POLYMERS FOR SUSTAINABLE HYDRAULIC VALVES TESTED IN WATER, GLYCEROL-WATER MIXTURE AND HYDRAULIC OIL

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Engineering polymers such as polyoxymethylene (POM) have proven to have very promising tribological properties and successfully follow high performance thermoplastics. The focus of our research is on testing and analysing POM for very demanding, harsh working conditions of high-speed hydraulic on/off valves. The samples were tested and compared to POM reinforced with 30 % carbon fibres in standard hydraulic oil ISO VG 46, water, and glycerol-water mixture at room and elevated temperature, and at different sliding speeds. The results showed good tribological properties for both polymers when lubricated with glycerol-water mixture, comparable to the results obtained in hydraulic oil but lower than those measured in water. However, the difference decreases at higher temperature. The results also showed an opposite trend of decrease in the coefficient of friction and increase of specific wear rate at lower sliding speed, with a similar trend at higher temperature.

Keywords: polymers, polyoxymethylene, glycerol, water, hydraulic valve



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1 Intruduction

The use of low weight and high strength polymers and polymer composites instead of metals, for manufacturing different fluid power elements and components has great potential for reducing components weight and energy losses [1]. Compared to traditionally used steel alloys, the strength-to-density ratio of reinforced polymer composites is 13.5 times that of steel [2]. In the recent study on hydraulic cylinders, the prototype based on the radial stiffness design method and composite structure has reduced weight by 56.86 % while maintaining the same performance as the conventional metal hydraulic cylinder [3]. Additionally, polymer composites have proven to produce very low coefficient of friction and specific wear rate at different loading regimes [4]. By combining the advantages of the new surfaces, materials, and lubrication technologies for friction reduction and wear protection in various equipment worldwide, energy losses caused by friction and wear could potentially be reduced by 18 % in the short term (8 years), or as much as 40 % in the long term [5].

Among different polymer composites, ultra-high performance polymers such as PEEK (Polyetheretherketone), high performance polymers such as PPS (Polyphenylene sulfide), engineering polymers such as POM (Polyoxymethylene), UHMWPE (ultra-high-molecular-weight polyethylene), PA (Polyamides) or commodity polymers such as PE (Polyethylene), PTFE (Polyeterafluoroethylene) have been investigated and analysed with different fillers, reinforcements for different loading conditions and applications [5]. From ultra-high-performance polymers down to commodity polymers, mechanical properties change in contrast to polymer price (representative polymers are compared to AISI 440C stainless steel [4–6] in Table 1).

POM is one of the 'middle range' polymers, with price up to 10 times lower, compared to ultra-high-performance polymers. It has low cost, low weight and low water absorption along with good tribological properties, which makes it one of the most commonly used engineering polymers [7, 8]. It can successfully follow both PPS and PEEK performance when used for gerotor gears, or even follows the performance of the classic metallic pressure relief valve [1].

Polymer group (representative polymer)	Density [kg/m ³]	Young modulu s [GPa]	Ultimate tensile strength [MPa]	Operating temperature [°C]	
Ultra-high-performance (PEEK)	~ 1.32	~ 4.2 - 8.1	~ 110	up to 250	
High-performance (PPS)	~ 1.43	~ 3.3 - 4.4	~ 75	up to 220	
Engineering (POM, UHMWPE, PA)	~ 1.13-1.5	~ 1.7 - 3.3	~ 40 - 80	up to 120	
Commodity (PE, PTFE)	~ 2.18	~ 0.5	~ 10	up to 100	
Stainless steel representative					
AISI 440 C	~ 8	~ 200	~ 760 - 1960	up to 1100	

