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ORIGINAL PAPER

Tribological Performance of UHMWPE and PFPE Coated Films on Aluminium Surface

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Abstract A thin layer of Ultra High Molecular Weight Polyethylene (UHMWPE) or UHMWPE + PFPE is coated onto cylindrical aluminium (Al) pin (4.6 mm diametre) surface with the aim of providing wear resistant coating on this soft and tribologically poor metal. The coefficient of friction and wear life of the coated samples are investigated on a pin-on-disk tribometre under different normal loads (394–622 g) and two sliding speeds (0.1 and 0.31 m/s) against uncoated Al disk as the counterface. Both coatings provide coefficient of friction values in the range of 0.02–0.2 as compared to 0.4–1.0 for uncoated Al. There is tremendous improvement in the wear life of the pin, with UHMWPE + PFPE film giving wear life approximately twice to thrice higher than that with only UHMWPE film. A thin polymer film is transferred to the disk surface during sliding providing very long-term wear life (continuous low coefficient of friction) despite visual removal of the film from the pin surface. The present films will have applications in gears and bearings as solid or boundary lubricants for automotive and aerospace component.

Keywords Tribology · Polymer coating · Aluminium · UHMWPE · PFPE

1 Introduction

Aluminium is a soft and ductile metal. However, its properties, such as lightweight, non-corrosive and high strength/modulus to weight ratios have made it (in various alloy forms) widely used material in the automobile and aircraft industries. The top oxide (Al_2O_3) layer on Al protects the metal against corrosion from environment; an additional important advantage with the use of Al in engineering. As for many other metals, Al does not have good tribological properties in dry state. It has low resistance to abrasion (due to low hardness) and galling (adhesion), and has high coefficient of friction when sliding on metals such as steel or itself. Oil/polymer coatings on Al for metalworking [1] were developed but the search on finding a suitable material coating to lower the coefficient of friction and improve the wear life for many other applications is ongoing. Work on boundary lubricants for Al-alloy sliding on steels was conducted as far back as in early 1960s [2]. It was found that chemically highly reactive aliphatic diesters are adsorbed on the surface of Al and thus help keep the two interacting metal surfaces separate. Also, some soft reaction products of Al and diester help fill the depressions between the asperities on the steel surface helping smooth sliding. The strong reactivity between the lubricant (e.g. I-cetene or$C_{14}H_{29}CH = CH_2$) and Al surface (freshly exposed due to initial wear) provided excellent boundary lubrication [3]. In this study, chemical reactivity, sufficient chain length and strong polarity of the lubricant were considered to be essential for excellent lubrication of the Al surface. Recently, attention has also shifted to provide a composite film (hard and soft) on light metals, such as Mg and Al, for better tribological performance with or without liquid lubrication [4]. Primary hard coating of TiO_2, or Al_2O_3, was provided with PTFE and MoS_2 particle mixed polymer coating as the second softer layer. There was considerable improvement in the wear life and reduction in the coefficient of friction for composite coated specimens

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when slid against 100Cr6 steel balls. Self-assembled monolayer of OTS (Octadecyltrichlorosilane) has also been considered as boundary lubricant on Al surface for automotive engine application [5].

The above literature survey has shown the importance of wear resistant thin coating on Al surface for many technological applications where tribology plays an important role. In the present study, we have coated Al surface with a thin layer of Ultra High Molecular Weight Polyethylene (UHMWPE). UHMWPE is coated on top of Al substrate using solution-based dip-coating technique, a very cost-effective method compared with thermal spray or CVD/PVD methods used in earlier research. The tribological properties such as the coefficient of friction and wear life are investigated. Dual composite layer, which comprises of UHMWPE and perfluropolyether (PFPE) films, has also been studied and the data for the coefficient of friction and wear life under the same experimental parameters are collected to compare the effectiveness of both types of polymer layers. UHMWPE is a good candidate material for thin coating because it is a very wear resistant polymer with low coefficient of friction against metals [6]. Also, UHMWPE is very efficient in forming thin transfer film on the counterface because of tribo-chemical actions, giving long wear life during sliding of coated Al against other metal surfaces. For the composite dual layer, PFPE is coated onto UHMWPE film to enhance the tribological properties. PFPE is chosen because it has properties such as chemical and thermal stability, low vapour pressure, low surface tension and good lubricity that are all necessary for better tribological performances [7].

