

Surface profiles and modulation of ultra-thin perfluoropolyether lubricant in contact sliding

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Received 7 April 2004

Published 28 July 2004

Online at stacks.iop.org/JPhysD/37/2247

doi:10.1088/0022-3727/37/16/005

Abstract

Deformation in shear and associated tribological behaviours of ultra-thin lubricants are of significant importance for the lubrication of magnetic hard disks and for other applications such as micro-electromechanical systems, nano-fluidics and nanotechnology. This paper presents the characteristics of the perfluoropolyether ultra-thin lubricant, in terms of its surface profiles when subjected to a contact sliding test. The results indicate that for a several-monolayers thick (~ 4.0 – 4.5 nm) lubricant film, sliding produces a considerable amount of surface roughness due to peaks of lubricant that persist during sliding; however, it can flow back or return to a smooth profile after a lapse of time when the sliding is stopped. For a monolayer-thin (~ 1.4 – 1.57 nm) film, the lubricant flow is restricted, and the rough profile created due to sliding persists and almost becomes permanent on the wear track. During sliding, due to high shear stress, a characteristic feature of lubricant profile modulation is observed. This modulation, or waviness, is due to the accumulation of lubricant in piles or islands, giving certain amplitudes and frequencies, which themselves depend upon the percentage of lubricant molecules that are chemically bonded to the substrate and the lubricant thickness. The results indicate that ultra-thin lubricants (monolayer and thicker) behave more like a semi-solid (having some sliding characteristics similar to those of rubbers) than a liquid when subjected to a high shear rate during contact sliding.

1. Introduction

Lubrication using an ultra-thin film of perfluoropolyether (PFPE) on a magnetic hard disk for data storage is a very effective way of reducing wear and friction between the disk and the slider. Wear may not be a major problem if the slider is continuously flying except during the start and stop phases in the landing zone. However, for ultra-high data density, as the flying height is reduced to only a few nanometres (5–10 nm), intermittent and sustained contact between the disk

and the slider outside the landing zone (i.e. in the data zone) is inevitable. Also, the possibility of contact recording cannot be realized without a proper wear-resistant lubrication system for the disk that is effective even at ultra-low thicknesses [1]. Therefore, technologically it is very important to understand and study the behaviour of ultra-thin lubricants. Besides wear, there is also the issue of lubricant surface profile changes due to disk/slider contact. Such profile changes, which often show peaks of lubricant, the so-called 'lubricant mogul' [2], have implications in slider–disk dynamics as very high peaks can generate vibration in the slider due to lube–slider hits. This

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type of lube behaviour will definitely affect the fluidity of the lubricant on the disk and thus lead to wear and contamination problems. The formation of a lubricant mogul can also introduce head–medium separation if the lube peaks are very high [3].

In addition to data storage, there are some other new applications of ultra-thin lubricants in micro-electro mechanical systems (MEMSs) or other kinds of micromachines where the thickness of the lubricant must not be more than several nanometres to a few micrometres. For example lubrication and static friction have been studied using PFPE as a lubricant (1–2 nm thick) for a micromotor fabricated of polycrystal silicon [4]. The fluidity of the lubricant on a solid substrate has a strong relation to the static friction (stiction) in micromotors. The very fundamental question of how molecularly thin/thick liquid films on a solid surface behave rheologically under applied shear stress is also important in molecular modelling and simulations work [5] as well in the area of nano-fluidics [6].

With these applications in mind, the current study was carried out to understand the behaviour of an ultra-thin lubricant upon contact sliding. This is a study of dynamic behaviour with an extremely high shear rate in contrast to several past studies, which have been carried out mainly for near-static conditions [7–9] or extremely low sliding speeds using atomic force microscopy (AFM) [10]. Experiments were conducted to observe the profiles of the lubricant (PFPE) immediately after a wear test and also after a rest period of 24 h for two film thickness ranges (1.4–1.57 nm and 4.0–4.5 nm). For each film thickness range, three different bonding ratios of the lube were adopted. PFPE is selected for our study because this lubricant is widely used in disk drive applications, and also this is a very important lubricant because of its low friction and excellent thermal and mechanical stability properties.

2. Experimental

The main contact sliding tests were conducted in a re-designed spinstand resembling the contact–start–stop (CSS) tester, with one difference, that the tests were conducted in the continuous sliding rather than CSS mode. The slider was a 3 (± 0.05) mm diameter glass ball glued to a metallic cantilever. The roughness of glass balls, measured using AFM on a 10 μm \times 10 μm scan, was approximately 4 Å. The micro-roughness of the glass ball surfaces did not vary much as they were from the same batch. A new glass ball, cleaned with acetone, was used for each experiment. The cantilever was attached to a force transducer for frictional force measurement. The metallic cantilever, which was calibrated for stiffness in the vertical direction, provided a means of applying a constant normal load to the glass ball during the test by simply pressing the slider against the disk. The frictional force was recorded continuously during the test from the strain outputs of the force sensor. During the wear test, the slider was in the seeking condition over the disk while the disk rotated at a constant rpm of 2000. This slider seek was approximately between the inner radius of 15.5 mm and outer radius of 20.5 mm for all wear tests. The frequency of seek was kept constant at 5 Hz. The seeking action was employed for the purpose of obtaining a wider wear track for easy measurement of the lube profile

inside the wear track. The slider seek, to some extent, also represented actual disk drive operation, where the slider has to seek on the surface of the disk to read or write information. A very detailed description on the experimental procedure is provided elsewhere [11].