Table 1: Sample properties

Usually, polymer composites are tested under dry or water lubricated conditions. However, hydraulic oil is commonly used lubricant for hydraulic applications. Nowadays, green lubricants are becoming mandatory in marine or forestry machinery [9], and extremely wanted in all different sorts of mobile machineries and industries. Typical answer to this quire, is in using pure water, or water with different additives, that correct water extremely low pressure-viscosity coefficient and corrosion problems [10, 11]. Glycerol is another interesting biocompatible alternative, that is main by-product in biodiesel production [12]. Although it has good mechanical and tribological properties, it also has almost 20 times higher viscosity compared to traditional mineral base oils [13]. Such a high viscosity is not particularly desired because there are greater energy losses due to the need for more energy to overcome the thicker lubricating film, resulting in lubricant degradation and possibly early failure of elements or the system. However, glycerol dissolves in water, and both high glycerol freezing point [14, 15], film thickness and viscosity can be controlled with an appropriate amount of water. In this way, even a so-called super-lubricity can be obtained, with a friction coefficient of less than 0.01 [16]. Glycerol aqueous solutions show good results in steel sliding contacts of rolling and sliding bearings [17, 18], under different boundary, mixed and elastohydrodynamic conditions [13, 16, 17]. In recent study of different polymer composites [19], environmentally acceptable lubricant proved to improve tribological properties of polymer-steel contacts. In our recent study, five different polymer composites were compared [20], and glycerol proved to be excellent lubricant, especially for three polymers with higher micro hardness.

The aim of this study is to analyse the tribological properties of pure POM, and to compare the results of polymer-steel contacts in conventional hydraulic oil ISO VG 46, pure water and glycerol + water solution. In addition, the experiments will be performed at room and elevated temperature, as expected in hydraulic applications. And finally, the results will be compared with our preliminary measurements on carbon fibre reinforced POM.

2 Materials and methods

2.1 Test samples

For the chosen type of ball-on-plate tribological tests, POM discs were cut from a 30 mm diameter rod with a thickness of 5 mm. RotoForce-3 automatic sample polishing and preparation machine was used, and samples were polished to a roughness of 0.1 μ m. The ball was a commercial bearing ball with a diameter of 25 mm made of hardened AISI 440-C stainless steel. Before starting the test, all samples, clamps and the bath were carefully cleaned.

2.2 Lubricants

Demineralised water was used as the reference lubricant. Glycerol (with \geq 99.5 % cleanness) was used as the base for the lubricant glycerol + water (G+W). Based on our preliminary experiments, glycerol with 40 % water in the mixture was used, as this mixture allowed the good lubricating properties of pure glycerol to be maintained at room temperature. The third lubricant used in the study is the commercially available, commonly used ISO VG 46 hydraulic oil. The parameters of the lubricants (Table 2) were determined with an automatic viscometer SVM 3001 (Anton-Paar).

Table 2: Lubricants	properties
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	Kin. Viscosity at 25 °C [mm²/s]	Kin. Viscosity at 80 °C [mm ² /s]	Density at 25 ∘C [g/cm ³]	Density at 80 ∘C [g/cm ³]
ISO VG 46	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

2.3 Tribological characterization

Measurements were carried out with a Cameron-Plint TE 77 high-frequency tribometer (Figure 1) in reciprocal mode. The average sliding velocity was set to 0.2 m/s and 0.05 m/s (frequency 40 Hz and 5 Hz, respectively, and stroke length 2.4 mm). The load was set to 50 N (90 MPa maximum Hertzian pressure). Before each test, the polymer disc was completely immersed in the selected lubricant. The thermoset was placed in the lubricant bath and a heating element was placed under the bath to check the temperature and keep it constant during the test (at a temperature of 80 °C). Special care was taken to maintain the lubricant level during the test so that the sample and ball were always fully immersed in the selected lubricant. After the final test, the contact sliding surface was marked on the ball using an electric pen.



Source: own.

Each test was repeated three times. The tests were conducted for 90 minutes based on preliminary tests that gave a stable value of the coefficient of friction.

2.4 Post-tribological analyses

The wear volume of the disc-like polymer plates was calculated from the dimensions of the wear tracks. The 3D profile of each calotte was determined and characteristic cross-sectional areas at different locations along the wear track were read [20] with digital microscope Hirox HRX-01. Same procedure was also used to determine the shape and dimensions of the wear marks on the steel balls.

3 Results

3.1 Wear and coefficient of friction

The average steady-state coefficient of friction in ISO VG 46 oil, glycerol + water mixture and water are presented in Figure 2.



Figure 2: Average coefficient of friction of POM at 40 Hz and 5 Hz in three different lubricants at: a) room temperature 25 °C; b) elevated temperature 80 °C.

