ON POLYOXYMETHYLENE COMPOSITE FOR SUSTAINABLE HYDRAULIC VALVES

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ABSTRACT

The aim of this study was to investigate the tribological properties of polyoxymethylene reinforced with carbon fibres which has proven to give comparable results to high performance polyetheretherketone, regardless their price difference. The results obtained in glycerol-water mixture were compared with the results of tests using conventional hydraulic oil and demineralised water as lubricant. The tests were performed at room and elevated temperature, as expected in hydraulic applications.

The results showed very low coefficient of friction and specific wear rate in glycerol-water mixture, comparable to the values measured in standard hydraulic oil (COF ~ 0.027 - 0.033, specific wear rate ~ 10^{-7} mm^3/Nm), and lower than measured in water (COF ~ 0.14, specific wear rate ~ 10^{-6} mm^3/Nm), at room temperature. At elevated temperature, coefficient of friction slightly increased in hydraulic oil and glycerol-water mixture, but decreased in water, and values become comparable for all lubricants. Specific wear rate significantly increased in hydraulic oil and glycerol-water mixture at elevated temperature, and became comparable to the specific wear rate measured in water. Based on results, both polyoxymethylene composite and glycerol-water mixture can be good alternative for standard hydraulic oil and steel tribo-pairs, leading towards excellent tribological properties.

Keywords: polymer composites, green lubricant, water, glycerol, friction, wear, hydraulics

1. INTRODUCTION

Hydraulic systems are widely used technologies in industry as high-power density systems that enable large forces, rigidity and endurance. The general challenge in improving the efficiency of a variety of sliding contacts is to reduce the coefficient of friction and control the wear mechanism for individual applications. This has often led to the development of new components or new materials and lubrication technologies [1]. Hydraulic systems are usually powered by standard mineral oil-based hydraulic oils. Today, we are aware that we have limited supplies of mineral oils, which are also harmful to nature and people, and require expensive disposal/storage after use [2]. Green tribology combines the classic challenges of tribology with an ecological approach that protects the environment and reduces health risks. One of the challenges on the way to sustainable hydraulics is the use of environmentally friendly green lubricants in combination with lightweight high-performance polymers, especially in the food industry, marine, automotive, aerospace, forestry and mobile machinery. These efforts and strategies for better wear protection and friction reduction in various equipment could potentially reduce such energy losses up to 40 % in the long term [3].

In the last decade, numerous studies have been conducted on the tribological properties of various high-performance polymer-based composites [3]. They have proven to be an excellent alternative to the classic elements made of steel, in various industrial applications for gears, pumps, cylinders, seals, bearings etc. [4–8]. These polymers have considerably higher strength-to-weight ratio compared to steel alloys, which implies potentially significantly lighter components. High-performance polymer composites based on polyetheretherketone (PEEK), polyphenylene sulphide (PPS), ultra-high molecular weight polyethylene (UHMWPE) or polytetrafluoroethylene (PTFE) have shown good tribological properties under dry conditions or in water [9]. Their tribological properties can be improved with various functional fillers that could extend their service life, or further reduce friction and wear, as well as improve the response at higher loads, sliding speeds, pressure or temperatures [10]. Polyoxymethylene (POM) is a commercially acceptable substitute, with up to 10 times lower price compared to ultra-high performance polymers mentioned above [11]. It shows low coefficient of friction (COF) and specific wear rates in water, especially when reinforced with various fillers (PTFE fibres or particles [12], hexagonal boron nitride nanoparticles (h-BN) [13], especially for higher loads). In our recent study POM reinforced with CF30 gave comparable results in pure glycerol and water to four different high performance polymer composites [14].

