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Project title: [**Advanced Research Training for the Biotribology of Natural and Artificial Joints in the 21st Century**]

Long Term wear characterisation using a 3 station multi directional pin on disk tribometer of thermoplastic nano composites prototypes, manufactured using AM and conventional methods.

Deliverable D5.7

Month Due: PM30

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Project coordinator name	Prof. Richard M Hall
Project coordinator organisation name	UNIVLEEDS
Report prepared by	PI Prof Nazanin Emami Ben Clegg Dilesh Raj Shrestha Luleå University of Technology, Sweden

Dissemination Level of Report

PU	Public	X
PP	Restricted to other program participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

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D5.7.1	2023-06-29	First Draft circulated to …	Judith Schneider, Richard Hall, Michael Bryant for further distribution
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D5.7	**2023-08-31**	**Submitted to Commission**	**JS (UNIVLEEDS)**

Some important notes:

Research title: Biocompatibility responses to newly developed carbon-based PEEK/UHMWPE-nanocomposites

ESR 5: Ben Clegg

Supervisor: Prof. Nazanin Emami, Lulea University of Technology, Lulea, Sweden

Co-supervisor: Prof. Joanne Tipper, University of Technology, Sydney, Australia

As per BioTrib grant agreement deliverable **D5.7: Long-term wear characterisation using hip simulator of thermoplastic nanocomposites prototypes, manufactured using AM and traditional method.**

Expected deliverables and reason for any changes:

The objective for this deliverable was to characterise the tribological and mechanical performance of AM printed polymers compared to their traditionally manufactured counterparts (both pins and disks). Any changes that have been more to the deliverable are only related to the material, as ESR4 moved to the more processable materials (PAEK Family) to ensure efficient research timeline and within the scope of the fields state of the art.

It was originally planned that this deliverable would be achieved via the use of a hip simulator to characterise the long-term wear mechanisms of experimentally developed polymeric components, in comparison to commercially available material.

Due to timings and early stages of the project for ESR5, this report will focus on the on-going experimental work using the multi directional pin on disk tribometer. This tribometer was designed recently together with Simulation Solutions, UK (manufacturer and supplier of hip simulators to both LTU and the university of Leeds). The configuration of this multidirectional pin on disc is designed for screening of polymeric component within orthopaedic application, using relevant loadings, velocities, test duration and material configurations. Which is an important step in the characterisation of experimentally developed material in comparison to commercially available components. The multi directional pin on disk tribometer is used to screen materials and material pairings to ensure that an optimised material combination is achieved before proceeding to the extensive hip simulator testing to clinically validate these screening with a more clinically representative tribometer.

Currently ESR5 is underway with their secondment to the university of Leeds and is carrying out training and assessing protocols for long term wear testing on hip simulators. During their time at the university of Leeds ESR5 will be undertaking the project of assessing wear of hip bearing materials under adverse loading profiles.

This will enable the ESR to gain knowledge of the processes and protocols required to then carry out similar and further testing at Luleå university of Technology during the rest of the project.

Contents

Executive Summary

This executive summary presents the key findings and objectives of a study focused on the long-term wear characterization of thermoplastic neat and composite prototypes manufactured using additive manufacturing (AM) and traditional methods, using a three station multi directional pin on disk tribometer.

The objective of the study is to evaluate the performance of experimentally developed thermoplastic neat and composite prototypes as potential load-bearing implants. The use of 3D printing technology allows to produce complex structures and customized designs, making it a promising approach for manufacturing implant components. The study specifically examines the influence of AM and traditional manufacturing methods on the long-term wear behaviour of these prototypes, to assess their suitability for load-bearing applications.

The study will include a comparative analysis between prototypes produced using AM and traditional methods. By examining both manufacturing approaches, the research aims to provide insights into the advantages and limitations of the AM method in terms of tribological behaviour and wear performance. This analysis will contribute to the development of optimized AM processes for load-bearing implant components in the biomedical field.

The specific objectives of the study include characterisation of the polymers and polymer composites, understanding the influence of processing parameters on the performance of printed components, developing a comprehensive understanding of the wear mechanisms in these prototypes, and experimentally developing 3D printable polymeric-based material filaments.

Thus, this project will focus on achieving following aims and objectives:

- To develop an understanding of the performance and wear particle characteristics of commercially available materials (UHMWPE and PEEK), both conventional and 3D printed, in varied loading conditions, using a pin-on-disk multidirectional tribometer.
- Understanding of the materials behaviour and biocompatibility of the development of novel self-lubricating and polymer and polymer composites with improved mechanical characteristics.

This executive summary highlights the importance of understanding the long-term wear characteristics of thermoplastic nanocomposite prototypes manufactured using AM and traditional methods. The findings of this study will contribute to enhancing the design and manufacturing processes of load-bearing implant components, ultimately improving patient outcomes in the biomedical field.

1) Introduction

The field of 3D printing, also known as additive manufacturing (AM), has gained significant popularity due to its versatility in fabricating intricate structures, production times, cost-effectiveness, and overall efficiency. This technology enables the creation of three-dimensional objects using a wide range of materials, including metals, ceramics, polymers, and composites.

The current market materials utilized in hip implants face increasing challenges due to a changing demographic with a decreasing age profile and declining patient health, particularly related to obesity [1]. This necessitates enhanced wear resistance to meet the longevity requirements of younger patients (<65 years old) who expect their implants to endure for longer durations [2]. Advancements in healthcare have increased life expectancy and led to a demand for hip implants with extended lifespans exceeding 20 years, allowing patients to maintain active lifestyles and avoid revision surgeries [3]. Improvements in surgical techniques and implant design have also contributed to the preference for hip surgeries in younger patients, emphasizing the need for materials that can withstand the demands of an active lifestyle [4]. Consequently, it is crucial to investigate material enhancements and develop novel materials that effectively mitigate wear-related failure modes, enhancing the overall performance and durability of hip implants in alignment with the evolving needs of the younger patient population.

