Tribological performance of DLC coatings on UHMWPE

V Martínez-Nogués1,*, F J Medel2, M D Mariscal1, J L Endrino3, J Krzanowski4, F Yubero5 and J A Puértolas1,2

1Department of Materials Science and Technology, Instituto de Investigaciones en Ingeniería de Aragón, I3A, Universidad de Zaragoza, C/ María de Luna 3, E-50018 Zaragoza, Spain.
2 Instituto de Ciencia de Materiales de Aragón, ICMA, Universidad de Zaragoza-CSIC, E-50018 Zaragoza, Spain
3 Instituto de Ciencia de Materiales de Madrid (CSIC). Sor Juana Inés de la Cruz, 3, Cantoblanco, E-28049 Madrid, Spain.
4 Materials Science Program and Department of Mechanical Engineering. University of New Hampshire, Durham, NH 03824 USA
5 Instituto de Ciencia de Materiales de Sevilla (CSIC- U. Sevilla). C/Américo Vespucio 49, E-41092 Sevilla, Spain.

*Email: enav@unizar.es

Abstract. Diamond like carbon (DLC) coatings were deposited by several methods (ion beam assisted evaporation, magnetron sputtering, filter cathodic arc, and plasma enhanced chemical vapor deposition) onto medical grade ultra-high-molecular weight polyethylene (UHMWPE) discs. The chemical characteristics and mechanical properties of the deposited DLC coatings were studied by Raman spectroscopy and nanoindentation, respectively. In addition, a set of tribological tests was conducted at human body temperature and under bovine serum lubrication against alumina balls. After testing, wear tracks were both visually inspected and documented using confocal microscopy. Visual inspection of the wear tracks confirmed that the DLC coatings were completely removed in all cases, the only exception being the DLC coating prepared by magnetron sputtering with thickness about 0.5 microns. Although this type of DLC coating exhibited the highest friction coefficient, and therefore it suggested a somewhat lower resistance to abrasive/adhesive wear conditions, no evidence of cracking or delamination was observed after the high contact pressure wear testing. This fact points out a good substrate-coating adhesion, and confirms magnetron sputtered DLC as a potential coating for orthopaedic applications.

1. Introduction

Ultra high molecular weight polyethylene (UHMWPE) is the “gold standard” for bearing surface in total joint arthroplasty due to its physical, chemical, and mechanical properties, as well as biocompatibility. However, UHMWPE is the softer material in total joint replacements and can exhibit...
wear-related problems and mechanical degradation after long-term post irradiation oxidation. The main problem is the generation of particles from its use in both articular and non-articular surfaces, which has been associated with osteolysis and implant loosening. The wear of UHMWPE on non-articular surfaces is also known as secondary wear and it is caused by micromobility in modular junctions due to insufficient locking during service. Although it was first detected in hip replacements, this problem affects knee replacements with polyethylene particle production estimations being 2-100 times the amount for femorotibial wear [1].

A solution to this problem could be to coat non-articular surfaces of polyethylene implants with low friction and wear resistant films. Diamond-Like-Carbon (DLC) coatings are potential candidates to reduce UHMWPE wear debris generation due to their excellent mechanical properties (hardness, wear resistance, friction), high chemical inertness and good biocompatibility. [2,3]

This study, we compared the tribological behavior of DLC coatings obtained by several deposition methods: ion beam assisted evaporation (IBAD), magnetron sputtering (MS), filter cathodic arc (FCA) evaporation, and plasma enhanced chemical vapor deposition (PECVD). The objective of this work was to determine the potential use of DLC coated UHMWPE to reduce the wear debris formation in non-articular surfaces.

2. Materials and methods

2.1. UHMWPE sample preparation

An extruded GUR 1050 UHMWPE (Perplas Medical Ltd., Lancashire UK) bar was used as raw material in the preparation of 20 mm diameter discs (3 mm thick). All disks were ground and polished using SiC papers up to a surface roughness equal to 0.15 ± 0.05 μm, measured using a SENSOFAR PLu 2300 optical imaging profiler.