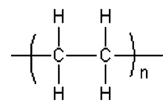
The coated samples are slid against a clean Al plate spinning at a certain speed with different normal load applied on the samples on a pin-on-disk apparatus.

2 Experimental

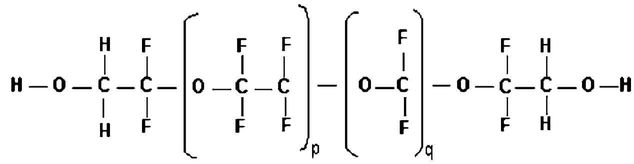
2.1 Materials

A long cylindrical aluminium rod (grade: alloy 1100 H14, Vickers Hardness = 85 HV) with the diameter of about 4.6 mm is cut into short pins of length 2 mm. The two ends are ground and polished with different grades of sandpaper to obtain a consistent roughness for all samples. UHMWPE polymer powder (Grade: GUR X143), supplied by Ticona Engineering Polymers, Germany, was provided by a Singapore local supplier. The solvent used to dissolve UHMWPE polymer powder is decahydronapthalin (Decalin). The structure for PFPE (Zdol 4000, molecular weight = 4,000 g/mol, monodispersed, ratio $p/q = 2/3$) used is shown below.

UHMWPE structure (with n of greater than 1,000,000),



PFPE Z-dol 4000:



The solvent used for PFPE is Hydrofluoropolyether (H Galden ZV) purchased from Ausimont INC. Other materials such as acetone (99.8%) and distilled water were used in the sample preparation for cleaning purposes.

2.2 Preparation of UHMWPE and UHMWPE/PFPE Dual-Film on Al Surface

Al pins were cleaned using distilled water and acetone in an ultrasonic cleaning bath. The UHMWPE polymer powder was dissolved in decalin. The solution was heated up to the temperature of 170 °C. The heating had to be maintained below 250 °C to prevent UHWMPE from decomposing. Magnetic stirrer was used to distribute the heat evenly in the solution to help speed up the dissolution process. After the solution turned from white colour to nearly transparent, which indicated complete dissolution, coating was carried out immediately. The samples were dip-coated using a dip-coating machine that can submerge and withdraw the sample from the solution at the speed of 2.1 mm/s. After submerging the sample in the solution, it was left to soak for 60 s before it was withdrawn out of the solution. The samples were dried in air for 60 s and heated inside a hot plate oven for 20 h at a temperature of ~100 °C. After the heat treatment, the samples were cooled down slowly to room temperature and kept in desiccator before proceeding to the tribological testing. The thickness of the film was measured by cutting a coated Al plate across the thickness and observing it on SEM. The thickness of UHMWPE is in the range of 80 μm (Fig. 1). As for the dual layer, UHMWPE coated samples were dipped into PFPE solution (0.2 wt.% PFPE in H Galden ZV solvent) with the same dipping condition as used for UHMWPE coating. The thickness of the top PFPE layer is in the range of 4–5 nm taking into consideration of the PFPE concentration used in the solution for dip-coating for other substrates.

2.3 Tribological Characterization

The samples were tested using a pin-on-disk tribometre. Figure 2 shows the set up of the tribometer. The sample is

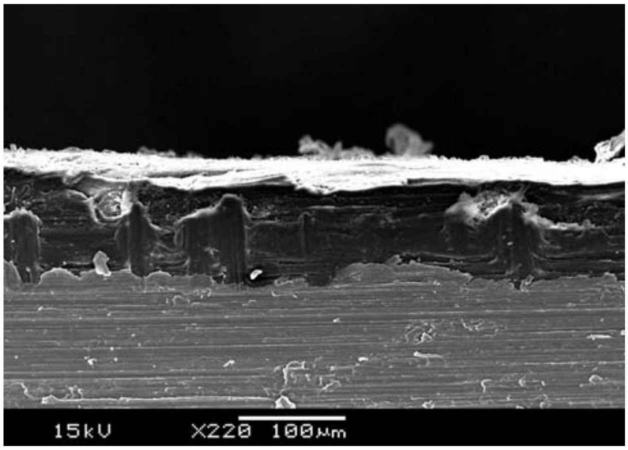


Fig. 1 Cross-sectional view of the UHMWPE film (top part) on Al surface. The thickness of the coating measured from the SEM images is in the range of 80 µm