3D printed polyetheretherketone (PEEK) and its potential composites hold significant relevance in medical filed. PEEK is a high-performance thermoplastic polymer known for its exceptional mechanical properties, biocompatibility, and resistance to wear and corrosion [5]. Leveraging the capabilities of 3D printing technology allows for the fabrication of PEEK-based components with complex geometries and tailored designs. Furthermore, the additive manufacturing process enables precise control over the internal structures and porosity of the implants, potentially leading to improved osseointegration and long-term stability [5].

The incorporation of reinforcing agents or fillers into the PEEK matrix, such as carbon based or ceramic nanoparticles, offers a means to further enhance the mechanical strength, stiffness, and tribological properties of the composite material [6]. By optimizing the distribution and alignment of these reinforcing agents within the PEEK matrix [7], it becomes possible to tailor the wear behaviour of the composite [8], making it particularly promising for addressing the challenges associated with implant wear and loosening. Polymer composite studies have shown positive outcomes for tribological and biological testing, at LTU, using UHMWPE as the matrix [9].

In summary, the combination of 3D printing technology, PEEK matrix, and potential PEEK based composites presents a promising approach to enhance the wear behaviour of hip implants. Through the customization and optimization of material properties, 3D printed PEEK and its composites offer the potential to address wear-related failure modes, extend the longevity of hip implants, and ultimately improve patient outcomes in the field of total hip replacements.

2) Experimental details

2.1) Material

The Materials used in this study are PEEK and PEEK filament **(**VESTAKEEP® i4 3DF-T) supplied by Evonik Industries AG, Germany. CoCrMo (ISO5832-12 Alloy 1, AST; F1537-11, ASTM F799-11, DePuy MS-10301000 Rev/) Supplied by Oracle Special Metals LTD, Basingstoke, UK.

GUR® ultra-high molecular weight polyethylene (UHMW-PE) grades, 1020-E, Celanese, TX, USA

2.2) Sample fabrication and Preparation

PEEK pins were machined from an extruded block of i4 PEEK and printed via FDM (CreatBot 300, China)

1020-E pins – compression moulded at LTU and machined from polymer block.

CoCrMo countersurfaces – hand polished to <10nm Ra confirmed using VSI (ZYGO, NEWVIEW 7300)

Polymer samples are then soaked until a measured mass equilibrium is reached. – 3D pins surface finish is left as Is from manufacture, and conventional pins are machined in this study.

As this is an ongoing project, below in **Table** 1, is a list of material bearing combinations that will lead to a better understanding of the optimal bearing combination with regards to wear and wear behaviours.

Table 1: Material bearing combinations, Planned and executed.

Pin	Plate	Completed/Planned
I4-PEEK	CoCr	✓ (1MC)
3D printed I4 PEEK	CoCr	✓ (1MC)
GUR1020-E	CoCr	✓ (0.66MC)
	3 months break for secondment at Leeds University (July-Sept 2023)	
E-XLPE	I4-PEEK	X
PEEK	PEEK	X
3D PEEK composite	CoCr	X
E- XLXPE	3D PEEK composite	X

*Last 4 combination of test series to be completed during autumn 2023.

Soaking:

Soaking PEEK samples prior to a tribological test is necessary to simulate real-world conditions and evaluate the material's performance in a hydrated environment. The material is soaked in accordance with ASTM F732 -17. This is to ensure that the polymer samples reach a stable mass before tribological testing begins. This is to prevent any discrepancies in the data from fluid absorption under pressure during the tests. A soak control is also used to determine and fluid mass uptake during the long-term testing.

Soaking Method:

- Clean samples and weigh before soaking. (As seen below)
- Ensure gloves are worn at all times when handling samples.
- Characterise samples before beginning the soak mass and surface profile.
- Immerse samples fully in DI water – using labelled containers.
- Place samples in a sealed desiccator in a temperature-controlled room
- Retrieve samples once a week to measure mass gain.
- The samples should be taken out of the soak for at least 30 minutes in a dust free environment to naturally dry (60 minutes allows for more stable and consistent measurements)
- Using gloves and tweezers weigh the samples on a clean balance (10±μm)
- Measure until 3 repeat readings are recorded.
- Re immerse in the DI water and place back in the desiccator and temperature-controlled room

Cleaning Samples:

This is to be carried out initially on the samples before soaking is commenced. And In between pin on disk cycles (every 0.33 million cycles) – to ensure the samples are weighed to the correct mass, (no particle or protein contamination).

In Accordance with ASTM F732 -17
Rinse with tap water to remove bulk contaminants.

- Wash in an ultrasonic cleaner in a solution of 1% detergent for 15 min.
- Rinse in a stream of distilled water.
- Immerse in De Ionised water for 10 min.
- Rinse in a stream of distilled water.
- Dry with lint-free tissue.
- Immerse in methyl alcohol (Note A6.1) for 3 min.
- Dry with lint-free tissue.
- Air-dry in a dust-free environment at room temperature for 30 min.

3) Testing parameters

Using the three station Multi directional pin on disk Tribometer (SimSol, Manchester, UK), screening tests were conducted to validate the wear factors of the recently developed machine by SimSol, compared to literature and to assess the wear behaviour of the AM and conventional polymers. Using the following parameters in **Table 2**, based upon ASTM F732 -17 standards, using 25% FBS joint solution.

Table 2: Pin on Disk configurations

X track distance	12.5mm
Y axis Distance	12.5mm
Total Distance	39.2699mm
Frequency	1Hz
Velocity	39.2699mm/s
Aspect Ratio of Track	1:1
Pin RPM	60RPM
Pin direction	Reverse to track motion
Force Applied	117.9N
Contact Pressure	3.06MPa

Surface characterisation techniques:

Surface profilometry:

VSI was used to visualize the wear scars in three dimensions aids in distinguishing between different wear modes and understanding their underlying mechanisms using the (ZYGO, NEWVIEW 7300)

SEM:

To determine specific wear mechanisms for the samples, SEM was used (Jeol JSM-IT300 Oxford Instruments (Aztec)).