At room temperature (Figure 2a), the results showed comparable values of the coefficient of friction of 0.028 and 0.031 in both ISO VG 46 hydraulic oil and glycerol + water mixture respectively. At lower frequencies, 60 % increase of coefficient of friction was measured in oil, and on contrary slightly lower value (16 % decrease) was measured in glycerol + water mixture. The lowest value was measured in glycerol + water mixture at 5 Hz (0.023). Compared to both oil and glycerol + water mixture case, 4 times higher coefficient of friction was measured in pure water. The highest measured value of coefficient of friction, at room temperature vas measured in water at 40 Hz (0.12). Additionally, the smallest change in measured coefficient of friction value was measured in water, compared to measurement in water at higher frequencies (~ 8 % decrease).

At elevated temperature (Figure 2b) the friction coefficients increased in hydraulic oil, at both measured frequencies, about 70 % increase. The highest measured value

at elevated temperature was in oil at lower frequency (0.077). In case of glycerol + water mixture, coefficient of friction showed the smallest change, compared to other two lubricants, namely at 40 Hz around 6.5 % decrease, and at 5 Hz almost 50 % decrease (the smallest measured coefficient of friction, 0.011). In case of water, significant decrease around 55 % of measured coefficient of friction was observed, at both frequencies.

The average calculated values of specific wear, based on analysed wear tracks in ISO VG 46 oil, glycerol + water mixture and water are shown in Figure 3.



Figure 3: Average calculated specific wear rate of POM at 40 Hz and 5 Hz in three different lubricants at: a) room temperature 25 °C; b) elevated temperature 80 °C. Source: own.

At room temperature (Figure 3a), the smallest specific wear rate was measured in glycerol + water mixture ($5.68 \times 10^{-9} \text{ mm}^3/\text{Nm}$) at higher frequency. Slightly higher specific wear rate was measured in oil ($2.42 \times 10^{-8} \text{ mm}^3/\text{Nm}$, ~ 4 times higher compared to glycerol + water mixture). The highest specific wear rate at higher frequency, was measured in water ($1.88 \times 10^{-7} \text{ mm}^3/\text{Nm}$, ~ 33 times higher compared to glycerol + water mixture). At lower frequency, specific wear rate increased, however the difference among lubricant decreased (same ordered of specific wear rate ~ $10^{-7} \text{ mm}^3/\text{Nm}$).

At elevated temperature (Figure 3b) increased specific wear rate was observed, in all tested lubricants. The highest increase (~ 90 times) was measured in glycerol + water mixture, on contrary lower increase in oil and water (~ 23 to 4.1 respectively).

However comparable specific wear rate was measured for all lubricants ($\sim 10^{-7}$ mm³/Nm). The same trend was observed at lower frequencies, when comparable specific wear rate was measured ($\sim 10^{-6}$ mm³/Nm).

3.2 Surface analyses

Polymer worn surfaces were observed with digital microscopy, and selected samples are presented in Figure 4 and 5. The surface appearance, wear track shape and length ($\sim 3300 \ \mu m$) are similar in all lubricants and at all tested conditions. However, the narrowest wear track was observed in case of oil at room temperature and at higher frequency ($\sim 823 \ \mu m$, Figure 4.I.a). The wear track is not significantly wider in glycerol + water mixture ($\sim 8 \ \%$ increase) at room temperature, although the scratches along the sliding direction are much more intense, especially in the middle of the wear scar (Figure 4.I.b). In case of pure water used at room temperature, both wear track width ($\sim 66.5 \ \%$ increase), the number and intensity of scratches is significantly higher (Figure 4.I.c).

At elevated temperature, there is no significant difference in wear track width among different lubricants used (~ 1600 μ m, Figure 4.II.a-c). This means, that the highest change observed in wear track, due to elevated temperature was observed in oil lubricated case, tightly followed by glycerol + water lubricated case. However, scratches along the sliding direction are not deep and intense in glycerol + water mixture (Figure 4.II.b) as they were in oil (Figure 4.II.a), or even more in water (Figure 4.II.a). This agrees with the smallest specific wear rate in the mixture at 80 °C, and relatively small differences among all three lubricated cases.

