Performance of Polymer Composites Lubricated with Glycerol and Water as Green Lubricants

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Abstract: The study analysed the tribological performance of five different polymer composites: polyetheretherketone reinforced with 30% carbon fibres—PEEK CF30, polyetheretherketone reinforced with 10% carbon fibres, 10% graphite and 10% polytetrafluoroethylene—PEEK MOD, polytetrafluoroethylene reinforced with 25% carbon fibres—PTFE CF25, polyoxymethylene with 30% carbon fibres—POM CF30 and ultra-high molecular weight polyethylene—UHMW PE. The polymers were tested under the sliding regime of a reciprocating stainless-steel ball on a polymer disc, with test parameters expected for hydraulic valves. Two environmentally safe lubricants were used: glycerol and water. The selected polymer materials and their tribological properties were compared based on the coefficient of friction and the specific wear rate. The worn surfaces were examined using scanning electron microscopy, and the transfer film was analysed using the energy dispersive spectroscopy technique. When tested in glycerol, a comparable and low coefficient of friction was measured for all polymers (~0.02). At the same time, a significantly lower coefficient was measured for all polymers in glycerol compared to water-lubricated conditions (~0.06–0.22). The polymers differed in the measured specific wear rate, which increases significantly in water for all polymers. A lower specific wear rate was measured for three polymers with higher microhardness: PEEK CF30, PEEK MOD and POM CF30. In water, PEEK CF30 showed superior tribological properties under harsh conditions but was well followed by POM CF30, which showed the most intense transfer film.

Keywords: polymer composite; green lubricant; glycerol; water; hydraulics

1. Introduction

Increased environmental awareness nowadays has led to an ecological transition, which aims to use both novel materials and green sustainable lubricants to replace the traditional dry- or oil-lubricated (mineral or synthetic) steel–steel contacts commonly found in most industrial sectors. The traditional focus on lower friction and specific wear under desired conditions, but with an added environmental approach, is of particular interest to forestry machinery, hydropower and marine, medical, textile and food, automotive and aerospace industries [1–3]. All this research and new practices can potentially both save energy and reduce pollution [4].

Particularly energy-efficient polymer-based composites are lightweight, recyclable, affordable and have good tribological properties. Among the various polymers, polymer plastics based on polyetheretheretone (PEEK), polyphenylene sulphide (PPS), polytetrafluoroethylene (PTFE) and ultra-high molecular weight polyethylene (UHMWPE) were tested intensively under dry sliding and water-lubricated conditions [5,6]. They have shown good mechanical performance at different loading rates, high strength-to-weight ratio and corrosion resistance. Their tribological properties and service life can be improved for different working conditions by using various functional fillers, fibre reinforcements or internal lubricants [7,8].

Among the various high-performance polymers, PEEK has been widely studied due to its high mechanical strength and stiffness, although it is light and easy to mould, which
makes it attractive for various demanding industrial applications [9]. It also has good thermal and chemical stability and excellent tribological properties [10]. These properties can even be improved when reinforced with carbon fibres CF in seawater [11–13] and in distilled water when reinforced with CF and PTFE [14]. However, additives in the form of glass fibres (GF) and bronze powder could not improve the effect of the reinforcement CF and the PTFE lubricant additive [13]. Although tested under various conditions, PEEK and its composites showed a low COF of 0.15 down to 0.03 and a specific wear rate of up to $1.66 \times 10^{-8} \text{mm}^3/(\text{Nm})$ in water [14–16]. PTFE also has a very low coefficient of friction of below 0.05 and high chemical resistance and temperature stability [17] but a higher average wear rate of $4 \times 10^{-5} \text{mm}^3/(\text{Nm})$ in distilled and seawater [18]. This can be improved by reinforcing the PTFE with CF, which can reduce the wear rate to $0.2 \times 10^{-5} \text{mm}^3/(\text{Nm})$ under dry conditions and even more in a water bath [19]. UHMW PE was recently studied and showed good tribological properties combined with thermal and chemical stability and corrosion resistance, especially in aquatic applications, even without various fillers typically used, due to its good self-lubricating properties at temperatures up to 80 °C, with coefficient of friction of 0.12 and specific wear rate down $1.45 \times 10^{-6} \text{mm}^3/(\text{Nm})$ [20–24]. Polyoxymethylene (POM) is another commercially and mechanically acceptable substitute for the high-performance thermoplastics mentioned above. It is generally very stiff, has good impact strength and shows a coefficient of friction of less than 0.1 and a low wear rate, especially in water [25], and can be further improved when reinforced with various fillers (PTFE fibres or particles [26,27], hexagonal boron nitride nanoparticles (h-BN) [28], especially for higher loads). There are already many different applications for the above polymers, such as gear pumps [28], cylinders, pistons, piston rods and sealings [29], hydropower bearings [2], gears [30] etc.