4) Results

Initial Results show a high variance in accuracy, for both the 3D printed material and the conventional. **Figure 1,** The results have separated into individual stations of the multi directional pin on disk tribo-meter to determine if there is a pattern of increased wear across the locations. Station 3 is the most predictable and is assumed that a representative wear behaviour is being exhibited on this station, which is represented more clearly in **Figure 2**. The trend of decreasing wear with time is not reported in literature as it is usually presented as an average overall wear factor for the duration of the test. The increased wear for both stations 1 and 2 is ascribed to contamination, within the individual cell of the station, leading to high volumes of abrasive wear, see **Figure 3**. The contamination of the cell could be credited to a number of sources, including particles in the air from construction and or other air borne particles in the lab. This type of contamination has been observed in practice of other pin on disk laboratories.

4.1) Wear of 3D printed PEEK vs Conventionally Manufactured PEEK

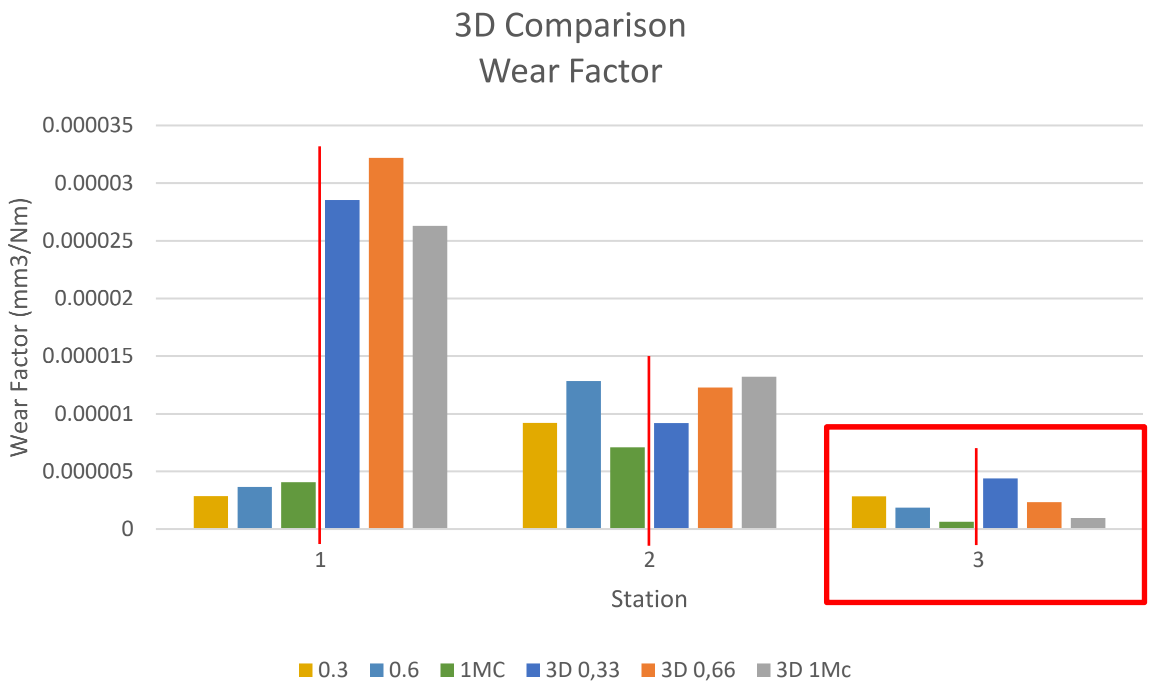

Figure 1 – Comparing the wear rates for each 1/3 million cycles for Conventional PEEK (left of red line) vs 3D printed PEEK (right of red line) for each station.

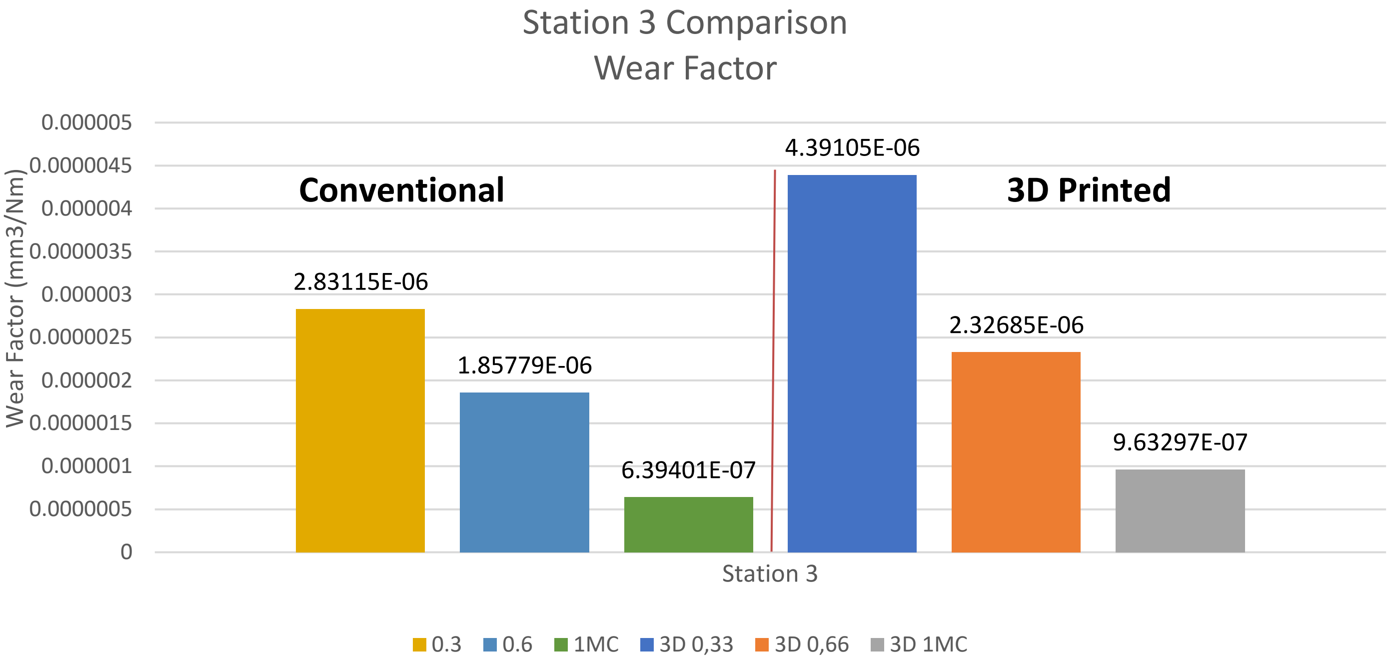

Figure 2 – Comparing the wear factor of conventional (Left) versus 3D printed (Right) over a timeframe of 1 million cycles, split into 0.33 million cycle intervals.