The magnetic disks used were supplied by Hitachi, Japan. According to the data provided by the supplier, these glass substrate disks had a hydrogenated diamond-like carbon (DLC) (H_2 40% and C 60% with 40–50% sp^3 structure) overcoat of thickness 3.5 nm. The DLC was deposited using the ion beam deposition technique by the supplier. The disks were used in as-supplied form, and no further treatment was given in our laboratory before the PFPE lubrication operation by dip-coating.

2.1. Sample preparation

Two lube thicknesses, one in the range of 1.4–1.57 nm and the other in the range 4.0–4.5 nm, were used for PFPE-lubricated DLC-overcoated magnetic hard disks. The lubes were coated using the dip-coating process using a solution of fractionated PFPE (Zdol 4000 with molecular weight 4000) in ultra-pure HFE7100 (a solvent supplied by 3M Co.). These sample disks had various thicknesses of the bonded and mobile lube layers. Lube bonding to DLC was achieved by a process of annealing (baking) the lubed disk in a clean room-compatible oven at 120°C for various time durations. Each disk was first dip-coated with lubricant to an experimentally optimized thickness followed by annealing and rinsing with the solvent. The annealing process provided a layer of bonded lubricant molecules by the reaction between the functional group of PFPE and the active sites on DLC, whereas the rinsing process removed any left-over mobile molecules. Thus, the above procedure provided a disk with only bonded molecules. The thickness of the bonded lubricant was measured using a micro-ellipsometer (see later for description). The same disk was then re-lubed to obtain a top layer of mobile lube molecules. The thickness of the mobile lubricant during re-lubrication was controlled by the dipping speed as the concentration of the lubricant in the solution used for dip-coating was the same. It is well known in the literature that the thickness of the lubricant is a strong function of the concentration and dipping speed. A great deal of experimentation was carried out prior to this study to determine exactly the dipping and annealing conditions that provided the desired thicknesses of the bonded and mobile layers. However, despite good control of the experimental parameters, some variation is expected for individual samples, and therefore the exact thickness of the bonded and mobile layers are reported for each sample used in this study. Table 1 summarizes the final lube thicknesses for the disks used in this study. The thickness of the mobile layer is simply the lubricant layer thickness deposited during re-lubrication after the annealing treatment. It may be noted that for two disks (Z1 and Z2) no annealing treatment was provided and the thickness of the bonded layer reported for these two disks corresponds to the bonding that takes place between PFPE and DLC naturally without any heat treatment. The ratio of bonded to mobile layers is basically the ratio of their individual thicknesses in the film. For each disk, both surfaces were tested in order to repeat each experiment at least twice.

Table 1. Total lubricant thicknesses for bonded/mobile ratio of disk samples.

Sample #	Bonded layer (nm)	Mobile layer (nm)	Total lube thickness (nm)	Bonded/mobile ratio	Thermal treatment
Z1	0.3	1.27	1.57	0.236	As lubed; no annealing
Z2	0.3	4.2	4.5	0.071	As lubed; no annealing
Z3	0.87	0.63	1.5	1.38	Annealed for 10 h
Z4	0.8	3.7	4.5	0.216	Annealed for 10 h
Z5	1.3	0.1	1.4	13.0	Annealed for 100 h
Z6	1.5	2.5	4.0	0.6	Annealed for 100 h

Please note that for sub-monolayer thickness (~ 0.7 – 0.8 nm is the monolayer thickness range for Zdol 4000 [12, 13]), the thickness refers to an average value measured within the spot size of the micro-ellipsometer. Such films may not be continuous but rather sporadic distributions of molecules on the surface. The term ‘mobile’ for a sub-monolayer film simply means that the PFPE molecules are chemically not bonded to DLC.

2.2. Test procedure

Each test started with the dip-coating of the disk, followed by the required amount of annealing for lube bonding. The duration of annealing varied, depending upon the thickness of the bonded layer required. After annealing, the disks were rinsed with the solvent, followed by measurement of the bonded lube thickness using a calibrated micro-ellipsometer. We used a spectroscopic ellipsometer with an incident angle of 70° and an elliptical spot size of $70 \mu\text{m}$ short diameter and $100 \mu\text{m}$ long diameter. The optical source in the ellipsometer was a He–Ne laser beam. Further, the refractive index value for PFPE used in the thickness calculation was 1.298 for both bonded and mobile lube. Although the optical properties of bonded and mobile lube will be slightly different due to polar end groups, this difference will be minimal and may not have a large effect on the lube thickness measured [14]. The calibration of the micro-ellipsometer was carried out using x-ray photoelectron spectroscopy (XPS), and details of the calibration procedure are presented in our earlier publication [11]. The disk was re-lubed by dip-coating to deposit a layer of mobile lubricant of specified thickness, followed by total lube thickness measurement. The disks were tested on the spindstand for wear of the lube. A constant normal load of 23 mN was applied to the slider during the wear test. Using a Hertzian contact and assuming the same values of the elastic modulus and Poisson’s ratio for the glass disk substrate and the glass ball, the contact pressure was calculated as ~ 70 MPa. The difference in the contact pressure due to uncertainty in the ball diameter of ± 0.05 mm did not make a difference in the pressure more than ± 1 MPa, which is well within the acceptable experimental error. The disk was rotated at a constant 2000 rpm for duration of 5 min to complete one wear test (~ 10000 disk revolutions). During each experiment the