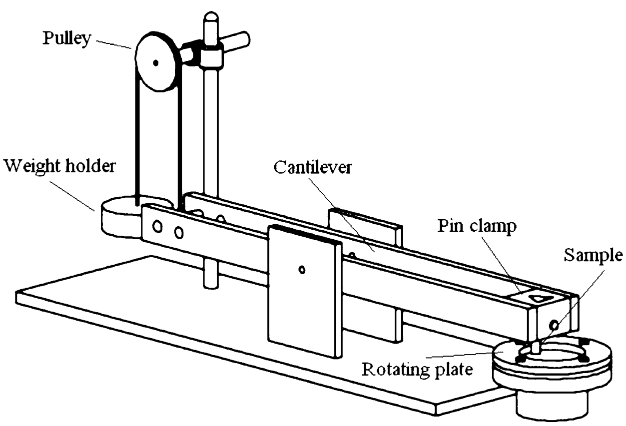


Fig. 2 Schematic of the pin-on-disk apparatus used for the tribological characterizations in this study

fixed in the pin clamp using two screws on one end of the double cantilever. The other end of the cantilever is attached to a pulley. Weight is applied to the string around the pulley which exerts a normal force onto the sample because of the moment about the pivot. The double cantilever has strain gauges attached for the friction force measurement. The cantilever was regularly calibrated for friction force during the course of this research to ensure consistency and accuracy of the results.

The pin samples were slid on a clean Al disk which had initial roughness (R_a) of 0.26 µm. These Al disks were polished using several different grades of sandpaper and cleaned using soapy water, distilled water and finally acetone to clear physical contaminants and water molecules. The disks were rotated at two different speeds of 0.1 m/s (low) and 0.31 m/s (high). The samples were also subjected to four variable normal loads with the wear track diametre on the disk of 2 cm. For each new test, a new clean Al plate was used. The wear life was defined as the number of cycles run before the surface of the Al pin was visually exposed near the coated areas. The same definition of wear life was applied for Al/UHMWPE and Al/UHMWPE/PFPE samples.

The wear track was then studied under scanning electron microscope (SEM) and Energy Dispersive Spectrometer (EDS). The EDS was used to study the polymer transfer from the samples to the Al plate by testing for carbon, hydrogen and fluorine. Profilometre was used to profile and measure the roughness the wear track and the surface of the pin samples.

3 Results and Discussion

3.1 Tribological Properties for UHMWPE Coating Layer

Figure 3 shows the coefficient of friction for bare Al and Al/UHWMPE. The bare Al surface shows the mean coefficient of friction of 0.6 and it fluctuates mostly between 0.4 and 1.0. This is a typical response of soft metal such as aluminium for which friction is high and wear of the metal starts almost instantaneously by seizure and galling if the counterface is of the same metal and by abrasive wear if the counterface is a hard metal. After coating UHWMPE onto the Al surface, the coefficient of friction is below 0.14 for most part which is much lower than that for the bare Al sample. It varies mostly between 0.04 and 0.10 depending on the normal load applied and the rotational speed of the Al plate. Some fluctuations in the coefficient of friction may happen for higher load and higher speeds with the coefficient of friction reaching up to 0.20. High load seems to give slightly high coefficient of friction. The coefficient of friction value for UHMWPE film is very close to the