The type of lubricant used is another aspect in the analysis of sliding contacts. Green lubricants are becoming mandatory in maritime and hydropower units. They are also increasingly desirable in forestry and mobile machinery [2] . Environmentally adaptable lubricants (EALs), such as vegetable oils, synthetic esters, polyalphaoleins, polyglycols and water, show low toxicity, excellent biodegradability and can be further improved tribologically by chemical modifications or by different anti-wear additives, antioxidants, etc.[15]. Glycerol is another good example of an environmentally friendly, non-toxic, biocompatible lubricant, which is main by-product of biodiesel production [16] . From an environmental point of view, glycerol could therefore be a better option for use in fluid power systems. Glycerol as a lubricant can potentially provide a very low coefficient of friction, enable low wear and reduce corrosion, although it has a very high viscosity, almost 20 times higher than traditional mineral based oils [17, 18]. Such high viscosity is not particularly desired, as it results in greater energy losses, more energy is required to overcome a thicker lubricating film, leading to lubricant breakdown and likely earlier components or system failures. However, since glycerol dissolves in water, the freezing point [19, 20], film thickness and viscosity of glycerol can be reduced by adding an appropriate amount of water. In this way, even a so-called liquid superlubricity can be obtained, with a friction coefficient of less than 0.01 reported [21]. Aqueous solutions of glycerol show good results in steel sliding contacts of rolling and sliding bearings [22, 23], especially when the water content is below 20 %, under different tribo-test conditions (different nominal stress and sliding speeds) [21]. Aqueous solutions of glycerol show good properties under boundary, mixed and elastohydrodynamic conditions [18, 22], although they are very sensitive to the water content under boundary lubrication conditions. When glycerol is used as a lubricant, there is data on a very low coefficient of friction even at higher contact pressures or sliding speeds between steel tribological couples [24]. So far, studies have mainly focused on the use of glycerol-aqueous solutions in conventional steel/steel contacts. Few studies address the simultaneous use of polymer composites and glycerol or similar green lubricants [14, 25].

Nowadays, it is very important to find an alternative solution for both innovative tribo-materials and for hydraulic fluids that are easier to obtain and that are safe for human health both in case of possible leakage and storage. The aim of this study is to analyse the tribological properties of commercially available pure POM and POM reinforced with 30 % carbon fibres (CF) in glycerol-water mixture. To evaluate such a green lubricant, we will compare the tribological properties of the selected polymer-steel sliding contact with wear and friction parameters in standard ISO VG46 hydraulic oil and the oldest environmentally adaptable lubricant, demineralized water. We will also compare and analyse their tribological properties at different working temperatures (room and elevated) and at two different loading speeds.

2. METHODS

2.1. Materials – samples and lubricants

For the tribological tests we prepared pure POM and POM reinforced with 30 % carbon fibers (POM CF30) samples. The polymer discs were cut from commercially available 30 mm diameter rod to a thickness of 5 mm. The polymer samples were polished in several steps using a RotoForce-3 automatic sample polishing and preparation device, to a final roughness of 0.1 µm. The ball was a commercially available, standard hardened bearing ball, 25 mm in diameter, made of AISI 440-C stainless steel. Before each test, the samples, clamps and ball were cleaned in ethanol and dried in air.

The first lubricant was commercially available, most commonly used ISO VG46 hydraulic oil. The second lubricant was a glycerol-water mixture. Commercially available redistilled glycerol, with a glycerol content ≥ 99.5 %, was used for preparation of 40 % glycerol and 60 % water (G+W) mixture lubricant. Based on our preliminary studies, by adding up to 40 % of water in the mixture, the good lubricating properties of pure glycerol remain, for a different polymer composites tested at room temperature. Demineralized water (W) was used as a third reference lubricant. The properties of selected lubricants were determined using an automatic viscometer SVM 3001 (Anton-Paar), which are in presented in the Table 1.

Table 1: Lubricants properties

Lubricant	Kin. Viscosity at 25 ◦C [mm^2/s]	Kin. Viscosity at 80 ◦C [mm^2/s]	Density at 25 ◦C [g/cm^3]	Density at 80 ◦C [g/cm^3]
ISO VG46	100	9	0.86	0.86
G+W	11.59	2.19	1.17	1.12
W	0.89	0.36	0.99	0.97

2.2. Tribological tests – experimental procedure

Tribological tests were performed on a Cameron-Plint TE 77 high-frequency tribometer (Figure 1). During the test, the steel bearing ball slides in a reciprocal mode on the polymer disk-like plate. The average sliding velocity was set to 0.2 and 0.02 m/s (frequency 40 Hz and 5 Hz, respectively, with stroke length 2.4 mm). The normal load was set to 50 N (90 -150 MPa maximum Hertzian pressure). Before each test, the polymer samples were completely immersed in the selected lubricant. The thermoset was placed in the lubricant bath, with a heating element under the bath to control the temperature and keep it constant during the test (at elevated temperature of 80 ^{o}C). Special care was taken to maintain the constant lubricant level during the test so that the tribo-pair was always fully immersed in the selected lubricant. After each test, the contact sliding area was marked on the ball with the help of an electric pen.