humidity of the test chamber was brought down to 6–7% relative humidity prior to each test. Such a low relative humidity will allow us to neglect any effect of meniscus formation during the tribological tests. In fact, studies have shown that the meniscus force remains very low for rough surfaces at relative humidities up to about 80% for low loads because the load is supported by only a few asperities [12]. Another point to note is that the meniscus effect is only for static friction, and for a dynamic test such as the current work, the meniscus effect can be safely neglected. The lube surface profile was recorded using the micro-ellipsometer immediately after the wear test (about 2 min time elapsing between the end of the wear test and ellipsometry) and after a rest period of 24 h to see the change in the profile due to lubricant diffusion and replenishment on the disk surface. It is important to note that the profile measurement after 24 h was not performed at exactly the same location on the disk as the one done just after the wear test. The lube profile was recorded in the radial (across the wear track) and circumferential (on the wear track) directions for a better assessment of the lube surface profile. The friction coefficient was also measured on the same disk, with one difference, that the slider was not kept in seeking motion during the friction test. This was to avoid fluctuations in the voltage signal of the strain gauges due to the seeking action. The friction test was carried out at a radius of ~ 15 mm for the disk rotating at 2000 rpm for 30 s duration. The coefficient of friction did not vary much during the 1000 cycles of rotation, and therefore an average coefficient of friction is reported in this paper. The glass ball was also observed after each wear experiment under an optical microscope to examine wear debris attached to the contact area. All experiments were conducted inside a class 100 clean room.

3. Results

3.1. Lube profile

Figure 1 shows the lube profile in the radial direction for disk samples Z1 (lube thickness ~ 4.5 nm) and Z2 (lube thickness ~ 1.5 nm). For each case, the profile is presented for immediately after the wear test and after a rest period of 24 h. For the 4.5 nm thick lube film it is seen that the lubricant profile is very rough after the wear test, but the lube tends to re-flow back to the valleys in the surface, giving a smoother profile after 24 h. The lubricant peaks, after wear, can be as high as 0.7–0.8 nm. Although the peaks have settled down after a rest period of 24 h due to lube re-flow, there is a clear general depression on the wear track when compared with the thickness outside the wear track. This may be because of the loss of lubricant due to lube pick-up by the slider. Lubricant replenishment from outside the wear track to the wear track is not complete to make up for this loss of lubricant from the wear track. The lube pick-up by the slider can be seen clearly in figure 2. This figure shows the slider (glass ball) surface after the wear test. The lube has extended far ahead, rising on the slider surface curvature, mainly because of the shear stress caused at the interface. It is interesting to note that the lubricant extends towards the leading edge of the slider.

Figure 3 shows the lube profile in the circumferential direction (on the wear track and in the direction of sliding)

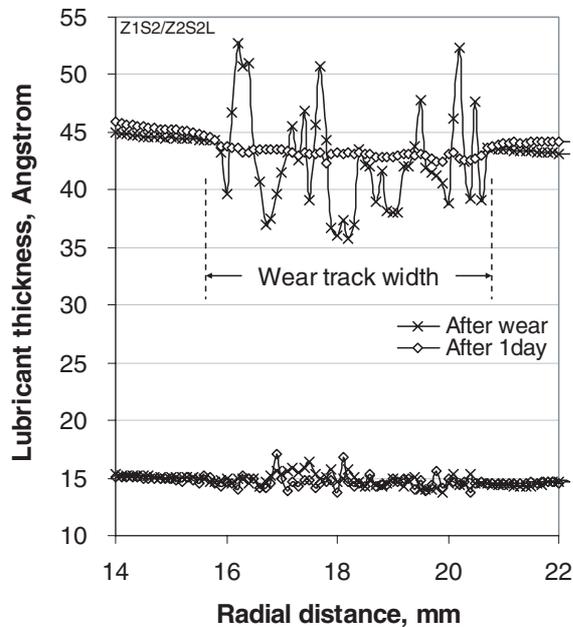


Figure 1. Radial (across the wear track) surface profile after wear test and after 24 h of rest period for 4.5 nm (upper curves) and 1.57 nm (lower curves) thick PFPE lubricants on magnetic hard disk.

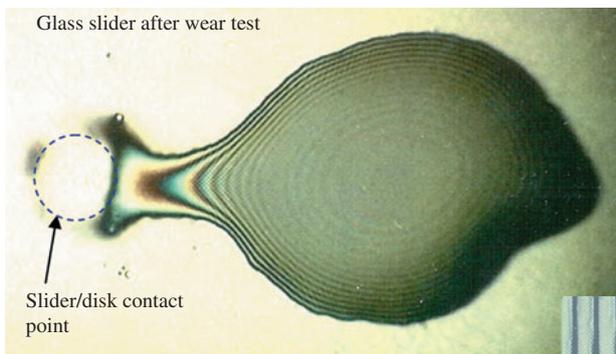


Figure 2. Optical image of the contact point on the glass slider used for sliding against 4.5 nm thick lube. The image shows extended flow of the lubricant on the glass surface during the initial part of the sliding. The direction of sliding is horizontally from left to right. (The spacing between the markings on the lower right-hand corner of the picture corresponds to 10 μm .)

