa were measured for the protrusions compared to a crystallinity of 0.49 and hardness of 0.037 GPa for the background, undeformed polyethylene. The hardness of the unused UHMWPE was consistently higher than that of the undeformed areas on a used pin. This is in contradiction to previous studies that have shown an increase in hardness and crystallinity following sliding of UHMWPE against CoCrMo in Ringer’s solution \[44\]. It should, however, be noted that the errors for both sets of measurements are larger than the differences. Higher crystallinity was also found at the hills of striations compared to valleys on retrieved tibial inserts using Raman spectroscopy \[45\].

The difference in hardness between protrusions and undeformed areas is in seeming contradiction to the results of Heuberger et al. who found no significant difference between the two areas \[46\]. However, in that study a nano-indenter was used to a penetration depth of 2 µm, a depth strongly influenced by ISE when using micro-indentation (Fig. 6). FT-IR was used to probe the chemistry of the UHMWPE surface and showed larger amounts of protein \[46\] than observed in this study. The micro-IR spectroscopy used here had a penetration depth of only about 0.1–1.8 µm at wavelengths of interest. This was too little to detect the layer of contamination trapped as the polyethylene is deformed on the surface, as detected with ToF-SIMS (Fig. 11). The infrared spectrum of the test fluid contains a strong peak at 1640 cm\(^{-1}\) that can be assigned to the amide I band of protein, the most abundant component of the fluid (Fig. 8a). The adsorbed contamination on the pin, measured with micro-IR, also contains a peak at approximately 1730 cm\(^{-1}\). This can be assigned to fully protonated EDTA \[47\]. The influence this may have on the wear rate and the formation of protrusions is unknown.

It can be postulated that the higher hardness of these protrusions results in a protection of the surface against wear, which will be more efficient on the smaller pins, where the protrusions show a higher coverage. As there was a lower coverage of protrusions on the larger pins, it can be postulated that the distribution of load on these leads to higher real CPs on the larger pins, which may in turn be responsible for higher wear factors.

A ploughing mechanism was proposed by Wang et al. to explain the shape of UHMWPE wear particles \[4\]. This involved a lip being formed by plastic deformation at the surface of the polymer. The formation of protrusions by plastic deformation has also been proposed by Saikko \[48\]. In plastic deformation it can be envisaged that the continuous change in direction leads to repeated folding of this “lip” to form the protrusions seen on the pins (Fig. 13). This proposal is supported by the evidence of sub-surface contamination within the protrusion seen in ToF-SIMS depth profiles (Fig. 11). Moreover, Heuberger et al. showed that the protrusions were strongly connected to the pins, rather than being loosely attached wear particles \[46\]. This was shown with scratch testing which, in some cases, led to the protrusions being torn out of the surface \[46\].

The surfaces of the UHMWPE components of explanted knee implants show extensive abrasive wear and pitting, the latter seldomly being seen in laboratory testing \[49\]. F. Ansari et al. have reviewed the influence of microstructure on wear and fatigue \[50\]. While a higher crystallinity has been shown to reduce fatigue crack propagation, it also increases delamination and pitting. Fatigue phenomena have not been observed in multi-direction POD testing, but it can be speculated that a higher crystallinity in the protrusions may encourage damage related to the brittleness at the surface.

Wear is strongly influenced by the combination of crystallinity and crosslinking, with increased crystallinity leading

---

**Fig. 12** 2D profiles taken from the 3D images of a pin 46 (13.8 mm) and b pin 26 (3.1 mm) on the same x and z scale. The 2D profiles of a range of pins is given in Supplementary Material.
to lower wear rates when the crosslinking is high [51]. In this study, changes to crosslinking were not examined.