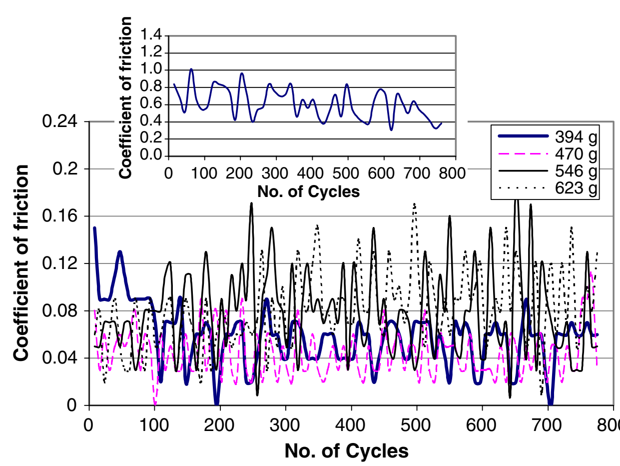


Fig. 3 Typical raw data for the coefficient of friction at low speed of 0.1 m/s for different normal loads. The graph in the inset is for bare Al pin on Al disk for 394 g normal load and sliding speed of 0.1 m/s

bulk value which indicates that a good coating was achieved. The mobility and flexibility of the UHMWPE backbone (polyethylene-based) makes it less resistant to the sliding motion. Also, PEs do not contain any bulky side group making this family of olefins most suitable for low-friction applications [8]. The film is able to withstand several hundreds of cycles of dry sliding demonstrating excellent adhesion with the substrate. Also, it is possible that there is some chemical bonding between the polymer and the aluminium substrate. There is an immediate (within few 10 s of cycle of sliding) transfer of a very thin layer of the polymer to the counterface (also Al) as sliding progresses. Thus, the actual tribological interaction in the present case is that between the coated film and the transfer layer (polymer-on-polymer). This situation provides the condition for stick-slip characteristics which has been observed in the sliding of polymer against polymer involving polyethylene (PE) and polymethylmethacrylate (PMMA) [9] and Acrylonitrile-butadiene-styrene against itself [10] in the absence of any liquid lubricant at the interface. Thus, even though the coefficient of friction is low, there is considerable level of stick-slip phenomenon experienced. The polymer-on-polymer type of contact is also responsible for the slight increase in the coefficient of friction at high load used; though this difference is small considering the fluctuations in the data for all loads. Higher load means increase in the contact area for soft contacts. For smooth contact and in the lower load range, the contact area is proportional to the load raised to power n, where n is greater than 1 ($A \propto W^n$) [10]. The contact pressure in the present case was in the range of 0.024 MPa for the lowest load and 0.0375 for the highest load used. The contact roughness was modified depending upon the amount of polymer transfer. Thus, higher contact area at higher load leads to slight increase in the coefficient of friction. This effect may stabilize if we increase the normal load further as there will be no more increase in the contact area when the load is considerable high, however, additional effect of frictional heating may change the frictional behaviour which needs to be investigated. Figure 4 shows the total number of sliding cycles run before the sample reached the failure point that is when the Al pin surface is partially exposed. The error bars shown in the graph represent the maximum and minimum values of the three tests. During the experiment, when the sample was presumed failed, the coefficient of friction did not change drastically. Instead it remained below 0.20 in all cases. Thus, the current definition of visual estimation of exposed Al pin surface is a grossly conservative value of the wear life of the polymer-coated pins. Despite this, the results show that UHMWPE coating improves the wear life of Al surface by several orders of magnitude. In general, higher normal load tends to lower the wear life. This is expected, as the coefficient of

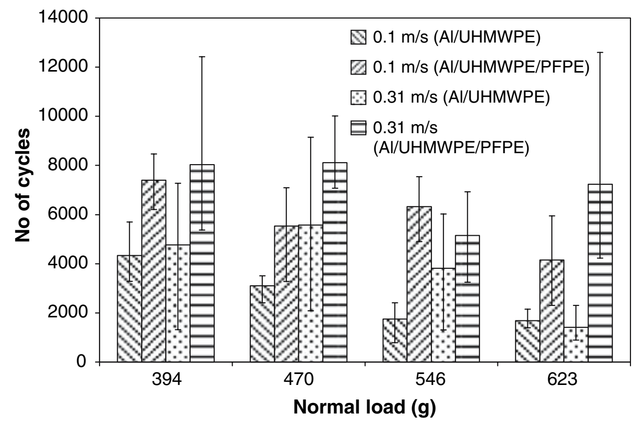


Fig. 4 Total number (average of three tests) of sliding cycles for different films on Al pin surface. The range shown on each bar indicates the scatter of the data for three repeats of the test. Two sliding speeds, as shown in the figure legends, were used for each normal load and film