(This figure is in colour only in the electronic version)

for the disk samples Z1 and Z2. The data in this figure show the profile just after the wear test and after a rest period of 24 h. For reference, the lube profile data for outside the wear track are also plotted. A very striking feature in the circumferential direction is the formation of a wavy lubricant profile pattern or lube thickness modulation for the 4.5 nm PFPE film. While the frequency of this modulation is very constant, the amplitude varies with almost the same maximum height of the peaks of the lube. For the case of 1.5 nm thick PFPE film, the modulation is not easily noticeable; however, some short-range waviness may be observed in some parts of the wear track. As was seen in the radial profile, the lube profile of the 1.5 nm thick film shows some lube peaks that are stable even after 24 h of the rest period. This indicates that for near-monolayer or lower thickness the replenishment characteristic

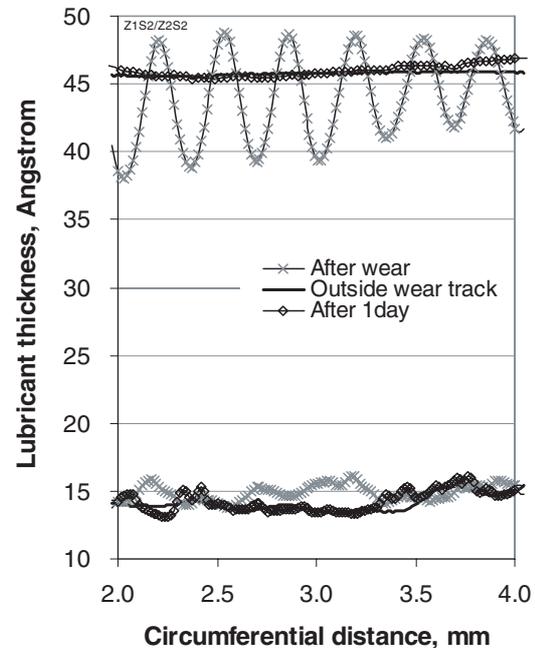


Figure 3. Circumferential (on the wear track) lube surface profile for the disk sample presented in figure 1. For the 4.5 nm thick lubricant (upper curves) there is modulation of the lube profile and there is almost complete lube replenishment after a rest period of 24 h. For the 1.57 nm (lower curves) the modulation is not very regular, and the recovery of the lubricant is not complete, with some lubricant peaks still existing after 24 h of rest period.

of PFPE is very limited. For the case of 4.5 nm thick PFPE film, the recovery of the lube is partially complete, with some near-permanent depletion of the lube on the wear track when compared with the outside track.

Figures 4 and 5 show radial and circumferential lube profiles, respectively, for disk samples Z3 (1.5 nm) and Z4 (4.5 nm). For these disks, the thicknesses of the bonded part are larger in comparison with those for the disks Z1 and Z2 (please see table 1). A larger thickness of the bonded layer for the same total lubricant film thickness may mean lower mobility of the molecules in the unbonded part. For the 4.5 nm thick film the lubricant is very rough just after the wear. This rough profile of the lube recovers to some extent, but to a much lesser extent than the ones shown in figures 1 and 3. Some larger peaks can be observed even after 24 h of rest period. For the 1.5 nm thick film the roughness after 24 h remains basically the same as the one after wear. It may be noted that the roughness of the lube outside the wear track for the 1.5 nm film is largely comparable with the profile inside the wear track. Figure 5 shows the wavy feature of the 4.5 nm thick film after the wear test. This feature is very similar to the one shown in figure 3, with the only difference that the frequency of occurrence of the waves is slightly smaller in figure 5. This means that the thickness of the bonded layer does influence the features of the lube modulation.

Figures 6 and 7 show radial and circumferential lubricant profiles for disk samples Z5 and Z6 with the thickness of the bonded layer 1.3 nm and 1.5 nm, respectively. With a very high percentage of bonding, the change in the roughness profile of the lubricant due to sliding wear is greatly reduced, as can be seen for both 1.4 and 4.0 nm thick PFPE films. For the 1.4 nm

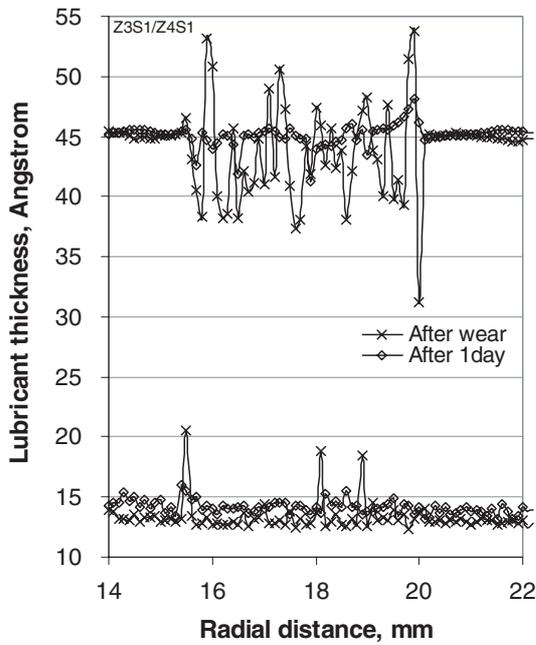


Figure 4. Radial surface profile for the lubes of thickness 4.5 nm (upper curves) and 1.5 nm (lower curves) with bonded-to-mobile ratio 0.216 and 1.38, respectively. The replenishment of the lube is not complete for both thicknesses even after 24 h of rest period.