The main requirements for modern environmentally acceptable lubricants (EALs) are to be both biodegradable and non-toxic under various operating conditions. Water alone is known as a non-flammable alternative with a strong cooling effect and is used in experiments as tap water, demineralised water or seawater. However, due to the corrosion sensitivity of the material and the almost 100 times lower kinematic viscosity of water compared to mineral oils, water affects the cost of the components involved [31]. It is usually mixed with various additives (wear protection, oxidation protection, friction modifiers) [32,33]. A similar approach to improving the physical and chemical lubricant properties also applies to commonly used natural oils, such as rapeseed, soybean, sunflower or castor oil [34,35]. Glycerol is another example of a non-toxic, biocompatible lubricant that is a major by-product of biodiesel production. Although it is the most abundant polyhydric alcohol in nature, it has often been neglected [36,37]. Unlike many conventional hydraulic fluids, which are based on mineral oils or synthetic compounds, glycerol is biodegradable and can be degraded by natural processes in the environment. This property reduces the risk of environmental pollution from leaks or spills in the hydraulic system. It can potentially produce a very low coefficient of friction, low wear and reduced corrosion, although it has a very high viscosity compared to conventional mineral base oils [36]. An even lower coefficient of friction was measured with aqueous glycerol solutions, especially with a water content of less than 20 wt.% within 40 s after the test. Water lowers the high viscosity of glycerol [38] and can simultaneously lower the freezing point of glycerol from +17 °C to −50 °C [39,40]. Since glycerol is highly hygroscopic, the coefficient of friction is already affected by the relative humidity of the environment, resulting in superlubricity in the range of 40 to 50% RH [36]. Aqueous glycerol solutions gave good results for both rolling and sliding bearing–steel contacts [41,42] under boundary, mixed and elastohydrodynamic conditions [36,41]. However, the results are very sensitive to solvent content and temperature [43], especially for boundary lubrication [44]. Similarly, light wear was measured in steel–steel contacts lubricated with glycerol with water and glycol, with a 50% lower coefficient of friction compared to gear oil [44]. All the above studies have investigated steel–steel contacts. Recently, various polymer–steel contacts expected in hydroelectric power plant bearings were tested in glycerol-based lubricant (with water and additives,
with unknown ratio) in water and under dry conditions [2]. The glycerol-based lubricant allowed the lowest measured coefficients of friction, with a reduction of up to 98%, and the lowest measured specific wear rates, reduced by up to an order of magnitude compared to dry conditions.

To be able to use such polymers and green lubricants in technical fields, it is necessary to investigate the tribological performance of these tribo-pairs under such conditions. The aim of this study is to investigate and gain better insight into the tribological properties of five selected polymer composites lubricated with glycerol and water as green lubricants. We compare the coefficient of friction, the wear rate and the wear mechanism that occurs in contact, as well as two different lubrication conditions. This will also lead us to more optimal operating conditions.

2. Materials and Methods

2.1. Materials

Five different polymers, namely: polyetheretherketone reinforced with 30% carbon fibres (PEEK CF30), PEEK MOD (PEEK reinforced with 10% CF, 10% graphite and 10% polytetrafluoroethylene), polytetrafluoroethylene reinforced with 25% carbon fibres (PTFE CF25), ultra-high-molecular-weight polyethylene (UHMW PE) and polyoxymethylene with 30% carbon fibres (POM CF30) were purchased as 30 mm diameter bars. The disc-shaped plate specimens were cut to 5 mm thickness, and finally, all specimens were polished to a roughness of 0.1 \( \mu \text{m} \) using an automatic device for polishing and preparing samples (RotoPol-21, RotoForce-3, Struers, Copenhagen, Denmark). Bearing balls made of hardened stainless steel (AISI 440-C) with a diameter of 25 mm were used as counterparts. All samples were thoroughly cleaned with medical benzene and ethanol and dried with dry compressed air. The properties of the materials used for the tests are listed in Table 1.