friction is also high for high normal loads and thus, the frictional heating effect can shear the film off easily. As for the sliding velocity effect, no definite trend could be picked up; however, compared to higher speed, lower speed might have higher wear life when the normal load is also low. This could be an effect of the slightly lower coefficient of friction for low speeds observed in our experiments. Overall, there is a clear effect of the normal load (contact stress) and sliding speed on the wear life of the coating. Figure 5 provides SEM images of the failed specimen and the wear track. The pin surface shows removal of the polymer film, whereas the wear track shows the presence of a transfer film, which is typical in polymers sliding against metals experiments. The EDS result on the wear track confirms the presence of carbon which is indicative of the presence of polymer transfer film. It was found that despite the observed removal of the polymer film from the pin surface, the coefficient of friction still remained low due to the formation of the transfer film on the counterface wear track which helped lubricate the surface. Therefore, wear of either of the Al surfaces did not start at this point. Keeping this fact in mind, we conducted extended sliding test beyond the above-defined failure point until the coefficient of friction started to rise beyond the steady state value. The data from the extended test will be presented in Sect. 3.3.

Figure 6 shows a UHMWPE coated pin surface after sliding for few hundred cycles but before the failure of the film from the surface. This image shows plastically deformed polymer film with few scratch marks due to the counterface roughness. Roughness profile of the film surface is also provided for reference. This type of polymer flow on the surface of UHMWPE bulk specimen is quite typical. It is the plastically flowing nature in the very top

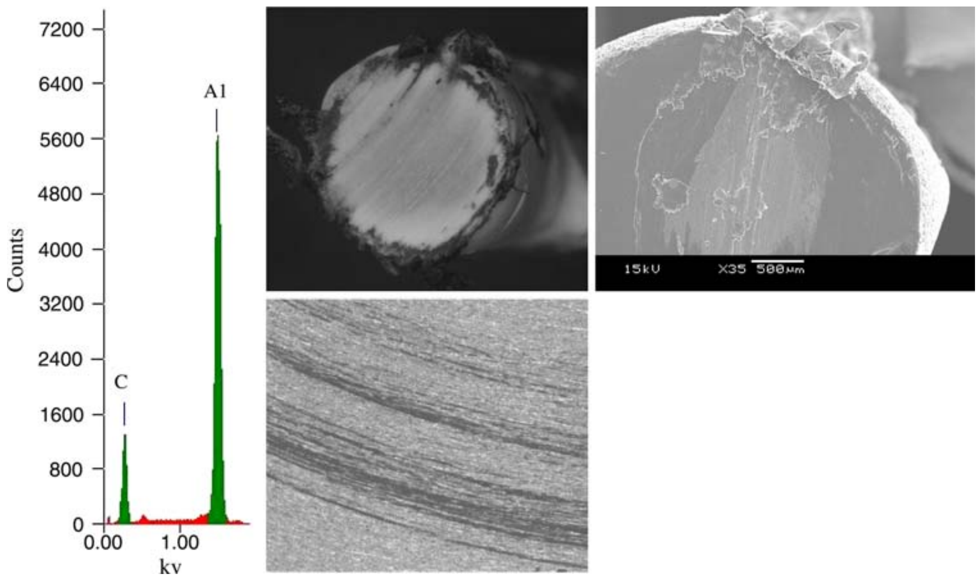


Fig. 5 Optical microscope images of the pin surface (top left) and the wear track (bottom) on the Al disk. On top right is the SEM image of the failed pin, showing accumulation of the polymer wear debris at the trailing end of the pin specimen. The Al and C peaks shown on EDS scans prove that the wear track had a polymer transfer film due to sliding which maintained low coefficient of friction even when the polymer coating on the pin surface appeared removed