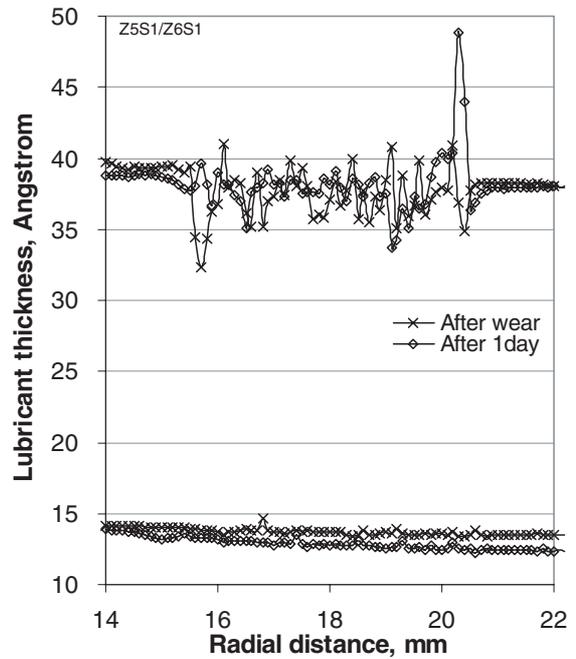


Figure 6. Radial surface profile for the lubes of thickness 4.0 nm (upper curves) and 1.4 nm (lower curves) with bonded-to-mobile ratio 0.6 and 13.0, respectively. Large peaks of lubricant are present for the 4.0 nm thick lube even after a rest period of 24 h.

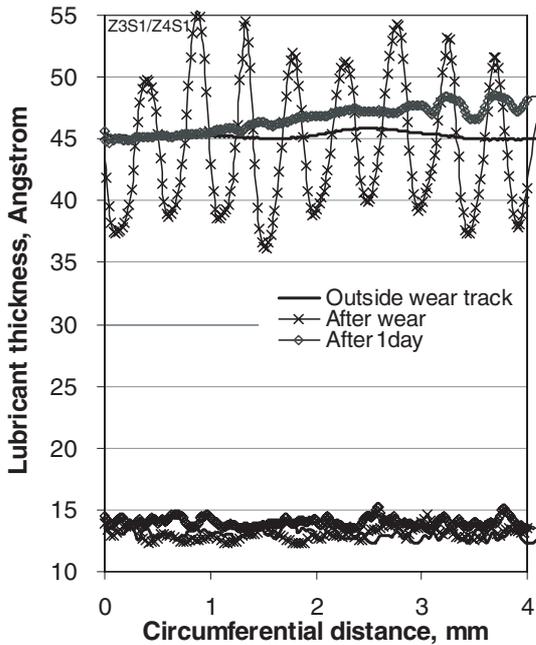


Figure 5. Circumferential (on the wear track) lube surface profile for the disk sample presented in figure 4. For the 4.5 nm (upper curves) thick lubricant there is modulation of the lube profile. The replenishment of the lube is not complete after 24 h of rest period. The 1.5 nm films (lower curves) show not much difference in the surface profile between each other, and the peaks do not tend to flatten with time.

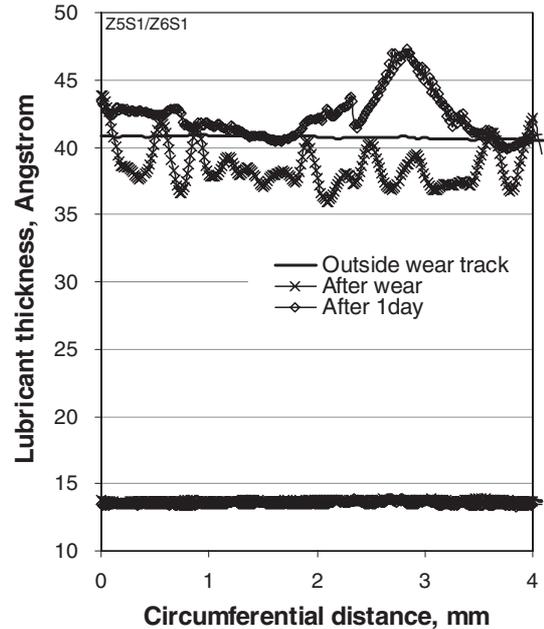


Figure 7. Circumferential (on the wear track) lube surface profile for the disk sample presented in figure 6. The lube thickness modulation is not very regular for the 4.0 nm thick lube (upper curves). The 1.4 nm thick lube (lower curves) shows almost no change in the surface profile due to wear because of the very high bonding ratio.

thick film there is almost no change in the lube profile even after the wear test at the given normal load. However, the 4.0 nm thick film shows some change in the profile after wear with several peaks. The frequency of these peaks is further

reduced compared with the previous two types of lube-bonded samples, and the peak heights are lower. However, occasional high peaks extending in height up to 8–9 nm may be seen at some parts of the wear track. For the high-bonded film, the recovery of the lubricant after the wear test is extremely slow