Table 1. Material properties of samples used and analysed in polymer–steel tribo-pairs.

<table>
<thead>
<tr>
<th>Name</th>
<th>Raw Material</th>
<th>Filler [wt%]</th>
<th>Modulus of Elasticity at 25 °C [GPa]</th>
<th>Poisson Coefficient ν</th>
<th>Water Absorption ISO 62 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer—plate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEEK CF30</td>
<td>PEEK</td>
<td>30% Carbon Fibres</td>
<td>6.8</td>
<td>0.38–0.44</td>
<td>0.02</td>
</tr>
<tr>
<td>PEEK MOD</td>
<td>PEEK</td>
<td>10% Carbon Fibres, 10% Graphite, 10% PTFE Fibres</td>
<td>5.92</td>
<td>0.38–0.44</td>
<td>0.3</td>
</tr>
<tr>
<td>POM CF30</td>
<td>POM</td>
<td>30% Carbon Fibres</td>
<td>3</td>
<td>0.35–0.49</td>
<td>0.01</td>
</tr>
<tr>
<td>PTFE CF25</td>
<td>PTFE</td>
<td>25% Carbon Fibres</td>
<td>1.1</td>
<td>0.46</td>
<td>0.05</td>
</tr>
<tr>
<td>UHMW PE</td>
<td>UHMW PE</td>
<td>/</td>
<td>0.76</td>
<td>0.4–0.42</td>
<td>0.01</td>
</tr>
<tr>
<td>Counterpart—ball</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AISI 440-C stainless steel</td>
<td>Carbon</td>
<td>16–18% Cr, max 1% Mn, Si, S, Mo</td>
<td>200</td>
<td>0.285</td>
<td>/</td>
</tr>
</tbody>
</table>

To get a better insight into the differences in the measured friction and wear data of the polymers, the micro-hardness was measured. The standard Vickers hardness (HV) tester (Leitz Miniload 2.0, Wild Leitz GmbH, Wetzlar, Germany) was used with an indentation force of 0.5 N, and each test was repeated at least six times.

2.2. Lubricants

Commercially available redistilled pure glycerol with a purity of more than 99.5% and demineralised water were used as EA lubricants. They were both analysed with an automatic viscometer (SVM 3001, Anton-Paar, GmbH, Graz, Austria). The kinematic
viscosity and density of the lubricants at room temperature, standardised to 40 °C, and the expected working temperature of 80 °C are shown in Table 2.

Table 2. The viscosity and density of glycerol and water at different temperatures.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>25 °C</th>
<th>40 °C</th>
<th>80 °C</th>
<th>25 °C</th>
<th>40 °C</th>
<th>80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>1.26</td>
<td>1.25</td>
<td>1.22</td>
<td>728.2</td>
<td>228.78</td>
<td>26.11</td>
</tr>
<tr>
<td>Water</td>
<td>0.99</td>
<td>0.99</td>
<td>0.97</td>
<td>0.89</td>
<td>0.66</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Measured at room temperature, glycerol has 815.8 times higher kinematic viscosity compared to water. Although the difference is smaller at higher temperatures, glycerol has a kinematic viscosity ~71.5 times higher than water at expected working temperatures in hydraulics. Given this difference, glycerol lubrication is expected to have much better tribological properties than water. If we compare glycerol with the standard hydraulic oil ISO VG 46, glycerol also has a much higher kinematic viscosity, from ~83 times at room temperature to ~2.4 times at higher temperatures, which means that both the coefficient of friction and wear should be very low.

Based on the polymers and lubricant properties (sample dimensions, radius) as well as the loading conditions (load, speed), the expected minimum lubricant film thickness was calculated and the characteristic film parameter (lambda ratio, λ) was calculated based on the Hamrock–Dowson equation [42,44]. The lubricants parameters for the calculation of the pressure viscosity index were assumed based on the literature [44]. In the case of glycerol, a mixed lubrication regime is expected, and in the water boundary regime [34,36,44].