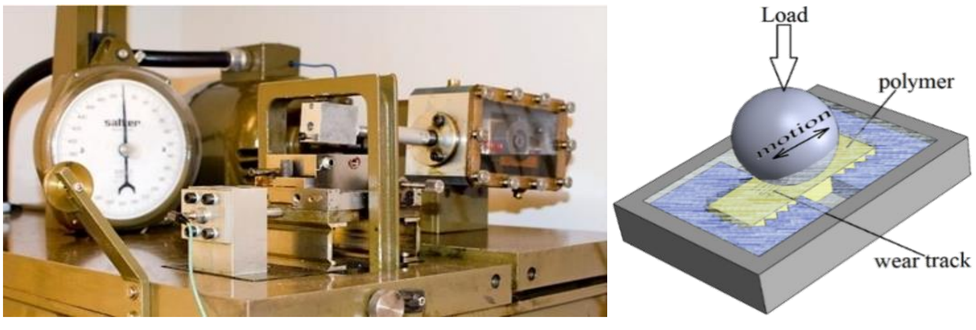


Figure 1: Scheme of tribological tests

During the tests, the current value of the friction coefficient was automatically recorded. The tests were performed for 90 minutes based on preliminary tests, which showed a stable value of the coefficient of friction was reached. Each test was repeated three times, and the average value of the steady-state friction coefficient is used for the comparison analysis.

2.3. Wear evaluation

The wear volume of the polymer discs was calculated from the dimensions of the wear tracks, which were measured using a 3D digital microscope with an additional nano-point confocal profilometer Hirox HRX-01 & NPS after the tribological tests. We determined a 3D profile for each calotte, from which the dimensions of the wear calotte and characteristic cross-sections were read on several characteristic locations along the wear track profile with Mountain Map software [14].The procedure is presented on Figure 2. The digital microscope also made it possible to determine the shape and dimensions of the surface films on the steel ball.

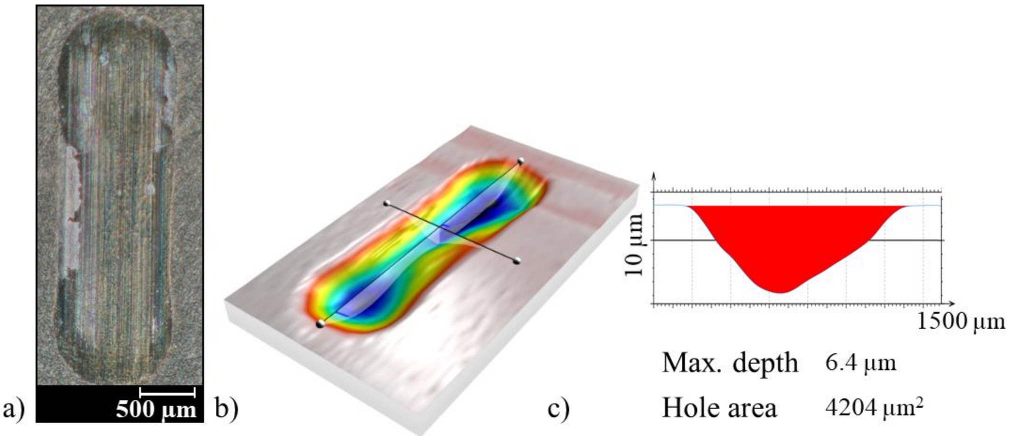


Figure 2. Procedure for wear analyses with a 3D digital microscope and Mountains Map software a) 2D digital image of worn surface's topography; b) 3D profile of worn volume; c) Measurement of cross-sectional area at a specific location.

3. RESULTS

3.1. Running in time

Figures 3 and 4 show the evolution of measured coefficient of friction during individual tests. When lubricated with ISO VG46 and G+W mixture, COF reaches a stable value very quickly, within the first 100 s of the test regardless the loading speed or temperature. The curves measured for POM follow the values measured for POM CF30. However, the COF measured in the water increases within the first 1000 s for POM, and for about 3000 s for POM CF30. Measured values for reinforced POM are considerably higher, and unstable compared to both pure POM and measurements in the other two lubricants.