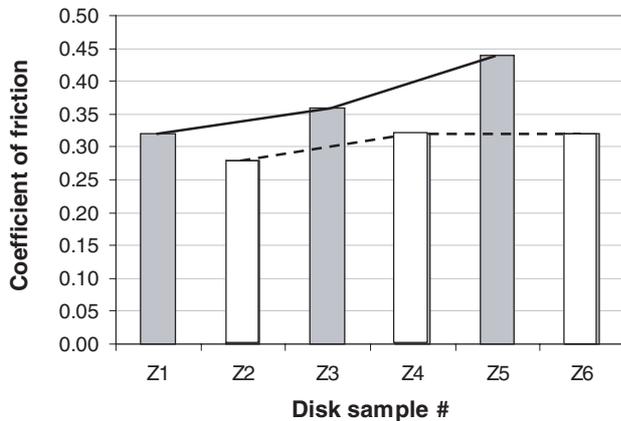


Figure 8. Coefficient of friction measured as an average in the first 1000 cycles of sliding for different disk samples. Refer to table 1 for lube thicknesses and the bonded-to-mobile ratio for each sample.

as we can see several of the lubricant peaks are still present even after a rest period of 24 h. The mobility of the lube is further reduced as the percentage of bonding is increased even if the total thickness is the same.

3.2. Coefficient of friction

In figure 8, the coefficient friction data are presented for each sample as indicated by the disk sample number. Disk samples Z1, Z3 and Z5 are for the 1.4–1.57 nm total lube thickness PFPE films with increasing percentage of bonded lube (shaded bars in figure 8). Disk samples Z2, Z4 and Z6 are for the 4.0–4.5 nm total lube thickness PFPE films with increasing percentage of bonded lube. It is seen that increasing the percentage of bonded lube tends to increase the coefficient of friction for the total thickness. A thicker film (thus a higher thickness of the mobile lube) provides a coefficient of friction slightly lower than that for thin PFPE samples. It has been found previously that the coefficient of friction is a complex function of the bonded lube and mobile lube thicknesses and probably strongly depends upon the ratio of the two [15].

3.3. Glass slider wear

The wear track of the disk samples did not show any presence of wear by ellipsometric measurement; however, wear debris was found on the surface of the glass slider after the wear test. The wear debris accumulated at the leading side of the slider, and the amount of wear particle is higher for the disk with a thicker bonded layer. The disks with 4.0–4.5 nm always showed some presence of lubricant, along with some wear debris particles that resembled micro-size glass particles from their optical properties. The amount of debris particles increases as the percentage of bonding increases for 4.0–4.5 nm films. The disks with a 1.4–1.45 nm total thickness of PFPE film showed a black-coloured residue with very little or no presence of liquid lubricant. Figure 9 shows typical glass surface optical images that were taken for disk samples Z5 and Z6. The image in figure 9(a) is for the glass slider slid against disk Z5, whereas figure 9(b) is for the glass slider slid against disk Z6. Although no analysis was carried out to determine the chemical nature of the wear debris, it is believed, from physical

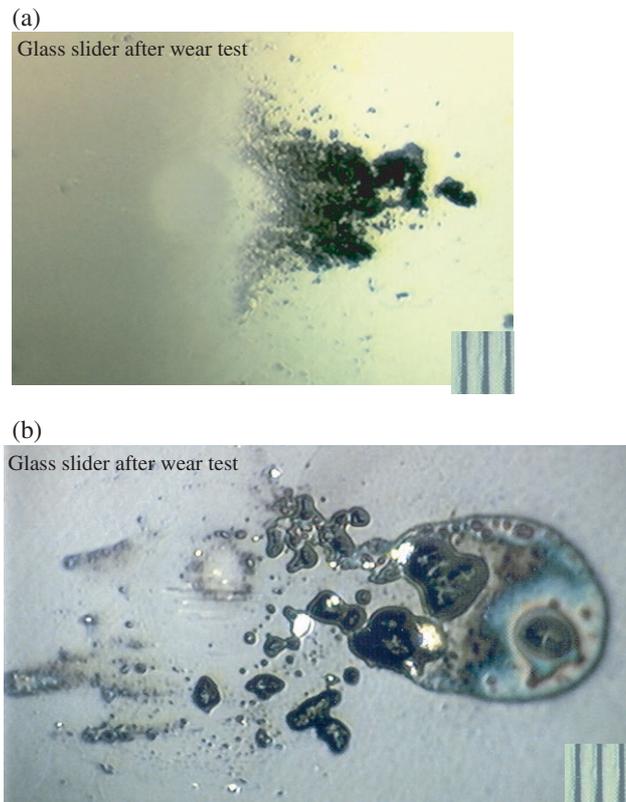


Figure 9. Optical images of the glass slider contact points showing wear debris when slid against (a) 1.4 nm and (b) 4.0 nm thick lubes with bonded-to-mobile lube ratios 13.0 and 0.6, respectively. The direction of sliding is horizontally from left to right. (The spacing between the markings on the lower right-hand corner of the picture corresponds to 10 μm .)

(This figure is in colour only in the electronic version)

appearances, that the wear debris consists of glass asperity fragments and degraded/un-degraded PFPE. The degradation of PFPE is caused mainly due to the frictional heating effect. The presence of PFPE on the glass slider after the wear test has been confirmed and reported by the authors in a previous study [11].