2.3. Tribological Tests

The tests with a reciprocal steel ball on a flat, disc-shaped polymer plate were carried out on a high-frequency tribometer (TE 77, Cameron Plint, Phoenix Tribology Ltd., Newbury, England) at room temperature (25 ± 1 °C). The samples were completely immersed in the lubricant during the test (Figure 1).

![Figure 1. Schematic view of the ball-on-plate tribo-test used in this study.](image)

The friction and wear tests were performed at a constant average sliding velocity of 0.2 m/s and a stroke length of 2.4 mm, which corresponds to the highest device frequency of 40 Hz. This frequency, in combination with the shortest apparatus stroke length, simulated the high-speed movement of a hydraulic on/off valve poppet movement in a housing. The applied load was 50 N, which corresponds to a maximum Hertzian contact pressure from 40 MPa (for UHMW PE) to 160 MPa (for PEEK CF30). The coefficient of friction was measured during the 90-min test. All tests were performed at least 3 times to ensure repeatability. The following results represent the average measured values with the corresponding standard deviation.
2.4. Wear Evaluation and Characterisation of Worn Surfaces

After the tribological tests, the dimensions and profiles of the worn polymer surfaces and the wear scars of the balls were characterised using a 3D digital microscope with a nanopoint scanner (Hirox HRX-01 and NPS, Hirox Europe, Limonest, France). The wear volume was obtained from the 3D profile of the worn surface (Figure 2) based on the average cross-sectional area and the worn surface length (Mountains@9 surface analysis software). The cross-sectional area was measured on several places along the profile, according to ASTM G133-05 and compared to 3D profilometry results. The sliding distance was calculated from the average sliding velocity and the time of the test. Based on the estimated wear volume divided by normal load and sliding distance, the specific wear rate was calculated. To further reduce the error and deviation of the calculated wear volume, special attention should be given to the measurement of the total length of the wear track [45].

![Figure 2. Procedure for wear track measurement on polymer sample: (a) 2D digital image of worn surface; (b) 2D scanned profile; (c) 3D profile of worn volume; (d) measured cross-sectional area on a specific location.](image)

In addition, the topography of the worn polymer and counter–ball surfaces was investigated, and elemental analysis (energy dispersive spectroscopy—EDS) was performed using a scanning electron microscope (SEM; JEOL, JSM IT100, Tokyo, Japan) at an accelerating voltage from 15 to 20 kV. For this purpose, the polymer plates were sputtered with a 15 nm thick gold coating (SCD005, Bal-Tec AG, Balzers, Liechtenstein).

3. Results

3.1. Hardness

The average values of the measured Vickers hardness (HV) of the tested polymers are shown in Figure 3. As expected, the highest hardness was measured for the high-performance thermoplastic PEEK CF30. A comparable hardness was measured for PEEK MOD and POM CF30, but ~30% lower than for PEEK CF30. In the case of PEEK MOD, the combination of carbon fibres, PTFE, and graphite significantly reduced the hardness of the PEEK matrix, as was also found in previous studies on PEEK with PTFE fillers [46]. POM, which is considered an engineering polymer compared to the high-performance polymer PEEK [6], but when reinforced with 30 wt% carbon fibres, follow the hardness of PEEK composites. The lowest hardness was measured for both PTFE CF25 and UHMW PE, ~83% lower compared to PEEK CF30. Although the measured data indicate differences between the polymers, the detailed composition of the materials (morphology, dimensions, and arrangement of the fillers) was not taken into account. The measured hardness only gives a better indication of the differences in the measured friction and wear data.
The average values of the coefficient of friction measured during the 90-min test for all polymers are shown in Figure 4. For all polymers tested, it was observed that the coefficient of friction reached a steady state shortly after the start of the test when lubricated with glycerol. However, when lubricated with water, the polymers reacted differently. The shortest run-in time was observed for UHMW PE (~300 s) and PTFE CF25 (~800 s), followed by a stable coefficient of friction. Both PEEK CF30 and POM CF30 reached a stable state from 1500 to 2500 s. On the other hand, PEEK MOD reached the maximum value within the first 500 s of the test but then showed fluctuations in the measured coefficient of friction of up to 10% during the test.