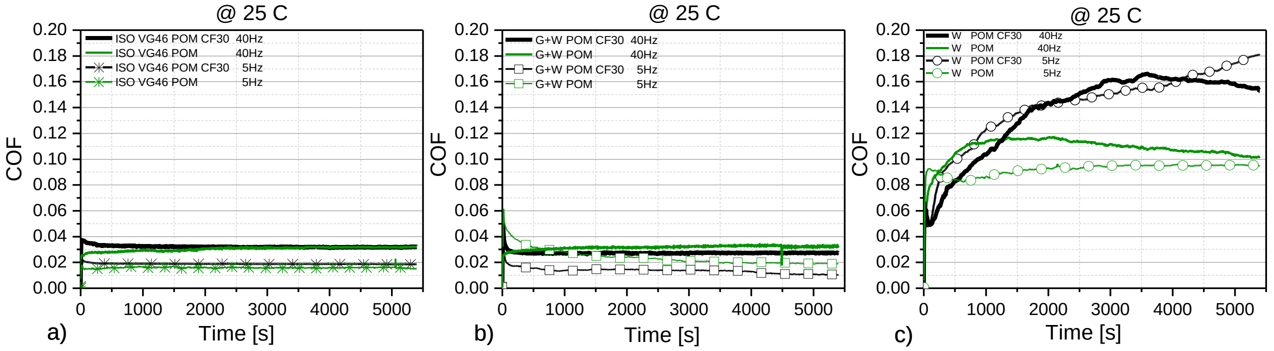


Figure 3: Coefficient of friction evolution during the tribological test of POM CF30 and POM in three different lubricants: a) ISO VG46; b) Glycerol + Water; c) Water all at room temperature

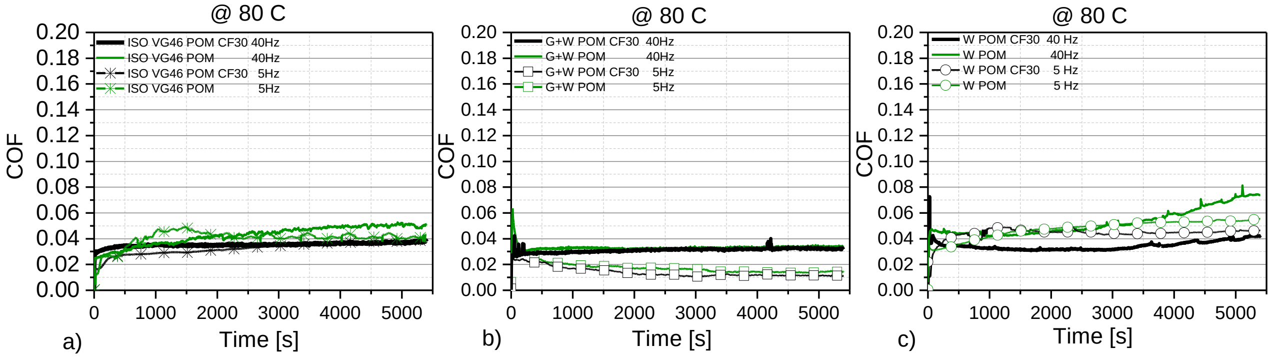


Figure 4: Coefficient of friction evolution during the tribological test of POM CF30 and POM in three different lubricants: a) ISO VG46; b) Glycerol + Water; c) Water all at 80 °C

Based on the results of measurements, the G+W mixture enables a good lubricating film, comparable to hydraulic oil. The increase in the measured average coefficient of friction observed in water indicates that the lubricating fluid film was not able to effectively separte friction surfaces of polymer plates and steel counterpart. Fluctuation observed in case of POM CF30 indicate, that reinforcements under such severe wear conditions incorporated additional instabilities.

3.2. Coefficient of friction

The average values of the steady-state coefficient of friction in ISO VG46 oil, G+W mixture and water are shown in Figure 5. The results showed comparable and low values of the coefficient of friction of 0.033 and 0.027 in the case of POM 30CF in oil and G+W mixture at room temperature. The measured values of the friction coefficient of POM CF30 in water are up to 6 times higher at room temperature.

It can also be seen from Figure 4 that the friction coefficients of the considered contacts in hydraulic oil and G+W mixture are comparable even in the case of lower sliding speed and at higher temperature. At a lower loading speed, there is a 40 % decrease in the coefficient of friction in the considered POM CF30 contacts in oil and G+W mixture. The decrease is smaller (10 %) at higher temperature in oil, and higher (60 %) in G+W mixture. Overall, COF increases at higher temperature in oil and G+W mixture, but not significantly.