4. Discussion

4.1. General lubricant surface profile analysis

The study presented in this paper has primarily focused on the behaviour of PFPE lubricant on a solid surface due to contact sliding actions when the thickness is in the range of a few nanometres. It has been shown that PFPE as a ultra-thin lubricant undergoes considerable change in roughness due to contact sliding. The peaks of the rough profiles are higher and more in number for a thicker film (4.0–4.5 nm); however, even for a monolayer-thin film (1.4–1.57 nm) some of the peaks can extend as high as 0.7 nm above the surface (figure 4). Because of the scaling (the X-axis is in the millimetre scale, whereas Y-axis is plotted in angstroms), it may be worth noting that the peaks shown in the figure are in fact islands of the lubricant accumulated due to the shearing action of the slider. The roughness of the lube without any bonding

to the disk (about 0.3 nm thickness is naturally bonded to DLC without any thermal annealing treatment) is, to a large extent, recovered after a prolonged rest for the thick film; however, it is not completely recovered if the film is thin, probably in the monolayer range. As the percentage of bonding is increased, the recovery of the lube after wear is extremely slow even for a thick layer of PFPE when the bonded-to-mobile lube ratio is 0.6. Thus, the benefits of bonded lube may be overshadowed by the fact that the lube surface profile will change near-permanent due to contact sliding. However, if we are working in the monolayer thickness, there is no measurable change in the roughness of the lube even due to contact sliding. The wear of the lube is considerable if the lube thickness is high; however, the wear tends to reduce when the lube thickness is around 1.4 nm. This may be because the bonded-to-mobile lube ratio is considerably higher for a thinner film than for a thicker film. Hence, the lubricant is strongly bonded to the DLC on the disk. For the normal load used in our case, wear of the carbon surface is not observed after 10 000 disk revolutions during the seeking type wear test of this study.

4.2. Lubricant profile modulation

It was observed in this study that under certain conditions of lubricant total thickness and bonded lube percentage, the lube thickness profile is modulated, presenting a wavy appearance in the circumferential direction. The modulation becomes less prominent in amplitude and reduces in frequency as the percentage of bonding is increased for the same total thickness of the lube. When the bonded/mobile lube ratio is very high, the modulation becomes irregular. This type of modulation has been observed also in the case of a slider flying on a PFPE-lubricated disk, where it was found that the wavelength of modulation is related to the linear sliding speed of the disk [3]. The present authors have also reported on the formation of a wavy lube surface profile on a PFPE ultra-thin lubricant due to sliding [16]; however, the current study provides a more systematic understanding of the effect for two different thicknesses of the lube and for different bonding/mobile ratios. The modulation in the lube patterning is a result of the shear stress applied due to contact between the slider and the lube surface. As the effective shear strength of the lube increases (due either to the reduction in the total lube thickness or to the increase in the percentage of bonding), there is a reduction in the amplitude and frequency of modulation. The changes in the surface roughness profile presenting a sinusoidal wavy pattern has been observed in a number of cases involving sliding of a hard surface on polymers (films or bulk), especially elastomers. Some interesting findings, for comparison with our results, may be cited, such as the Schallamach waves in rubbers [17], stick–slip type features for organic monolayers [18], wall–slip and extrusion instability in polymers [19] and de-wetting effects for PFPE [20]. Out of these effects, the de-wetting effect is ruled out in our case as the lube profile modulation is very regular and follows some definite frequency and amplitude for the two cases of lube thickness presented in this study. Waltman *et al.*'s [20] work on de-wetting showed that the lube roughness due to de-wetting is very irregular and shows spotty features on the surface. This is in contrast to our current and previous results [16], where final roughness of the lube has

a sinusoidal feature. Second, let us consider the case of wall–slip and extrusion instability, which is shown when a polymer is extruded through a nozzle or capillary. Such an instability, which is a function of the extrusion velocity and temperature, appears on the surface of the extrudate in the form of a regular rough feature known as ‘shark-skin’. Extrusion instability is a result of the characteristic stick–slip motion for viscous (non-Newtonian) fluids, which is caused by the adhesion of the polymer molecules with the wall and eventual fracture when the stress exceeds a certain critical value. Though the stick–slip mechanism in extrusion instability is now generally accepted, the exact nature of the polymer molecules within molecular thickness from the wall surface is not well understood [19]. A high compressive stress experienced by the polymer during the stick in the exit zone gives rise to relaxation and stretch during tensile deformation immediately after the exit zone. Polymers under this kind of situation behave like rubber. Thus, the stick–slip motion manifests as shark-skin on the surface of the extrudate. A similar mechanism of stick–slip was observed in the classical work by Schallamach [17] on the frictional work dissipation in rubber, which is now known as ‘Schallamach wave’. Stick–slip features have also been found for liquid monolayers on solid surfaces [18], where it is believed confined polymer liquids of thickness in the monolayer range behave like rubber. The frictional energy dissipation for such systems involves Schallamach waves and plastic deformation in addition to elastic hysteresis loss. Both the extrusion instability and the Schallamach wave are highly dependent upon the relative speed of the sliding surfaces, temperature and some intrinsic nature of the materials involved, which may increase or decrease adhesion between them. Koudine and Barquins [21] have also found that the nature of the Schallamach wave on a solid rubber surface also depends upon the thickness of the rubber if it is coated on a substrate [21].

Following the evidence available in the literature on the effects of stick–slip motion in sliding on polymers and its various manifestations, it is plausible that in our experiments also the lubricant profile modulation of PFPE is in some way related to the stick–slip motion between the glass slider and the film. Since the thickness of the film is extremely low this may mean that the shear rate experienced by the film is extremely high. The nominal shear rate for a liquid between two plates in relative motion is given as $8v/D$, where v is the relative velocity and D is the gap between the plates [19]. Since D is very low (only a few nanometre), while v is in the range of 3.2–4.3 m s⁻¹, the shear rate could be expected to be of the order of 10¹⁰ s⁻¹. Thus the liquid in the monolayer thickness range could undergo structural changes and behave like rubber due to the very high imposed shear rate, as found for other confined polymeric liquid systems [18] and polymer films [22].