Delamination has been observed in microscopy images of retrieved UHMWPE components [52]. Similar observed structures on retrieved implants are “striations” commonly detected on retrieved polyethylene bearings [53]. However, such striations appear as parallel hills and valleys of fibers oriented along the sliding direction [54] compared to the more scattered protrusions resulting in a pimplered surface observed here. There are also reports of structures described as “folding” [55]. It is possible that folding, striations, and the protrusions are the result of a similar mechanism of repeated plastic deformation. However, the flat-on-flat contact in the POD wear tests is very different from the contact in vivo conditions and will be strongly influenced by a small misalignment. It can therefore not be concluded that the formation of such protrusions occurs and influences wear and surface damage in artificial joints. In order to determine the significance of these protrusions in vivo and whether changes to the hardness or crystallinity accompany their formation, it would be necessary to section explanted material for further analysis such as micro or nano-testing of mechanical and chemical properties.

5 Conclusions

As in previously reported studies of UHMWPE, the wear factors reported here increased with increasing CS and decreasing CP. During multidirectional POD wear testing, protrusions were formed on the articulating polyethylene surfaces. The size of these protrusions and their coverage of the surface varied, with smaller pins subjected to higher CP showing a higher coverage of larger protrusions. As the crystallinity and hardness of these structures were higher than those of the background areas without protrusions, it is suggested that they protect the surface from wear, contributing to lower wear rates for smaller pins. The composition of the protrusions was shown by ToF-SIMS to be UHMWPE, except for a narrow, enclosed band within the structure that could be assigned to surface contamination through the lubricating fluid. It can be speculated that this layer marks the contact between the deformed protrusion and the original surface of the material.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11249-022-01660-w.

Acknowledgements The authors would like to thank Krzysztof Wieczerek, (Empa, Thun) and the Swiss Federal Laboratories for Materials Science and Technology for funding this project. Additionally, we would like to express our gratitude to Zimmer Biomet for providing the UHMWPE pins.

Author Contributions MD carried out the pin-on-disk experiments and worked on the manuscript. RC carried out the surface analysis and worked on the manuscript. BW was involved in experimental design, supervision of modeling, and worked on the manuscript. RH and TI assisted in the design and setup of the pin-on-disk measurements and provided support in the interpretation. KW and Bill Taylor provided expertise and support for the experiments and analysis of result.

Funding Open Access funding provided by Lib4RI – Library for the Research Institutes within the ETH Domain: Eawag, Empa, PSI & WSL. Funding was supplied by the Empa Research Commission.

Declarations

Conflict of interest There are no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. You may do so, for any purpose, without further permission beyond the licence terms. The article's Creative Commons licence and any additional terms available at https://creativecommons.org/licenses/by/4.0/.