On the contrary, in water COF does not change significantly at lower loading speed. However, measured COF decreases at higher temperature for both POM CF30 (4 times) and pure POM (2 times) in water, and measured values become comparable to values measured in hydraulic oil and G+W mixture.

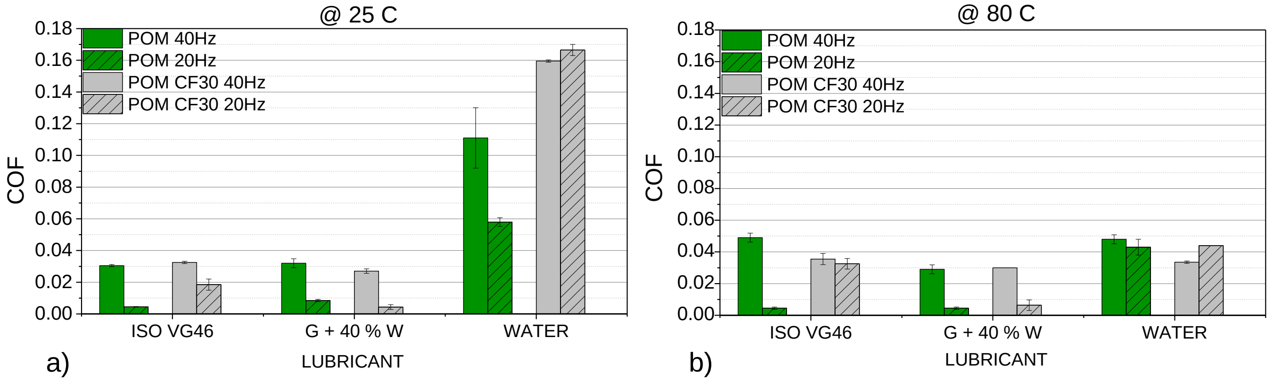


Figure 5: Average values of coefficient of friction ± sd of POM CF30 tested in three different lubricants: a) at room temperature; b) at 80 °C.

3.3. Specific wear rate

Based on the cross-section measured along the 3D profile and overall dimensions of the wear track, we calculated the specific wear rate of the polymer discs in contact with the steel ball, in the case of using hydraulic oil ISO VG46, G+W mixture and demineralized water as lubricants, which is shown in Figure 6.

Specific wear, like the coefficient of friction, is comparable when using ISO VG46 hydraulic oil and G+W mixture, and most values for POM CF30 are in the range of 10^{-7} mm^3/Nm, and in the range of 3 x 10^{-8} mm^3/Nm for pure POM. The specific wear rate in both lubricants is lower than measured in water (~ 3 - 6 x 10^{-6} mm^3/Nm for POM CF30, ~ 3 x 10^{-7} mm^3/Nm for pure POM), at room temperature.

Specific wear rate significantly increased in hydraulic oil and glycerol-water mixture at elevated temperature, and became comparable to the specific wear rate measured in water (~ x 10^{-6} mm^3/Nm).

Specific wear is in general higher at lower sliding speed in for all lubricants tested.