This should not occur in a clean PEEK on CoCrMo system due to the variance in hardness of the materials. The abrasive wear can be seen on the SEM, **Figure 4**, with the majority of scratches in the direction of pin rotation working from the inner edge of the wear track out to the middle and edge of the wear track. There are also some scratches that can also be seen perpendicular to that of the pin rotation motion.

Focusing on Station 3, it can be observed that preliminary test results show that 3D printed PEEK can be comparable to that of conventionally manufactured.

4.2) Damaged surface profiles:

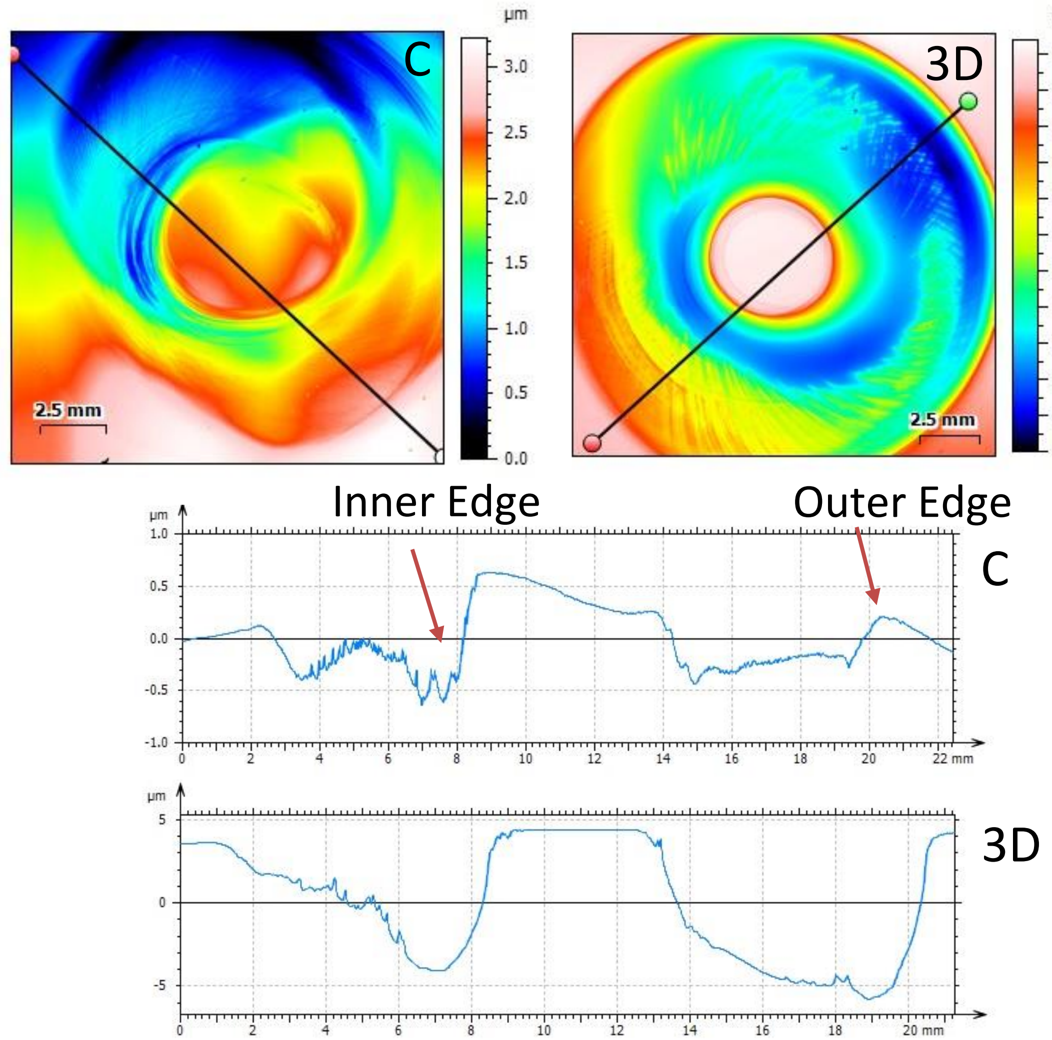

Figure 3 - CoCrMo Countersurfaces for Conventional (C) and 3D Printed (3D) PEEK (Station 2 and Station 1 Respectively, as these were the highest wearing stations) and the wear profiles for each.