References

1. Kim, K.T., Lee, S., Ko, D.O., Seo, B.S., Jung, W.S., Chang, B.K.: Causes of failure after total knee arthroplasty in osteoarthritis patients 55 years of age or younger. Knee Surg. Relat. Res. 26, 13–19 (2014)
2. Oparaugo, P.C., Clarke, I.C., Malchau, H., Herberts, P.: Correlation of wear debris-induced osteolysis and revision with volumetric wear-rates of polyethylene: a survey of 8 reports in the literature. Acta Orthop. Scand. 72, 22–28 (2001)
3. Bragdon, C.R., O’Connor, D.O., Lowenstein, J.D., Syniuta, W.D.: Importance of multidirectional motion for the wear of polyethylene in the hip. In: Transaction of the Annual Meeting of Society of Biomaterials in Conjunction International Biomaterials Symposium, vol. 1, p. 582 (1996)
4. Wang, A., Stark, C., Dumbleton, J.H.: Mechanistic and morphological origins of ultra-high molecular weight polyethylene wear debris in total joint replacement prostheses. Proc. Inst. Mech. Eng. H 210, 141–155 (1996)
5. Saikko, V.: A multidirectional motion pin-on-disk wear test method for prosthetic joint materials. J. Biomed. Mater. Res. 41, 58–64 (1998)
6. Saikko, V., Calonius, O., Keränen, J.: Effect of slide track shape on the wear of ultra-high molecular weight polyethylene in a
pin-on-disk wear simulation of total hip prosthesis. J. Biomed. Mater. Res. B 69, 141–148 (2004)
7. Turell, M., Wang, A., Bellare, A.: Quantification of the effect of cross-path motion on the wear rate of ultra-high molecular weight polyethylene. Wear 255, 1034–1039 (2003)
8. Korduba, L.A., Wang, A.: The effect of cross-shear on the wear of virgin and highly-crosslinked polyethylene. Wear 271, 1220–1223 (2011)
9. Wang, A.: A unified theory of wear for ultra-high molecular weight polyethylene in multi-directional sliding. Wear 248, 38–47 (2001)
10. Lee, R.K., Korduba, L.A., Wang, A.: An improved theoretical model of orientation softening and cross-shear wear of ultra high molecular weight polyethylene. Wear 271, 2230–2233 (2011)
11. Wang, A., Sun, D.C., Yau, S., Edwards, B., Sokol, M., Essner, A., Polineni, V.K., Stark, C., Dumbleton, J.H.: Orientation softening in the deformation and wear of ultra-high molecular weight of polyethylene. Wear 204, 230–241 (1997)
12. Galvin, A., Kang, L., Tipper, J., Stone, M., Ingham, E., Jin, Z., Fisher, J.: Wear of crosslinked polyethylene under different tribological conditions. J. Mater. Sci. Mater. Med. 17, 235–243 (2006)
13. Abdelgaied, A., Liu, F., Brockett, C., Jennings, L., Fisher, J., Jin, Z.: Computational wear prediction of artificial knee joints based on a new wear law and formulation. J. Biomech. 44, 1108–1116 (2011)
14. Abdelgaied, A., Fisher, J., Jennings, L.M.: A comprehensive combined experimental and computational framework for pre-clinical wear simulation of total knee replacements. J. Mech. Behav. Biomed. Mater. 78, 282–291 (2018)
15. Saikko, V.: Effect of contact area on the wear and friction of UHMWPE in circular translation pin-on-disc tests. J. Tribol. 139, 2–6 (2017)
16. Kandemir, G., Michler, J.: The influence of contact stress on the wear of cross-linked polyethylene. Proc. Inst. Mech. Eng. H 232, 1008–1016 (2018)
17. Kang, L., Galvin, A.L., Fisher, J., Jin, Z.: Enhanced computational prediction of polyethylene wear in hip joints by incorporating cross-shear and contact pressure in additional to load and sliding distance: effect of head diameter. J. Biomech. 42, 912–918 (2009)
18. Saikko, V.: Effect of contact pressure on wear and friction of ultra-high molecular weight polyethylene in multidirectional sliding. Proc. Inst. Mech. Eng. H 220, 723–731 (2006)
19. O’Brien, S.T., Bohm, E.R., Petrik, M.J., Wysz, U.P., Brandt, J.M.: An energy dissipation and cross shear time dependent computational wear model for the analysis of polyethylene wear in total knee replacements. J. Biomech. 47, 1127–1133 (2014)
20. Heuberger, R., Wahl, P., Krieg, J., Gauthier, E.: Low in vitro third-body wear on total hip prostheses induced by calcium sulphate used for local antibiotic therapy. Eur. Cells Mater. 28, 246–257 (2014)
21. Baykal, D., Siskey, R.S., Haider, H., Saikko, V., Ahlroos, T., Kurtz, S.M.: Advances in tribological testing of artificial joint biomaterials using multidirectional pin-on-disc testers. J. Mech. Behav. Biomed. Mater. 31, 117–134 (2014)