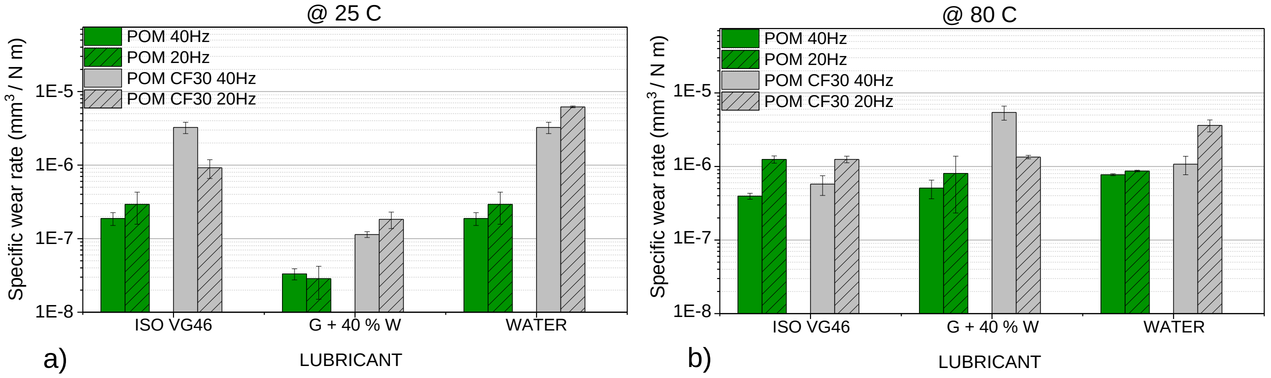
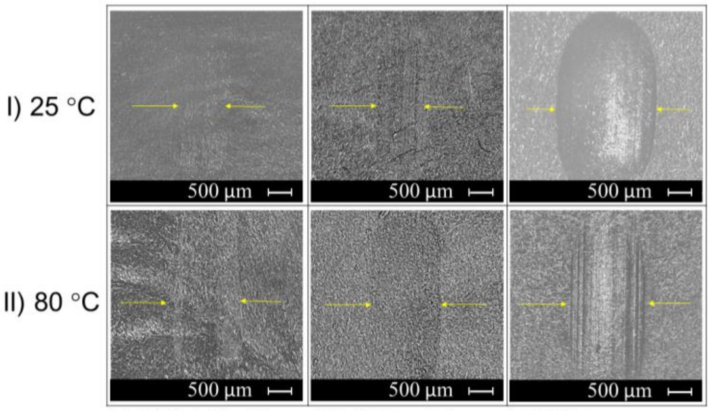


Figure 6: Average value of specific wear rate ± sd of POM CF30 tested in three different lubricants a) at room temperature; b) at 80 °C

3.4. Worn surfaces analyses

Selected worn surfaces of the polymer samples observed by optical microscopy are presented in Figures 7 and 8. The surface appearance of POM 30CF is similar in shape and size (width ~900 µm, length ~3500 µm) in ISO VG46 oil (Figure 7.I.a) and G+W mixture (Figure 7.I.b). The wear track is only approximately 2 times wider at elevated temperature (width ~1400 µm). The wear mechanisms of POM composites in oil and G+W mixture are similar; lubricants form film thick enough to separate surfaces in contacts. However, the narrowest wear track was observed in case of oil at room temperature and at higher frequency (~ 936 µm, Figure 6.I.a). The wear track is not significantly wider in glycerol + water mixture (~ 8 % increase) at room temperature, although the scratches' along the sliding direction are observed, especially in the middle of the wear scar (Figure 7.I.b). In case of pure water used at room temperature, both wear track width (~ 2.5 times increase), the number and intensity of scratches is significantly higher (Figure 7.I.c).

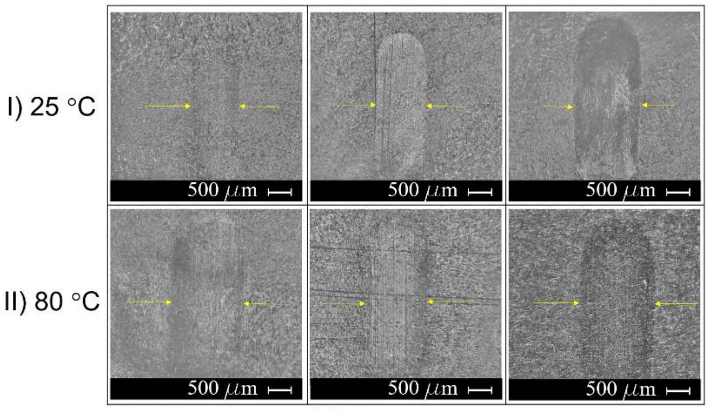
At elevated temperature, the worn surfaces are on average 50 % wider at approximately the same length (Figure 7.II.a/b) in oil and G+W mixture. On contrary, in the water scratches become more intense, although overall wear track width does not change significantly.