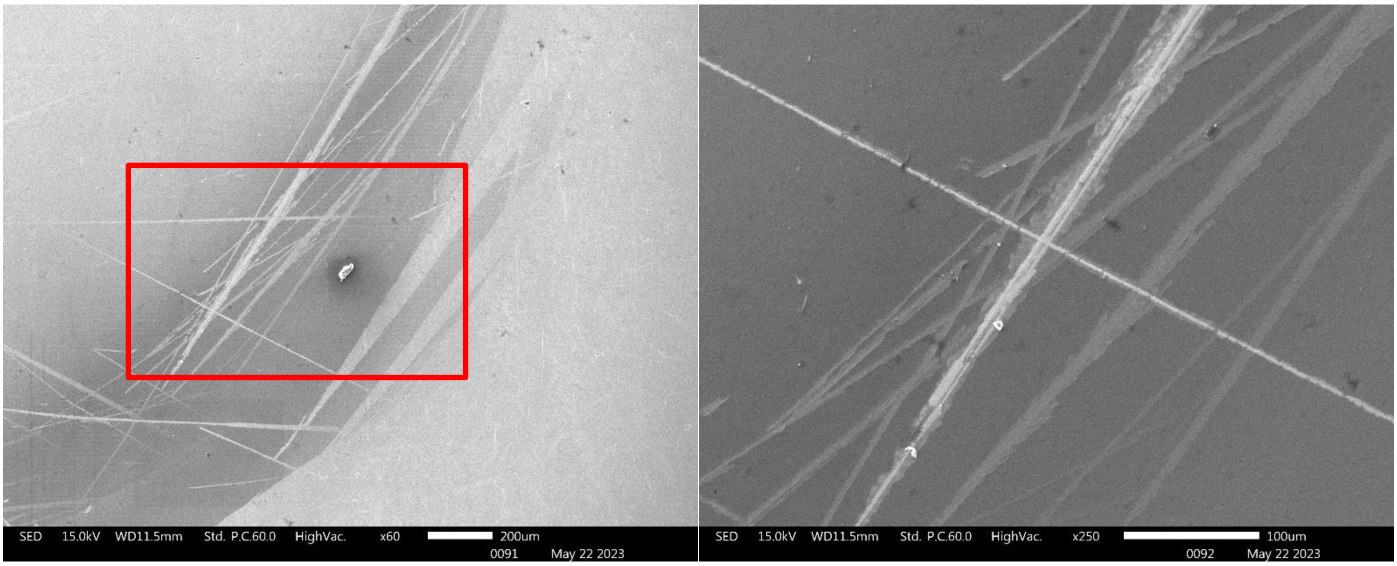

Figure 4 – SEM image of the damaged CoCrMo surface shown in **Figure 3.C.** Right image is a magnification of the red zone

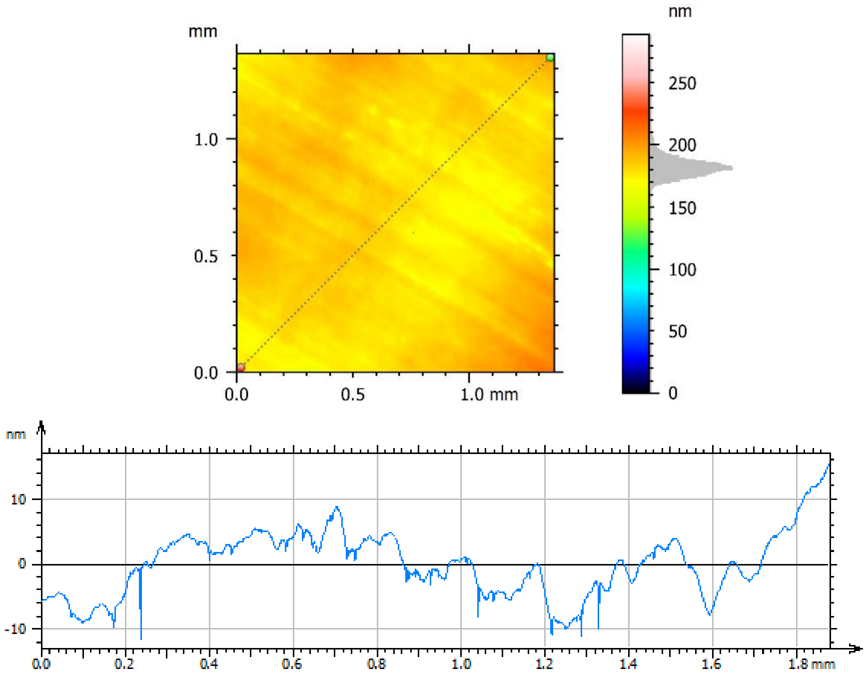

Figure 5 – mirror polised CoCrMo countersurface before testing

The Damaged surface shown in **Figure 3,** show heavy abrasive wear of the metallic countersurface. With the countersurface for the 3D printed material showing x10 deeper wear scars, reflected in the higher wear of the polymer sample, **Figure 1.** The countersurface for the conventional PEEK, **Figure 3C**, exhibits a slight waviness across the surface, leading to a deeper wear scar on the northwest corner, this needs to be examined to understand if this attributes to the increased wear. Wear scars can also be seen to begin at the inner edge of the wear track and spin spiral outwards to the edge of the track, in line with the pin rotation movement.

The mirror polished samples are shown in **Figure 5**, to confirm that the scratches were not there previously and caused by external influences. with a profile and surface roughness of <10nm.

4.3) Surfaces Profiles for Station 3:

As seen on **Figure 6,** the wear scars are more uniform compared to the higher wearing samples. With concentric circles in line with the translation motion of the load cell bed, rather than with the pin rotation. The wear scars are again deeper for the countersurface of the 3D material, however this time only by a factor of two. It is noticeable that there is a tendency for the wear scar to deepen on the inner edge of the wear track.