2.2. DLC coatings

The DLC films were deposited on pristine UHMWPE by several techniques: IBAD, MS, FCA and PECVD. The samples included in this study were labelled as M1-M7, as shown in Table 1, where their thickness and average roughness Ra are included.

| Sample | Deposition method | Thickness (μm) | Ra (μm) |
|--------|------------------|----------------|---------|
| M1     | IBAD             | 0.10           | 0.96    |
| M2     | IBAD             | 0.50           | 2.86    |
| M3     | MS               | 0.25           | 0.10    |
| M4     | MS               | 0.49           | 0.18    |
| M5     | FCA              | 0.13           | 0.15    |
| M6     | FCA              | 0.10           | 0.10    |
| M7     | PECVD            | 0.70           | 0.20    |

Samples M1 and M2 were synthesized at room temperature using the IBAD technique. The evaporation was performed from a single graphite source in combination with Ar⁺ bombardment using a Kaufmann type source. Likely, the high roughness observed in these samples was due to localized heating effects induced by the Ar⁺ ions at the surface of the UHMWPE substrates. Samples M3 and M4 were prepared using MS from a pure graphite target at room temperature with grounded substrates. Samples M5 and M6 were synthesized using a “triggerless” mini-gun designed to operate in pulsed mode. The pulses used in the production of carbon plasma were 100 Å and had a duration of 5 ms per second, the plasma stream produced by the source is injected into a 90-degree filter to
remove most of the macroparticles which were formed during the cathodic arc process. During the deposition of the FCA DLC samples, the substrates were pulsed polarized at -1000 V with a duty cycle of 15%. PECVD technique was made in a RF capacitive coupled reactor with plate parallel electrodes. DLC layers of 700 nm were deposited on pristine substrates using acetylene, Ar and H₂ gas mixture and 200 V bias voltage.

The local bonding characteristics of the DLC films were studied with Raman spectroscopy with visible (523 nm) excitation. Spectra were collected using a Horiba Jobin Yvon HR800 system equipped with a CCD camera and a confocal microscope. The laser spot was focused on the sample surface using a 50x objective with short-focus working distance.

2.3. Nano-hardness profiles

In-depth hardness profiles of coated samples were obtained using a nanoindenter XP MTS system. The maximum load used in the tests was 2.0 mN. The indentation rate was 5 nm/s.

2.4. Wear experiments

A ball-on-disk tribometer (CSM instruments; Peseux, Switzerland) allowed assessing wear resistance and monitoring the coefficient of friction for each system. Wear tests were performed in a sample per material group working with a rotation vessel which contains UHMWPE disks immersed in bovine serum (B-9433, Sigma Aldrich). The counterpart was a stationary 6 mm diameter ball made of alumina with a nominal roughness of 0.050 ± 0.002 μm, whereas the load applied to the ball was 5.23 N. The radius of the circular track was 4 mm and the sliding speed was 0.05 m/s. The environment temperature was set to 37 ºC, to simulate body temperature. Assuming hertzian contact, the previous loading conditions gave an approximate contact pressure of 37 MPa, which is in the range of peak contact stresses (≥30 MPa) found for some contemporary tibial inserts. Wear rates were measured after 26400 meters sliding distances. After each wear test, disks were removed from the tribometer and underwent a cleaning protocol following guidelines included in ASTM F2025.

Confocal microscopy was performed using a SENSOFAR PLU 2300 optical imaging profiler to evaluate worn disk surfaces. A total of four line measurements diametrically opposed were carried out on the wear tracks of each sample. The average of the registered worn areas was used to calculate the corresponding wear factor.

The volume loss corresponding to the track profile was evaluated taking into account the plastic deformation suffered by the polyethylene disks under applied loads during wear tests. By virtue of the shape memory effect, UHMWPE heated to high enough temperature recover the original shape that has been previously lost due to mechanical deformation. The recovery of plastic deformation after wear testing was achieved by heating samples at 120 °C for 36 hours. Preliminary tests confirmed that some DLC coated samples demonstrated no removal of the DLC layer after tribological testing, but they exhibited wear tracks exclusively due to permanent plastic deformation. This permanent plastic deformation was not completely recovered after the thermal treatment. Thus, the average worn area after the heating process was corrected taking into account the non-recoverable plastic deformation arise in the sample where the DLC layer remains.

3. Results and discussion

3.1. Chemical characterization of the DLC coatings

Figure 1 show the typical Raman spectra registered for the thickest DLC-coated UHMWPE samples considered in this study.
Figure 1. Typical Raman spectra corresponding to thick DLC coatings deposited by several techniques on UHMWPE.