22. ISO 14243-1:2009: Implants for Surgery—Wear of Total Knee-Joint Prostheses—Part 1: Loading and Displacement Parameters for Wear-Testing Machines with Load Control and Corresponding Environmental Conditions for Test. ISO, Geneva (2009)
23. ASTM F732-17, Standard Test Method for Wear Testing of Polymeric Materials Used in Total Joint Prostheses. ASTM International, West Conshohocken (2017)
24. Huang, J.B., Hong, J.W., Urban, M.W.: Attenuated total reflectance Fourier transform infra-red studies of crystalline–amorphous content on polyethylene surfaces. Polymer (Guildf.) 33, 5173–5178 (1992)
25. Lorenz, L., Chudoba, T., Makowski, S., Zawischa, M., Schaller, F., Weihnacht, V.: Indentation modulus extrapolation and thickness estimation of Ta–C coatings from nanoindentation. J. Mater. Sci. 56, 18740–18748 (2021)
26. Chudoba, T., Schwallier, P., Rabe, R., Breguet, J.-M., Michler, J.: Comparison of nanoindentation results obtained with Berkovich and cube-corner indenters. Philos. Mag. 86, 5265–5283 (2006)
27. Bano, S., Iqbal, T., Ramzan, N., Farooq, U.: Study of surface mechanical characteristics of ABS/PC blends using nanoindentation. Processes 9, 637 (2021)
28. Gulmine, J.V., Janissek, P.R., Heise, H.M., Akcelrud, L.: Polyethylene characterization by FTIR. Polym. Test. 21, 557–563 (2002)
29. Krimm, S., Liang, C.Y., Sutherland, G.B.M.: Infrared spectra of high polymers. II. Polyethylene. J. Chem. Phys. 54, 549–562 (1966)
30. Slouf, M., Arevalo, S., Vlkova, H., Gajdosova, V., Krälik, V., Pruitl, L.: Comparison of macro-, micro- and nanomechanical properties of clinically-relevant UHMWPE formulations. J. Mech. Behav. Biomed. Mater. 120, 104205 (2021)
31. Hagemann, H., Snyder, R.G., Peacock, A.J., Mandelkern, L.: Quantitative infrared methods for the measurement of crystallinity and its temperature dependence. Polyethylene. Macromolecules 22, 3600–3606 (1989)
32. Fontana, L., Santoro, M., Bini, R., Vinh, D.Q., Scandolo, S.: High-pressure vibrational properties of polyethylene. J. Chem. Phys. 133(20), 204502 (2010)
33. Rugg, F.M., Smith, J.J., Bacon, R.C.: Infrared spectrophotometric studies on polyethylene. I. Structure. J. Polym. Sci. 13, 535–547 (1954)
34. Gleen, W., Peterlin, A.: Infrared studies of drawn polyethylene. Part I. Changes in orientation and conformation of highly drawn linear polyethylene. J. Macromol. Sci. B 4, 473–489 (1970)
35. Saikko, V.: In vitro wear simulation on the RandomPOD wear testing system as a screening method for bearing materials intended for total knee arthroplasty. J. Biomech. 47, 2774–2778 (2014)
36. Kang, L., Galvin, A.L., Brown, T.D., Jin, Z., Fisher, J.: Quantification of the effect of cross-shear on the wear of conventional and highly cross-linked UHMWPE. J. Biomech. 41, 340–346 (2008)
37. Barbour, P.S.M., Barton, D.C., Fisher, J.: The influence of stress conditions on the wear of UHMWPE for total joint replacements. J. Mater. Sci. Mater. Med. 8, 603–611 (1997)
38. Galvin, A.L., Kang, L., Udofia, I., Jennings, L.M., McEwen, H.M.J., Jin, Z., Fisher, J.: Effect of conformity and contact stress on wear in fixed-bearing total knee prostheses. J. Biomech. 42, 1898–1902 (2009)
39. Mazzucco, D., Spector, M.: Effects of contact area and stress on the volumetric wear of ultrahigh molecular weight polyethylene. Wear 254, 514–522 (2003)
40. Hill, M.R., Catledge, S.A., Konovalov, V., Clem, W.C., Chowdhury, S.A., Etheridge, B.S., Stanishevsky, A., Lemons, J.E., Vohra, Y.K., Eberhardt, A.W.: Preliminary tribological evaluation of nanostructured diamond coatings against ultra-high molecular weight polyethylene. J. Biomed. Mater. Res. B 85B, 140–148 (2008)
41. Bortel, E.L., Charbonnier, B., Heuberger, R.: Development of a synthetic synovial fluid for tribological testing. Lubricants 3, 646–684 (2015)
42. Kaddick, C., Wimmer, M.A.: Hip simulator wear testing according to the newly introduced standard ISO 14242. Proc. Inst. Mech. Eng. H 215, 429–442 (2001)
43. Kampouris, A.K., Konstantinidis, A.A.: On the interpretation of the indentation size effect (ISE) through gradient theory for Vickers and Berkovich indenters. J. Mech. Behav. Mater. 25, 161–164 (2016)
44. Mazszybrocka, J., Cybo, J., Fąckowiak, J.E., Krzemień, K.: Change of micromechanical properties of polyethylene induced
by a tribological process in polymer/metal system. Mater. Sci. Forum 513, 75–84 (2006)