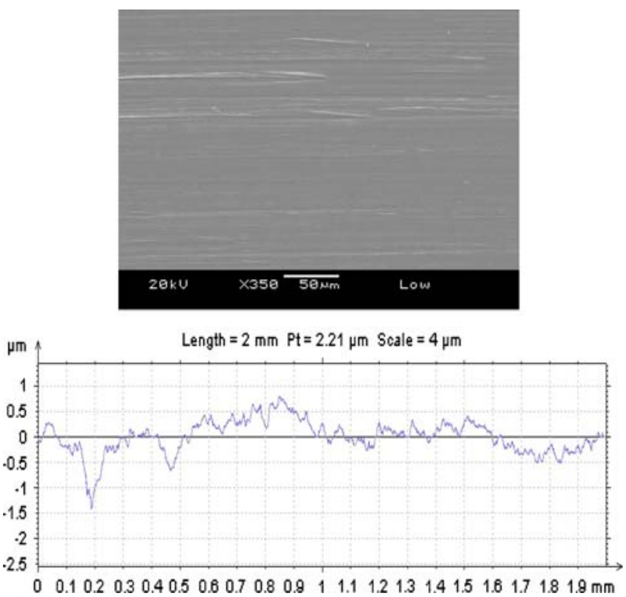


Fig. 6 SEM image of the UHMWPE film surface on the pin during sliding before failure. The profile at the bottom shows the surface topography of the film

surface of this polymer which is responsible for low shear stress with high wear durability. It is interesting that the low sliding velocity condition gives slightly smoother surface of the film during wear giving low coefficient of friction for the same normal load. The friction mechanism involves both adhesive and ploughing (abrasive) components. In the steady-state sliding condition, the adhesive component of the friction mechanism is more dominant due to transfer film which forms as very thin layer on the counterface within few 10 s of sliding cycles. The wear mechanism is that of plastic deformation (a viscous flow for thermoplastics) of the film and subsequent removal from the pin surface. Some pile-up of the deformed and ejected polymer film was observed at the trailing end of the pin as shown in the SEM image of Fig. 5.

3.2 Friction and Wear Life for UHMWPE/PFPE Coating

Figure 7 presents coefficient of friction as a function of the sliding cycles for the dual UHMWPE/PFPE coating on Al pin surface for different loads and the sliding speed of 0.1 m/s. The coefficient of friction remains very low as observed for only UHMWPE film with much fewer fluctuations in the data. This is because of the lubricating action of PFPE which provides a smooth sliding due to very low shear stress. Thus, in the presence of PFPE, stick-slip phenomenon is minimized to an extent. The consolidated wear life for UHMWPE/PFPE film can be seen in Fig. 4. This figure shows approximately 1.5–2 times higher

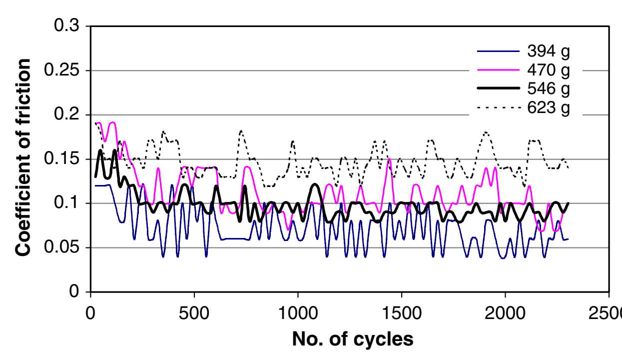


Fig. 7 Coefficient of friction as a function of the number of sliding cycles for UHMWPE/PFPE film on Al pin surface. The data presented here are for lower sliding velocity (0.1 m/s) and different normal loads as mentioned in the graph

wear life for UHMWPE/PFPE coated Al pin over only UHMWPE coated ones. For this case also, the coefficient of friction remained low at the time of film failure as defined above. Wear of the film up to this stage is mainly because of severe plastic deformation within the film and the transfer layer