The Raman spectra exhibited the characteristic G (due to the bond stretching of all pairs of sp$^3$ atoms in rings and chains) and D (breathing modes of sp$^2$ atoms in rings) peaks at 1530-1590 cm$^{-1}$ and at 1330 cm$^{-1}$, respectively. The spectra were analysed by peak fitting and a linear background subtraction. Three values were extracted from the fitting process, the position $w_G$ and full-width at half maximum $\Delta_G$ of the G peaks, and the ratio between intensities of the D and G peaks, $I_D/I_G$.

The first parameter $w_G$ is mainly related to the sp$^3$ content in the DLC material. On the other hand, $\Delta_G$ is sensitive to structural disorder (bond angle and bond length distortion), and $I_D/I_G$ is related to the size of the sp$^2$ clusters organized in rings [4, 5]. The values obtained for the thickest DLC coatings considered in this study are shown in Table 2 (Raman analysis of the thinnest coatings were not attempted due to strong interferences with the signal originated at the UHMWPE substrate).

| Sample | M2 | M4 | M7 |
|--------|----|----|----|
| IBAD   | 1589 | 1594 | 1542 |
| $w_G$ (cm$^{-1}$) | | | |
| $\Delta_G$ (cm$^{-1}$) | 77 | 116 | 130 |
| $I_D/I_G$ | 0.87 | 0.71 | 0.66 |

The coatings prepared by IBAD and MS showed values of $w_G$ of about 1590 cm$^{-1}$. These high values are usually correlated with films with high content of nanocrystalline graphite [4, 5]. The corresponding values of $\Delta_G$ are consistent with the presence of sp$^2$ clusters smaller than 2 nm. Regarding the film prepared by PECVD, the value of $w_G$ is consistent with highly disordered amorphous hydrogenated DLC (about 20% at.) with 30-40% of sp$^3$ bonds [4, 5].

3.2. Nano-hardness

Figure 2 shows the nanoindentation hardness depth profiles obtained for DLC coated UHMWPE samples. Qualitatively, a similar behavior was observed for all the DLC coatings. The influence of the
soft UHMWPE substrate was typically observed at indentation depths as shallow as 20 nm. Although M7 (PECVD) showed slightly higher hardness profile values than DLC coatings obtained using other deposition methods, this could be due to its higher thickness since its initial surface hardness value is one of the lowest (~3 GPa) of the series. Nano-hardness tests performed on MS samples (M3 and M4) had the highest start-up value of ~26 and ~15 GPa (range not shown in Fig. 2), respectively with a further decrease up to around 0.2 GPa. The difference in the measured hardness between M3 and M4 could also be related to the difference in thickness and the influence of the soft substrate since the same tendency appears in M5 and M6 with the thicker coating showing the higher hardness values. The sample deposited by evaporation (M1) had an initial surface hardness close to 10 GPa and its hardness profile decreased to the value expected for virgin UHMWPE (~0.01 GPa) for depths shallower than those of the rest of the films. Nanoindentation depth profile values could not be collected for M2 sample due to its high surface roughness.

In agreement with [6], sample M7 had the lowest ID/IG ratio, so its sp\(^3\) content is higher than in the rest of the samples. Due to this fact it shows better mechanical properties (higher hardness) during the measuring profile, as we shown in Figure 2.

![Figure 2. Hardness profiles of the DLC coatings deposited on UHMWPE](image)

3.3. Friction

The friction coefficient versus sliding distance obtained during ball-on-disk tests are shown in Fig. 3. Sample M5 (FCA) presented the lowest friction coefficient (~0.10) at the beginning of the run and remained practically constant after a sliding distance of 25000 meters. This value is similar to that obtained for the uncoated UHMWPE substrate using identical tribological conditions [7]. The sample deposited using MS displayed the highest friction coefficient, around 0.30, and it remained above 0.25 for the entire run, indicating that the coating was not removed from the substrate during the test. The evolution of the friction coefficient of the samples obtained using PECVD and IBAD methods revealed a different tribological behaviour. Both of them started at 0.25, but the friction coefficient values tend to decrease during the test to 0.20 and 0.15 respectively after the running-in period. This points out that the DLC coatings deposited by these two methods worn out after a sliding distance of 16000 and 6000 m, respectively. Likely, the same mechanism occurred in the sample deposited by FCA. In this case, the thickness of the coating was so thin that was probably partially removed during the running-in stage yielding a low friction coefficient.
3.4. Wear
Confocal microscopy images of the wear tracks (Fig. 4a-g) were obtained for the seven coated UHMWPE discs after tribological testing (26400 meters of sliding distance). All the samples showed wear tracks featuring grooves parallel to the sliding direction. These grooves are typical of an abrasive wear process, likely produced by the contact between alumina ball and DLC asperities. In the case of M4, the only sample in which the coating remained practically intact after the entire test, the micrograph showed a lighter colour, due to the presence of the DLC layer, but still similar abrasive grooves. However, the wear track of the PECVD sample showed a mixed behaviour since it was partially covered by DLC fragments, indicating that, in this case, the DLC coating had been fragmented and partially removed in some areas.