The results show that the tests in glycerol and water are based on a different wear mechanism. Glycerol proves to be an effective lubricant for all polymers under the conditions tested. In water, however, the differences in the mechanical properties of the polymers tested, both the polymer matrix and the fillers, are highlighted.
3.2.2. Coefficient of Friction for Different Polymers

The average values of the measured coefficient of friction obtained from the tribological tests of the polymers are shown in Figure 5.

![Coefficient of friction for different polymers](image)

**Figure 5.** Coefficient of friction of tested polymers in water and glycerol.

In glycerol, a very low coefficient of friction was measured for all tested polymers, the lowest for PEEK CF30 and UHMWPE, around 0.023 and the highest for POM CF30, around 0.03. In glycerol, there was no significant difference between the measured coefficients of friction of the different polymers.

In water, the coefficient of friction increased significantly for all polymers tested compared to the glycerol-lubricated conditions. The smallest coefficient of friction was measured for UHMW PE, around 0.06, with a 2.8 times increase compared to the glycerol lubrication regime. The highest increase in the coefficient of friction was measured for PEEK MOD (8 times), followed by PEEK CF 30 (7.8 times). A significantly lower (up to 3.5 times for PE) and stable coefficient of friction, indicating effective lubricating properties of glycerol compared to water-lubricated conditions, was similarly observed in a recent study on polymers for hydropower bearings [2].

3.2.3. Specific Wear Rate for Different Polymers

The average values of the specific wear rate of the tested polymers are shown in Figure 6.

![Specific wear rate for different polymers](image)

In the experiments conducted in glycerol, the lowest specific wear rate was measured for the high-performance grade PEEK CF30, but interestingly PEEK CF30 was followed by PEEK MOD and the commercially affordable grade POM 30CF, with a specific wear rate in the same order of magnitude ($10^{-6}$ mm$^3$/Nm)). The highest wear rate ($10^{-6}$ mm$^3$/Nm)) was measured for the PTFE CF25. A significantly higher specific wear rate compared to the first three composites was also measured for UHMW PE, as both PTFE CF25 and UHMW PE had significantly lower hardness values compared to the other three composites.

When tested in water, the specific wear rate increased for all polymers tested compared to glycerol-lubricated conditions. Interestingly, the lowest change in specific wear rate was observed for UHMW PE (only two times), similar to the study on reinforced UHMW PE, which was tested in EAL and water [2]. The highest increase in specific wear rate was measured for PEEK MOD (300-fold), indicating that the combination of fillers used does not produce a synergistic effect in reducing wear or the coefficient of friction for the high-performance PEEK matrix, as is the case when only carbon fibres are added (PEEK CF30). The most promising result was again provided by PEEK CF30, with a specific wear...
rate of $9.5 \times 10^{-7}$ mm$^3$/(Nm). In addition, POM CF30 successfully followed both PEEK CF30 and UHMW PE in water under much harsher test conditions ($\sim 2 \times 10^{-6}$ mm$^3$/(Nm)) and a comparable specific wear rate of about $3.4 \times 10^{-6}$ mm$^3$/(Nm) was measured. Both PEEK MOD and PTFE CF25 showed a specific wear rate in a higher order of magnitude ($\sim 10^{-5}$ mm$^3$/(Nm)) compared to the other polymers.

![Graph showing specific wear rate of polymers in water and glycerol.](image)

**Figure 6.** Specific wear rate of tested polymers in water and glycerol.

### 3.3. Digital Microscopy and SEM

To be able to compare the wear tracks of the polymers in glycerol and water, typical wear scars are shown in Figure 7a–e. As can be seen from the figure, the wear scar is narrow and difficult to be detected for all polymers when lubricated with glycerol, except for the polymer PTFE CF25. The first three polymers (Figure 7a–c) have a comparable wear scar width, while PTFE CF25 and UHMW PE have a wear scar up to 2.8 wider. In water, the intensity and width of the wear scars increased for all polymers. However, the smallest change in wear scar width was observed for PEEK CF30, followed by POM CF30, which is consistent with the measured specific wear rate (Figure 6). The greatest change in wear scar dimensions when lubricated with water was observed for PEEK MOD. Although scratches in the sliding direction were present in glycerol, the exact edge of the wear scar was difficult to identify with the digital microscope. Based on the measurements (Figures 5 and 6) and the observed wear scars (Figure 7), glycerol was able to form a film thick enough to divide the contact areas and protect the polymers, especially PEEK CF30, PEEK MOD and POM CF30, from severe wear.