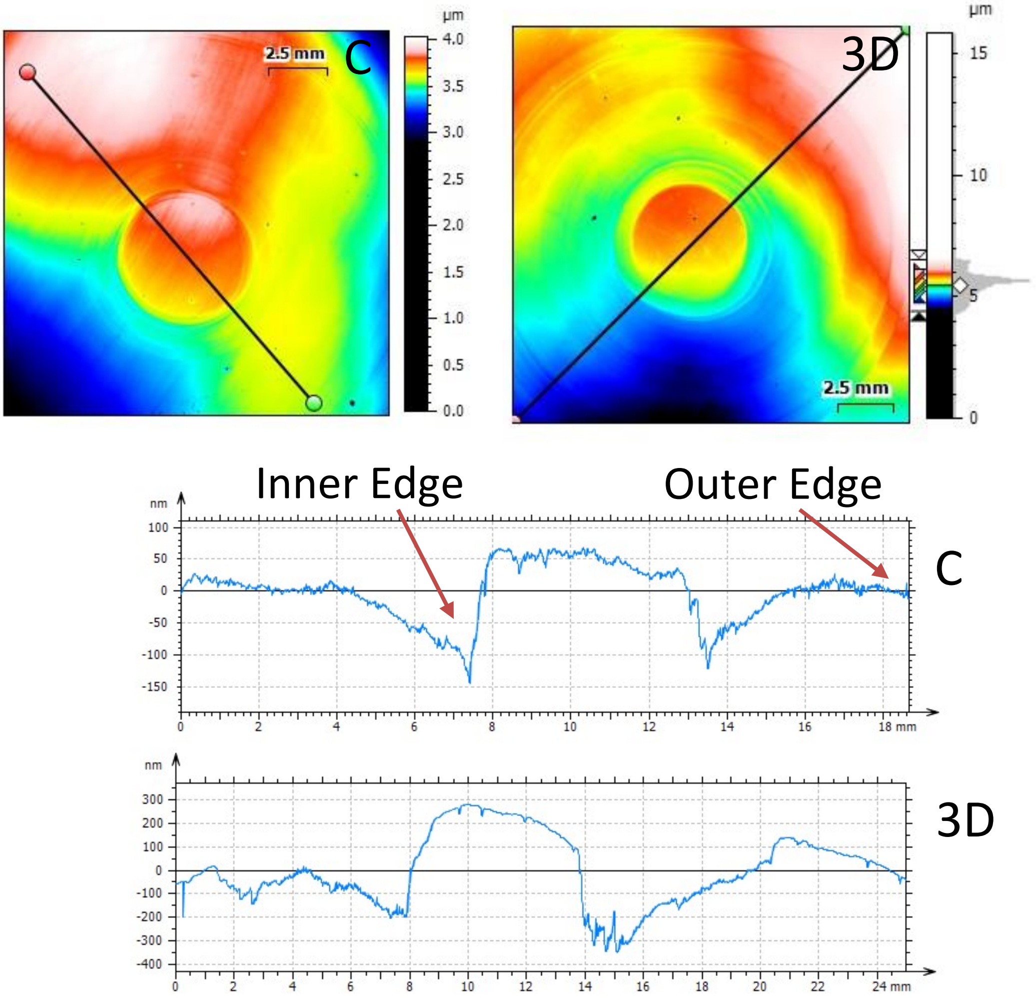

Figure 6 - CoCrMo Countersurfaces for Conventional (C) and 3D (3D) Printed PEEK (Station 3) and the wear profiles for each. The inner and outer edges of the wear track are labelled for context.

4.4) Pin surfaces Pre and Post Testing:

The following section shows the articulating surface characteristics of the polymer pins before and after the testing procedure. It is clear from **Figure 7,** that the surface profile of the samples varies greatly. With the conventionally manufactured PEEK showing concentric circle machined pattern with significantly less variation in the asperity profile. Ranging from an average of ±10µm from the average profile. Whereas the 3D printed surface varies from +100µm to -50 µm.

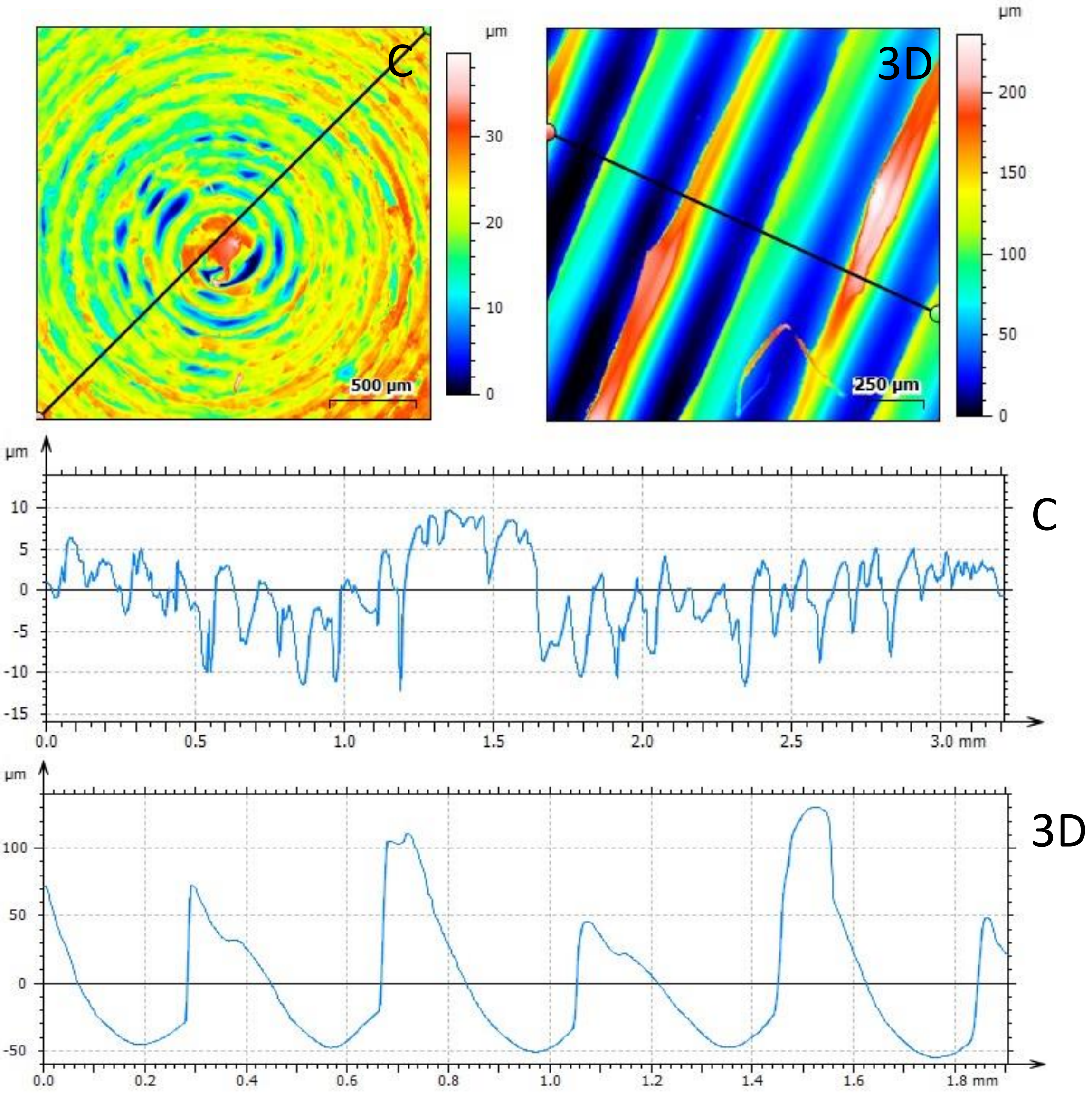

Figure 7 – Pre-test contact surfaces for conventional (C) and 3D (3D) printed PEEK, and their respective wear profiles.