(a) ISO VG 46 (b) GW mixture (c) Water

Figure 7: Digital images of worn POM CF30 polymer surfaces at (I) room and (II) elevated temperature, lubricated with: (a) Oil ISO VG46; (b) Glycerol-water mixture; (c) Water all at 40 Hz

At lower frequency (Figure 8.a-c) there was no significant difference in the wear track dimensions among oil and G+W mixture at both temperatures, in water the wear track was slightly (~ 10 %) wider. The main difference was observed in wear mechanism since the wear scratches along the sliding direction are more intense in case of G+W mixture, especially at higher temperature (Figure 8.II.b). This agrees with considerably higher specific wear measured in POM CF30 at elevated temperature, compared to oil or water (Figure 6.b). At elevated temperature, wear track width was comparable among lubricants (~ 1522 µm, Figure 8.II.a-c), and not significantly changed compared to room temperature conditions. The difference was in the scratch's intensity and depth, being the least intense in case of oil.



(a) ISO VG 46 (b) GW mixture (c) Water

Figure 8: Digital images of worn POM CF30 polymer surfaces at (I) room and (II) elevated temperature, lubricated with: (a) Oil ISO VG46; (b) Glycerol-water mixture; (c) Water all at 5 Hz

4. DISCUSSION AND CONCLUSONS

In this study we have analysed the possibility of using an affordable engineering polymer POM CF30 in combination with a G+W mixture as a green lubricant as a potential tribo-pair for hydraulic applications. For reference and comparison, the same contacts were tested in ISO VG46 hydraulic oil and demineralised water, as the most widely available green base lubricant. The experiments were performed with parameters that correspond to seat on-off valves, and according to the experiment equipment limits. Using such polymer composites could potentially enable lighter hydraulic components, with excellent tribological properties. Additionally, new additive technologies could enable relatively quick prototyping accompanied with new component design. The tests were conducted at room temperature and elevated temperature, as expected in hydraulic applications, with the samples fully immersed in the selected lubricant. The tests were performed at two different sliding speeds.

Glycerol is an alternative lubricant whose annual production exceeds the demand for the same. Our recent study proved good tribological properties of pure glycerol for five different polymer composites [14]. Among observed composites, POM reinforced with 30 % carbon fibres successfully followed high performance PEEK reinforced with 30 % carbon fibres by tribological performance.

The results of this study show low values of the coefficient of friction of POM CF30 when G+W mixture is used as lubricant, at room temperature and elevated temperature and at both frequencies tested. The values of the coefficient of friction were similar when comparing G+W and ISO VG46 hydraulic oil. At room temperature, the coefficient of friction was up to 6 times higher in water than in oil and G+W mixture. At elevated temperature, however, the difference was not significant, although the lowest value was measured in the G+W mixture (0.03). At lower frequencies, a similar trend of COF decrease in the G+W mixture and oil was observed.

The specific wear rate was also lower in the G+W mixture and hydraulic oil, especially at room temperature (~ 10^{-7} mm^3/Nm). When comparing G+W mixture and hydraulic oil with water as lubricant, we measured one order of magnitude higher specific wear rate. At higher temperatures, the difference between the lubricants decreased as an increase in the specific wear rate was observed. At lower frequencies, a higher specific wear rate was observed, which is related to the more intense scratches observed. However, at higher temperatures, all specific wear rate values increased and there was no significant difference between the lubricants (the order of x 10^{-6} mm^3/Nm). Water proved to be a less effective lubricant at both frequencies and at room temperature compared to a G+W mixture and compared to water. At higher temperature, however, the difference decreased significantly.

Compared to the measurements of pure POM, in our recent study, a similar trend was observed in the measured coefficients of friction (influence of water, higher temperature, or lower frequency), but higher values of COF were measured overall for pure POM than for POM reinforced with 30 % CF. In contrast, lower values of specific wear rate were observed for pure POM compared to reinforced POM. This effect is probably due to the fact that in the case of reinforced POM the carbon fibres carry most of the applied load, but at the same time the thinning of the fibres indicates a fracture of the POM matrix and a higher wear rate [27]. However, further elemental or spectroscopic analysis of the worn surfaces is required to discuss the difference in detail. Based on the current measurements, POM CF30 gives excellent tribological results in both hydraulic oil and a G+W mixture and can be considered as a potential material or even a combination of material and lubricant for hydraulic applications where low load and high frequency are expected.

NOMENCLATURE

EAL	Environmentally adapted lubricants	
POM	Polyoxymethylene	
PEEK	Polyetheretherketone	
PPS	polyphenylene sulphid	
UHMWPE	ultra-high molecular weight polyethylene	
PTFE	polytetrafluoroethylene	
CF	Carbon Fibre	
G+W	Glycerol + Water mixture	
W	Water	
COF	Coefficient of friction	/

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