3.3 Extended Wear Test Results

Due to the consistently low coefficient of friction, even when the film appeared to have been partially removed from the pin surface, we conducted sliding test between the coated Al pin and the Al disk until the coefficient of friction started to fluctuate drastically and value increased above the steady state value of 0.2. An example of the raw friction coefficient data in this type of extended sliding test is shown in Fig. 8. With this new definition of failure point, the number of cycle that the sample can run before failing is at least thrice higher than the previous definition of failure; Fig. 9. The new results proved that the polymer transfer film on the counterface still remained in the sliding interface and thus lubricated the two sliding components. This is an important aspect of soft polymeric solid lubricant as the interface dynamics continues to be favourable for high wear life coupled with low coefficient of friction. From Fig. 9 it is not clear if the sliding speed used in this study had any influence on the extended wear life. For lower normal load, the wear life is high for higher sliding speed, however, any firm conclusion at this stage would be difficult due to the large scatter of the data.

SEM images of the pin surface and the wear track after extended wear test is shown in Fig. 10, which shows near complete removal of the polymer film from the pin surface after an extended wear test. The wear track still has the transfer film as seen from the SEM image and EDS result

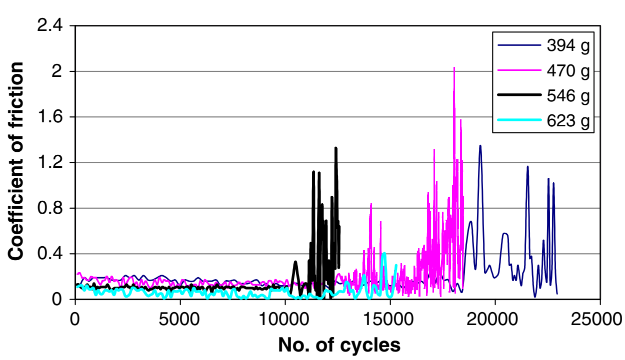


Fig. 8 Coefficient of friction as a function of the number of sliding cycles in extended sliding test beyond the point of partial removal of film from the pin surface for the UHMWPE/PFPE film coated pins. The sliding velocity was 0.1 m/s and the normal loads were as mentioned in the graph

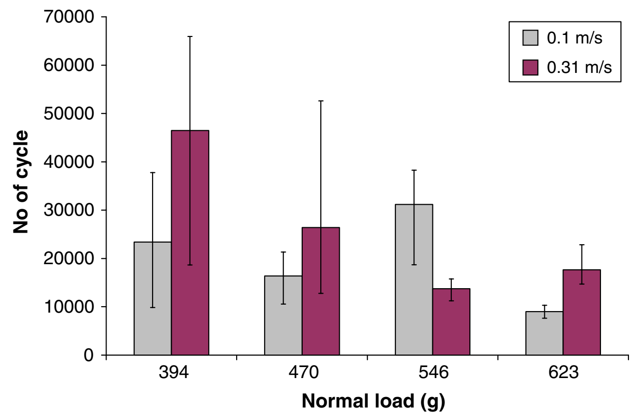


Fig. 9 Wear life of UHMWPE/PFPE film in extended sliding test for two sliding velocities and different normal loads

which shows the presence of carbon, oxygen and fluorine. The presence of oxygen is indicative of the exposed Al surface that has been oxidized and also of the oxidation of the transferred polymers (UHMWPE and PFPE). Scratches can be seen both on the pin surface and the wear track which is a result of severe adhesive and abrasive wear of the surfaces as the effect of polymer transfer film wears off leading to Al on Al contact.

Failed specimen showed evidence of degraded (possibly charred) polymer debris at the pin trailing end and on the disk surface (along the wear track). This infers that the polymer's molecules undergo sever plastic deformation during the low-friction steady-state regime. Severe plastic deformation within the film and the transfer layer can