Figure 8 shows the post-test surface profile of the PEEK pin. As seen the pin surface is uniformly smooth with only minor undulations. The characteristics of the pins were homogeneous across all stations and materials, independent of the wear factor.

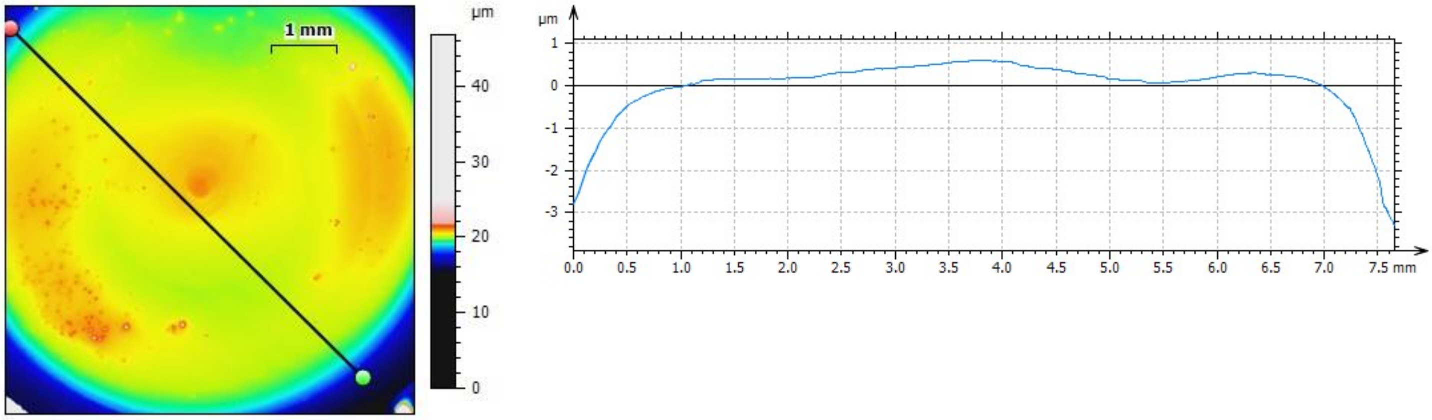

Figure 8 – Post-test surface characteristics of PEEK pin. 3D Pin shown above along with wear profile.

From **Figure 9** it can be seen that both the compressive yield strength and compressive modulus of the 3D printed material is less than that of the conventionally manufactured material. With a reduction of 7Mpa in compressive yield strength and 1GPa in compressive modulus. This reduction in mechanical property explains the decrease in tribological performance.

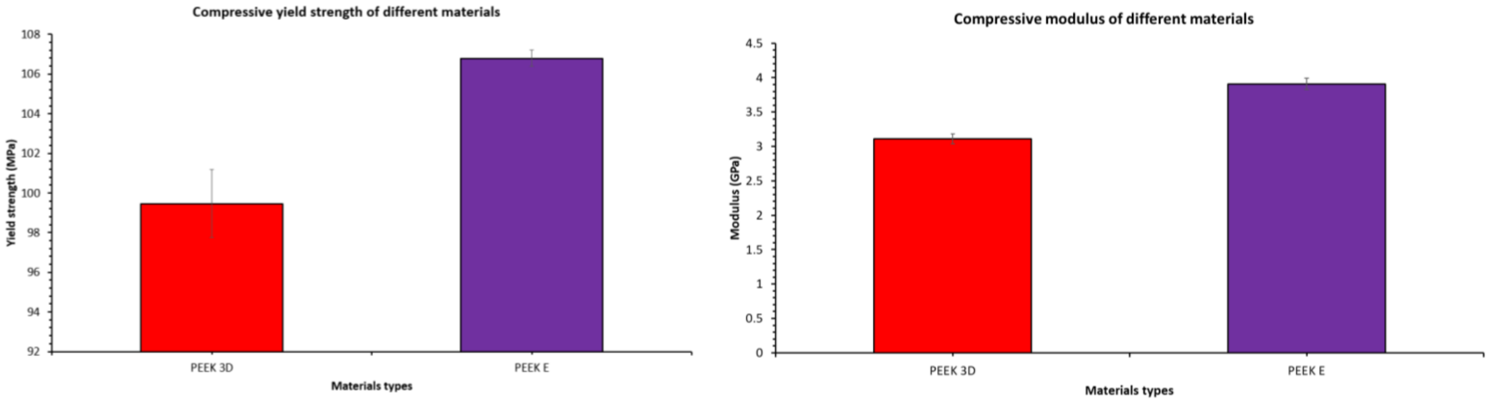

Figure 9 – comparing both Compressive Yield strength (Left) and Compressive modulus (Right) of 3D printed and Conventionally manufactured PEEK.

4.5) Soaking of Material

To obtain accurate and stable measurements over long cycle testing for polymer materials, they must be soaked in accordance with standards (ASTM F732-17). This will allow for suitable time for the polymer to uptake fluid and stabilise. If the polymer is not stabilised before the test has begun, then the samples can uptake fluid during the test due to expose to lubricating fluid. Also, there is an axial load applied to the samples during testing, as such this can cause extra fluid uptake and mass gain for the sample, a stabilised polymer should minimise this effect, leading to more accurate and repeatable results. This study is interested to see if the 3D printed parts vary in time to reach equilibrium in soaking when compared to their conventionally manufactured counterparts.

From **Figure 10**, it can be seen that the conventional PEEK reaches equilibrium at around 50 days, with literature suggesting 98% of fluid absorption occurring after 30 days [5]. The same trend occurs, but at over a much shorter period for the 3D printed PEEK at around 10 days.