45. Rad, M.E.: Volumetric Wear Assessment and Characterization of Striated Pattern of Retrieved UHMWPE Tibial Inserts. Master’s thesis, University of Illinois at Chicago. https://www.semanticscholar.org/paper/Volumetric-Wear-Assessment-and-Characterization-of-Bahonar/cc0e7ae4c4f6022ef1011014b4d9740e802fb8c3 (2015). Accessed 20 July 2022

46. Heuberger, R., Bortel, E.L., Sague, J., Escuder, P., Nohava, J.: Shear resistance and composition of polyethylene protuberances from hip-simulating pin-on-disc wear tests. Biotribology 23, 100139 (2020)

47. Langer, H.G.: Infrared spectra of ethylenediaminetetraacetic acid (EDTA). Inorg. Chem. 2, 1080–1082 (1963)

48. Saikko, V.: Analysis of wear produced by a 100-station wear test device for UHMWPE with different contact pressures. Tribol. Int. 171, 107560 (2022)

49. Harman, M., Affatato, S., Spinelli, M., Zavalloni, M., Stea, S., Toni, A.: Polyethylene insert damage in unicondylar knee replacement: a comparison of in vivo function and in vitro simulation. Proc. Inst. Mech. Eng. H 224, 823–830 (2010)

50. Ansari, F., Ries, M.D., Pruitt, L.: Effect of processing, sterilization and crosslinking on UHMWPE fatigue fracture and fatigue wear mechanisms in joint arthroplasty. J. Mech. Behav. Biomed. Mater. 53, 329–340 (2016)

51. Bracco, P., Bellare, A., Bistolfi, A., Affatato, S.: Ultra-high molecular weight polyethylene: influence of the chemical, physical and mechanical properties on the wear behaviour. A review. Materials (Basel) 10(7), 791 (2017)

52. Knowlton, C.B., Bhutani, P., Wimmer, M.A.: Relationship of surface damage appearance and volumetric wear in retrieved TKR polyethylene liners. J. Biomed. Mater. Res. B 105, 2053–2059 (2017)

53. Harman, M., Cristofolini, L., Erani, P., Stea, S., Viceconti, M.: A pictographic atlas for classifying damage modes on polyethylene bearings. J. Mater. Sci. Mater. Med. 22, 1137–1146 (2011)

54. Wimmer, M.A., Andriacchi, T.P., Natarajan, R.N., Loos, J., Karlhuber, M., Petermann, J., Schneider, E., Rosenberg, A.G.: A striated pattern of wear in ultrahigh-molecular-weight polyethylene components of Miller-Galante total knee arthroplasty. J. Arthroplasty 13, 8–16 (1998)

55. Liza, S., Haseeb, A.S.M.A., Abbas, A.A., Masjuki, H.H.: Failure analysis of retrieved UHMWPE tibial insert in total knee replacement. Eng. Fail. Anal. 18, 1415–1423 (2011)

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.