In contrast, the wear scar in water is clearly defined for all polymers with clearly defined edges, but also with a distinct central part of the wear scar. In the central part of the wear scar, where the sliding velocity and the contact area are most constant, there are stronger scratches, especially for PEEK CF30, PEEK MOD and UHMW PE (Figure 7a,b,e). To get a better insight into the wear mechanism, SEM images were taken at the edge of the wear scar and in the central part of the wear scar (Figure 7a–e).

At PEEK CF30, the edge of the wear scar is clearly defined and shows adherent material. There are scratches in the direction of sliding and carbon fibres exposed at the surface but well integrated into the PEEK matrix. As we move to the central part of the wear scar, the scratches become more intense and denser, indicating an abrasive wear mechanism. Although the carbon fibres are fine-defined, they are well integrated into the PEEK matrix, indicating that they are capable of bearing the load. This is consistent with the lowest increase in the specific wear rate of PEEK CF30 in water, compared to the glycerol regime, but also with the lowest specific wear rate in the water among the polymers tested.
Figure 7. Wear scar of tested polymers (a) PEEK CF30; (b) PEEK MOD; (c) POM CF30; (d) PTFE CF25; (e) UHMW PE in water and glycerol with accompanied SEM images of wear scar edge (inside wear scar on the left, outside of wear scar on the right) and central part of polymer wear scar in water.
In the case of PEEK MOD, although the edge of the wear scar is pronounced, the scratches are not as intense as in PEEK CF, and the surface of the scar is smoother, probably due to the presence of PTFE and graphite, known as good solid lubricants. There is also evidence of destruction of the PEEK matrix, which means that adhesive wear is present. In the central part of the wear scar, there are signs of severe destruction of the matrix, accompanied by strong scratches in the sliding direction. The fibres are broken and partially pulled out of the material. PTFE and graphite incorporated as reinforcement in PEEK MOD are well-known solid lubricants and are, therefore, often added to high-permanence PEEK to improve tribological properties, especially under dry sliding conditions [13,17,46–49]. In our experiments, however, PEEK MOD could not follow PEEK or POM, which were reinforced with CF, especially under harsh conditions in water. The images of SEM show that the PEEK matrix in PEEK MOD does not have good interfacial adhesion of CF (as in the stable PEEK CF30) and that there is evidence of severe damage to the graphite sheets. In addition, PTFE could possibly be responsible for the lower hardness of PEEK MOD compared to PEEK CF30 [13,48] and has been shown to be very sensitive to contact pressure [11,50]. The right combination of fillers also improves the properties of the composite, and PTFE with CF alone has a good synergistic effect, which is compromised by the addition of additional fillers [13]. At POM CF30, the edge of the wear scar is clearly defined, with wide scratches in the sliding direction and reinforcing fibres well integrated into the matrix but also well exposed. In the central part of the wear scar, the scratches are more intense and cracks in the matrix near the fibres are also evident. Although the fibres are covered with adherent material and can carry the load, the matrix is not as stable as the PEEK CF30 matrix and starts to crack. This is probably why we measured a comparable but higher specific wear rate than PEEK CF30.

In the case of PTFE CF25, the wear scar is the largest, but at higher magnification, only signs of micro-delamination of the matrix can be seen, with no clear difference between the worn and the original surface. In the central part of the wear track, pale scratches in the sliding direction are also present.

In the case of UHMW PE, the surface of the wear scar looks smoother than the untreated material outside the wear track. Only in the middle part of the wear track are deep, abrasive grooves present in the sliding direction, indicating strong delamination of the matrix.