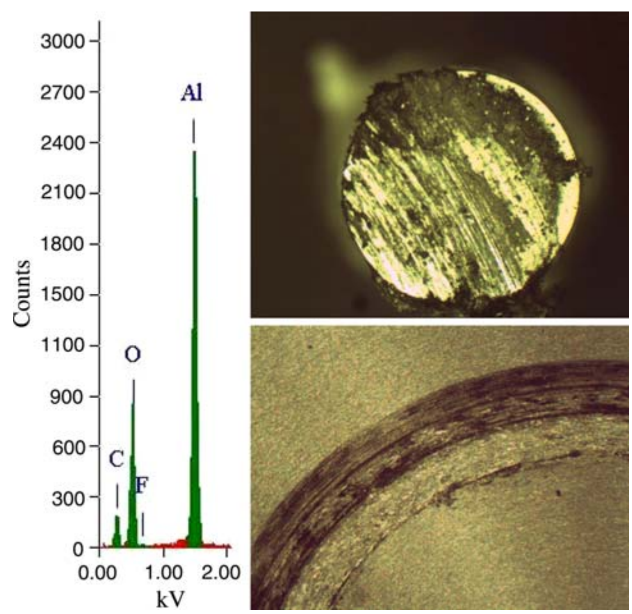


Fig. 10 Optical microscopic images of a failed UHMWPE/PFPE coated pin specimen (top) and the corresponding wear track (bottom) after an extended sliding test. The EDS scan on the left shows the presence of carbon, fluorine and oxygen along with Al peaks

finally bring about degradation of the polymer which is linked to interfacial temperature effect (frictional heating) and mechanical scission of the molecules. Degraded forms of the polymer are brittle and can fracture easily with subsequent easy removal from the interface due to dynamic situation.

The reason of how PFPE helped to increase the wear life was explained in earlier paper on Si/UHMWPE/PFPE [6]. UHMWPE does not contain any reactive chemical groups to bond chemically with PFPE. Due to high roughness and fibrous nature of the UHMWPE coating, the molecules and fibres of the polymer on the surface can trap PFPE inside its gaps and between asperities. With the initial roughness of the UHMWPE of 1.866 μm, it is able to trap PFPE molecules easily. It is also possible that under tribological conditions some tribo-chemical reactions help to bond PFPE molecules to UHMWPE, however this fact would require more work to prove. PFPE is a thermally stable liquid lubricant (extensively used in the lubrication of magnetic hard disk in data storage application) with thermal stability up to 370 °C and high viscosity [11], and hence its presence helps in prolonging the low friction condition and high wear life of the film. However, the effect of PFPE wears off after a long period of sliding due to evaporation of the liquid lubricant and shearing and removal along with the UHMWPE film. The present results show great promise of using UHMWPE overcoated with PFPE as a solid lubricant on Al surface or as a boundary lubricant in a liquid environment, when Al is to be used as the structural (load bearing) material.

4 Conclusions

In this study, UHMWPE was coated onto Al (pin) substrate and tribological properties for single UHWMPE film and dual film of UHMWPE + PFPE were investigated in dry sliding against a clean Al disk. The coated samples were subjected to four different normal loads varying from 394 to 622 g and two different sliding speeds of 0.1 and 0.31 m/s. The coefficient of friction and the number of cycles before the samples failed were recorded. From this study, we conclude that

(1) UHMWPE reduces the coefficient of friction from 0.6 for bare Al to below 0.20. With this low coefficient of friction, the wear life of the Al pin improves from instant wear to 1,000 cycles or more. UHMWPE forms strongly adhering film on the Al surface and can be used for any grade of Al as the actual bonding is between the polymer and the top Al_2O_3 layer of Al.

(2) After coating PFPE onto UHMWPE film, the composite film produces the same coefficient of friction as Al/UHMWPE. As for the wear life, the PFPE overcoated samples could run twice to thrice longer than Al/UHMWPE samples. These wear tests did not show reduction in the coefficient of friction even when the film was visibly partially removed from the pin surface. Transfer film was formed on the counterface that helped reduce friction and protect the interface from wear.

(3) The extended wear test for as long as the coefficient of friction remained in steady-state and low value gave wear life from two to five times higher than the previous definition of film failure. Overall, lower load and lower sliding velocity gives low coefficient of friction and longer wear life for all cases. The present coatings show excellent promise to be used as boundary lubricants in liquid lubrication environment or as solid lubricants on Al surface.

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