The wear performance of the samples included in this work is summarized in Table 3. After the recovery process, some samples, M5 and M7 (NW-PE), showed a negligible wear of the PE when the DLC coatings were removed from the substrate.

The most relevant result was that the MS coating with ~0.5 μm in thickness, M4 (NW-DLC), did not exhibit signs of fragmentation or coating delamination after 26000 m of sliding distance in the described tribological conditions. The performance was better than that shown for other DLC coated UHMWPE samples with similar thickness but obtained by other methods (IBAD or PECVD). The joint interpretation of friction and wear results confirmed that, despite the comparatively lower abrasion resistance as reflected by the high friction coefficient, the 0.5 μm thick MS DLC layer presented a strong substrate-coating adhesion. Thus, M4 was able to endure the high contact pressure conditions and the predominant fatigue wear mechanism of the present tribological test.
Figure 4. Confocal microscopy images of the wear tracks corresponding to a) M1, b) M2, c) M3, d) M4, e) M5, f) M6 and g) M7.
Table 3. Wear rate of DLC coated materials after 26400 m sliding distance, where NW-DLC means samples without DLC wear and NW-PE means no measurable wear over the PE.

| Sample | Wear rate x10^-7 (mm^3/Nm) |
|--------|-----------------------------|
| M1     | 1.1 ± 1.0                   |
| M2     | 2.5 ± 1.8                   |
| M3     | 1.7 ± 0.3                   |
| M4     | NW-DLC                      |
| M5     | NW-PE                       |
| M6     | 0.7 ± 0.5                   |
| M7     | NW-PE                       |

4. Conclusions
Remarkable wear test results were obtained for DLC-coated UHMWPE disc prepared using the radio frequency magnetron sputtering (RF-MS) technique with high content of nanocrystalline graphite and thickness of ~0.5 μm. Even though the friction coefficient of these MS DLC-coated UHMWPE samples were the highest of the set. The excellent wear behavior observed, with no delamination or chipping even after 26000 meters sliding distance, confirms the potential of these nanocrystalline graphite rich DLC coatings on UHMWPE for some orthopedic applications.

Acknowledgment
The authors are grateful to A.Anders (LBNL) and I. Jimenez (ICMM) for deposition of DLC coatings by filter cathodic arc and by IBAD techniques. We thank the Ministry of Science and Education of Spain (projects MAT2006-12603-C02-01 and CONSOLIDER-INGENIO CDS2008-0023 for financial support. JLE also acknowledges Spanish MICINN Project FIS2009-12964-C05-04.

References
[1] A.R. Rao, G.A. Engh, M.B. Collier, S. Lounici. J.Bone Joint Surg. Am. 84-A (10) (2002) 1849-1855.
[2] R.K. Roy, K.R.Lee. J.Biomed Mater. Res.B: Appl. Biomater. 83(1)(2007) 72-84.
[3] R. Hauert. Tribol.Int 37 (11-12) (2004) 991-1003.
[4] J. Robertson, Materials Science and Engineering R 37 (2002) 129.
[5] C. Casiraghi, A.C. Ferrari, J. Roberson, Phys. Rev. B72 8 (2006) 08540.
[6] F.X. Liu, Z.L. Wang. Surface coating Technology. 203 (2009) 1829-1832.
[7] J.A. Puértolas, V. Matinez-Nogués, M.J. Martinez-Morlanes, M.D. Mariscal, F.J. Medel, C. López-Santos, Y. Yubero. Wear 269 (2010) 458-465