When analysing counter ball surfaces, the wear scar with transfer film is present in water for all polymers except for UHMW PE. The wear scars on the ball surfaces are shown in Figure 8a–d, together with the SEM images and the elemental mapping of the marked areas of the transfer films. The wear scar on the counterface was the smallest at PEEK CF30, which is consistent with the smallest specific wear rate measured (Figure 5) and the most stable polymer matrix with fine-integrated fibres (Figure 7a). This is followed by the counterface wear scar for PTFE CF25, which corresponds to the material with the lowest measured hardness. For POM CF30 and PEEK MOD, a much larger area of counterface wear scar was measured (2.7 to 6 times). In all cases, grooves in the sliding direction are present, and in some of them, a transfer film can be seen. The presence of carbon in the form of scratches in the valleys of the counterface proves the transfer film, according to the elemental analysis, although it can be from (PEEK, POM, PTFE) polymer or the reinforcements [51]. Further detailed analysis would only allow us to determine the exact origin and structure of the transfer. Based on the current analysis, the thickest transfer film was found for POM CF30, which is consistent with the relatively low coefficient of friction measured for POM CF30 compared to the two PEEK polymers, which have comparable microhardness. In the case of UHMW PE, which has excellent tribological properties in water [21], we used pure polymer without reinforcements in our study. Therefore, no continuous transfer film could be found, similar to the results of previous studies [52].
4. Discussion and Conclusions

In this paper, we have analysed the tribological properties of five polymer composites that are considered high-performance or excellent engineering polymers [53]: PEEK CF30, PEEK MOD, POM CF30, PTFE CF25 and UHMW PE. The polymers were compared based on their tribological performance under glycerol and water-lubricated conditions as two basic sustainable lubricants. The tribological tests with the reciprocating steel–ball on polymer disc tests were performed with parameters simulating the movement of a poppet in hydraulic valves. Following the tribological tests, wear tracks were analysed, which provided a better understanding of the tribological mechanisms involved.

In order to understand and compare five very different tested composites, it is possible to analyse different factors that can potentially affect COF or/and wear rates, such as...
intrinsic material parameters (size and orientation of reinforcement fibres/particles, the roughness of specimens, etc.) and extrinsic parameters (temperature, pressure, hydrothermal ageing, load, sliding velocity, sliding time) that are part of studies on polymers or lubricants [6,8,34,53]. The results of the tribological tests performed in glycerol prove glycerol’s excellent performance as a lubricant, which agrees with recent studies of steel–steel tribo-pairs in glycerol and different glycerol solutions [36,38,41,42,44]. The coefficient of friction was very low, ~0.02 and comparable for all polymers tested. All polymers performed significantly better in glycerol, especially the high-performance PEEK composites and POM CF30. PEEK CF30, PEEK MOD and POM CF30, as polymers with higher and comparable measured microhardness, showed a lower specific wear rate compared to PTFE CF25 and UHMW PE. We assume that glycerol can form an effective lubricating film in this case.

In water, under harsh lubrication conditions, the mechanical properties of the individual materials were exposed. Under water-lubricated conditions, both the coefficient of friction and the specific wear rate increased significantly for all polymers tested. The high-performance polymer PEEK CF30 showed the lowest specific wear rate, interestingly followed by the affordable engineering polymer POM CF30. Both showed stable polymer matrices with well-integrated carbon fibres and abrasion as the main wear mechanism. However, POM CF30 showed a lower measured coefficient of friction under water-lubricated conditions, probably due to the transfer film on the ball mating surface. Both PEEK MOD and PTFE CF25 showed a significantly higher specific wear rate in water, indicating cracking in the matrix and adhesion as the predominant wear mechanism. Materials with lower hardness retained a lower coefficient of friction, since both PTFE and UHMW PE are known to be good solid lubricants [20,47]. However, they could not match the low specific wear rate of stiff high-performance materials reinforced with CF. For harsh lubrication conditions, either a different reinforcement should be considered for PTFE and UHMW PE, or they should be used for different loading conditions.

For the three polymers tested with higher measured microhardness, namely PEEK CF30, PEEK MOD and POM CF30, glycerol can be used as a base lubricant to reduce both the coefficient of friction and specific wear compared to water-lubricated conditions. Glycerol was not as effective in reducing the specific wear of UHMW PE and PTFE CF25.

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