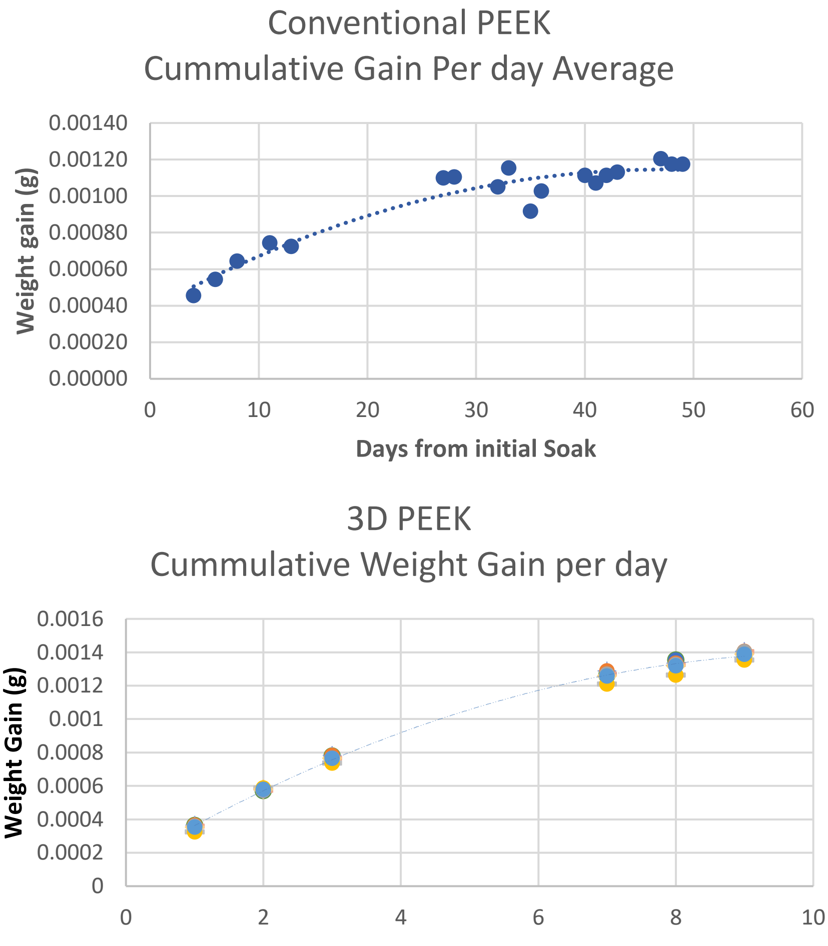

Figure 10 – Weight gain profiles for Conventional and 3D Printed PEEK taken from an average of four pins.

5) Discussion:

When discussing the slightly high wear nature of the PEEK against CoCrMo. It must be considered that each individual multi directional pin on disk has highly varied outputs due to their loading and motion characteristics. Other studies have used pins with a maximum rotation of ±55° [10,11] Also, this study has initially conducted testing at a higher contact pressure, of 3.06MPa, still within the recommended standard (ASTM F732 -17). PEEK is known to be susceptible to higher wear with increasing contact pressures [10,12]. The effects of contact pressure variance are an aim for future work within this project. It should be stated again that this is an ongoing work and many other materials pairing will be investigated to finalise the most suitable combination. PEEK will be tested both as pins and disks (countersurfaces) in order to understand the wear mechanisms as an acetabular cup and femoral head.

The First 0.33MC of testing, brings the highest variance in mass loss for the samples. As the length of the test increases the more comparable the two samples become. The author ascribes this behaviour mainly due to the surface profile of the 3D printed material, with an increased surface roughness compared to the conventionally manufactured sample. There is also a difference in the direction/pattern of the roughness, with the conventional sample showing concentric circles and the 3D parallel lines. Both factors will contribute to the increased material loss for the 3D printed sample in the first phase of testing. Once the surface has initially worn and become smooth and uniform the wear profiles become increasingly comparable.

FDM-printed PEEK falls short in terms of mechanical properties compared to conventionally manufactured material, suggesting inferior wear performance [13]. This was also confirmed by mechanical testing in house at LTU shown in **Figure 9**.

However, **Figure 2** demonstrates comparable wear performance, which could be attributed to the porosity of the printed material. The porosity may enable the absorption and redistribution of joint fluid, potentially creating a hydraulic effect. These factors might contribute to the comparable wear performance despite the lack of mechanical properties.

The abrasive wear due to the contamination, seen in **figure 3 & 4**, can be seen with scratches and wear scars matching the direction of the spinning pin, showing that the pin is carrying debris within the surface leading to abrasive ploughing across the CoCr countersurface. This was confirmed by the author, as when resetting the track profile post-test, a scratch in the same profile was observed. When looking at the inner edge wear, **figure 6,** it is a repeating occurrence for both set of materials. This wear characteristic can be attributed to an edge loading effect, as the pins have a bevelled shoulder from a 9-7Ømm diameter, however this will not eliminate the effect entirely. Another reason may be a slight offset with the pin to the countersurface, leading to increased edge loading of the sample.

The effect of porosity is also seen with the soaking of both PEEK materials, with the AM PEEK showing a mass increase of up to four-fold gain per day. However, this leads to the material reaching an equilibrium at a much faster rate. This can be attributed to an increased surface area of the material and porous structure. There is an average porosity of <1.2%, within the LTU 3D printed samples.

6) Conclusion:

- FDM-printed PEEK exhibits higher wear under multi directional conditions, with the 3 station in this report denoting slightly higher linear mass loss than previous studies [10,11] .
- Initial testing shows higher mass loss for 3D printed samples due to increased surface roughness compared to conventionally manufactured samples.
- Abrasive wear and scratches indicate contamination, leading to abrasive ploughing across the countersurface.
- Repeat studies are needed to validate the possible comparative wear performance of 3D printed PEEK versus Conventionally manufactured PEEK.
- Further research is needed to optimize surface roughness, porosity, and mechanical properties for improved wear resistance in additively manufactured PEEK materials.

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