At lower frequency (Figure 5.a-c) there was no significant difference in the wear track dimensions among lubricants at both temperatures. At room temperature the wear track width (~ 1148 μ m, Figure 5.I.a-c) was wider compared to the tests at higher frequency and room temperature in oil and glycerol + water mixture, and on contrary tighter in case of water. The main difference was observed in wear mechanism since the wear scratches along the sliding direction are the least intense in case of glycerol + water mixture (Figure 5.I.b). They are the most intense and frequent in case of oil (Figure 5.I.a), and the widest and deepest in case of water (Figure 5.I.c). This agrees with the smallest specific wear rate in the mixture, yet there were small differences among different lubricants (Figure 3.a). At elevated

temperature, wear track width was comparable among lubricants (~ 1522 μ m, Figure 5.II.a-c), and not significantly changed compared to room temperature conditions. Again, the difference was in the scratch's intensity and depth, being the most intense in case of oil and the least intense in case of glycerol + water mixture.



Figure 4: Digital images of POM wear tracks after sliding against still ball at: I) room and II) elevated temperature when lubricated with: a) ISO VG 46 oil; b) glycerol + water mixture; c) water at 40 Hz.

Source: own.



Figure 5: Digital images of POM wear tracks after sliding against still ball at: I) room and II) elevated temperature when lubricated with: a) ISO VG 46 oil; b) glycerol + water mixture; c) water at 5 Hz.

Source: own.



Figure 5: Sample. Source: own.

Surface analysis showed that at lower frequencies, in the case of all three lubricants, the wear track is also present on the bearing ball (Figure 6) at both temperatures. The transfer film dimensions (almost regular circle) are comparable among lubricants. The width is smaller at room temperature ($\sim 800 \,\mu$ m, Figure 6.I.a-c), compared to elevated temperature ($\sim 1300 \,\mu$ m, Figure 6.II.a-c). At room temperature, the scratches were the most intense in water, while at elevated temperature some scratches could be observed in oil.

4 Discussion and conclusion

This study investigated the possibility of using an affordable engineering polymer POM in combination with a glycerol + water mixture as a green lubricant as a potential polymer/steel tribo-pair for hydraulic applications. For reference and comparison, the same contacts were tested in typical ISO VG 46 hydraulic oil and demineralised water, the most widely available green base lubricant. The experiments were performed with parameters that correspond to the seat on-off valves, which could potentially become lighter and have excellent tribological properties. The tests were conducted at room temperature and elevated temperature 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. Because of its high viscosity, glycerol has already been used in research on steel/steel tribological contacts [18, 21]. Recently, an environmentally friendly commercial glycerol-based lubricant has been used in the literature to study the tribological properties of modern commercial polymer materials and compared with water and dry contact [19]. The glycerol-based lubricant further improved the tribological properties of the observed materials. Our recent study also proved good tribological properties of pure glycerol for five different polymer composites [20]. 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 the POM /steel contact when glycerol + water 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 glycerol + water mixture and ISO VG 46 hydraulic oil. At room temperature, the coefficient of friction was about 3.7 times higher for water than for oil and glycerol + water mixture. At elevated temperature, however, the difference was not significant, although the lowest value was measured in the glycerol + water mixture (0.029). At lower frequencies, a similar trend was observed, although the coefficient of friction in oil increased at lower frequencies and, in contrast, decreased in the glycerol + water mixture and in pure water.

The specific wear rate was also lowest in the glycerol + water mixture, especially at room temperature (5.68 x 10^{-9} mm³/Nm). However, the results were comparable to those obtained with hydraulic oil. When comparing glycerol + water mixture and oil with water as lubricant, we measured one order of magnitude higher specific wear rate. At higher temperatures, the difference between the lubricants decreased almost completely and an increase in the specific wear rate was observed (the order of x 10^{-7} mm³/Nm). At lower frequencies, a higher specific wear rate was observed, which is related to the formation of a transfer film that was present on the steel ball in all tests at lower frequencies. 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} mm³/Nm). Water proved to be a less effective lubricant at both

frequencies and at room temperature compared to a mixture of glycerol and water and oil. At higher temperature, however, the difference decreased significantly.

In our previous study, POM, which was reinforced with 30 % carbon fibres, was tested under similar conditions [20], and in our preliminary study the tests were repeated at elevated temperature. A similar trend was observed in the measured coefficients of friction (influence of water, higher temperature, or lower frequency), but higher values 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 [22]. However, further elemental or spectroscopic analysis of the worn surfaces is required to discuss the difference in detail. Based on the current measurements, pure POM gives excellent tribological results in both hydraulic oil and a glycerol-water 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.

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