The lube profile modulation observed for an ultra-thin lubricant may be related to the stick–slip motion for tribological contacts, however, with one difference. The stick–slip observed for rubber and thin polymer films has shown much a shorter wavelength (a few microns) of surface roughness modulation. However, as one can see in this work, the wavelengths are much larger than a few microns. This discrepancy may be attributed to the velocity effect and a hypothesis that the transition from the liquid to the rubbery

phase may be reversible, which means that the reversible transition from liquid to rubbery phases can happen within different shear rate ranges. Thus, a rubbery behaviour coupled with some shear flow is possible when a slider is constantly sliding on the same track. The constant stick–slip motion, in the present case, gradually causes the lubricant to accumulate at certain parts on the wear track, leading to the characteristic waviness in the lube profile. Once such lubricant pile-up occurs on the wear track. This feature remains on the track as long as the sliding process continues because of the continuous slick–slip motion between the slider and the disk. Once a precursor of surface pile-up is formed during the initial stages of sliding, more and more lubricant molecules can be stopped and accumulated until the height of the pile-up is so high that it cannot sustain further piling up and the molecules move further. This process may take only a few revolutions before a steady state feature of the lube surface profile is achieved. As observed in our study, the process of formation of wavy feature on the surface is highly dependent upon the thickness and bonding/mobile ratio of the lubricant. The waviness feature can disappear for a thicker lube with low bonded/mobile ratio after sliding is stopped and the disk is left at rest for the lubricant to replenish the depleted areas. This relaxation is mainly a diffusion-controlled phenomenon, which has been studied extensively [23, 24]. Thus the amplitude of this type of lube modulation, which is apparently permanent during the sliding process, may have some effects on the possible vibration of the slider due to the roughening effect on the disk and even on the wear of the slider as the lube, which is present on the disk, behaves as a semi-solid with characteristics resembling those of a rubber. Wear of slider materials is quite common with these applications.

4.3. Wear debris formation

Wear debris formation is a major challenge of head–disk interface tribology as well as for other types of applications. Even at a very small load of 23 mN (giving a contact of around 71 MPa) there is considerable amount of wear debris formation, which accumulates at the leading edge of the slider. The constituents of the debris are, with high probability, glass asperities broken during the initial part of sliding, PFPE lubricant and some charred organic compounds formed due to the oxidation of PFPE at the sliding contact. The amount of wear debris increases for a thinner lube, which may indicate that the problem of wear debris formation and contamination of the system may increase as we reduce the total thickness of the lube and as we increase the bonded/mobile ratio. Therefore, though lube bonding increases the wear resistance properties of the lube itself, a high percentage of lube bonding may not be very desirable from the point of view of wear debris formation as a result of slider wear. Slider wear for alumina sliders used in hard disk drives has been recognized as a major problem in operating the head–disk interface at a very low flying height [1].

5. Conclusions

Contact sliding tests were carried out for two film thickness ranges (4.0–4.5 nm and 1.4–1.57 nm ranges) with varying bonded/mobile lube ratios of PFPE film on magnetic hard disk

sliding against a 3 mm diameter glass ball slider. The lube profile after contact sliding and the coefficient of friction were measured for all the tests. The following conclusions may be drawn from the current study:

1. The roughness of the lube during sliding is much higher for a thicker lube in comparison with a thinner lube. The roughness tends to settle after the disk is left stationary, due to lube replenishment, very easily for the higher thickness. For lube in the range of monolayer thickness (1.4–1.57 nm) the mobility of the lube molecules is largely restricted.
2. A higher bonded-to-mobile lube thickness ratio for the same total thickness of the lube shows little change in the surface roughness profile due to contact sliding; however, peaks and islands of the lube, once they are formed, do not flow back easily to replenish depleted parts of the wear track.
3. The higher thickness of the lube shows a characteristic surface profile modulation, the amplitude and frequency of which tend to decrease as the bonding ratio is increased. Such a regular and continuous lube profile modulation is not seen for the thin PFPE film.
4. The wear of the glass slider is higher for the thinner lube and increases as the percentage of lube bonding is increased for both the thickness ranges employed in this study.
5. Ultra-thin lubricants appear to behave as semi-solids as the flow is largely restricted, which is confirmed by the stable peaks at various locations for 1.4–1.57 nm thickness lubricant. The wavy feature on the disk persists during sliding and does not change because the lubricant molecules become semi-rigid for a high shear rate condition.

Acknowledgments

This collaborative research between National University of Singapore (NUS) and the National Institute of Advanced Industrial Science & Technology (AIST), Tsukuba, Japan was made possible by a visiting fellowship provided to one of the authors (SKS) by the NUS-JSPS New Scientific Exchange Programme. Also, a research grant provided by NUS Nanotechnology & Nanoscience Initiative (NUSNNI) (Research Grant #: R-265-000-132-112) to SKS has helped this research in various ways.

References

- [1] Khurshudov A and Waltman R J 2001 Tribology challenges of modern magnetic hard disk drives *Wear* **251** 1124–32
- [2] Pit R, Marchon B, Meeks S and Velidandla V 2001 Formation of lubricant ‘mogul’ at the head/disk interface *Tribol. Lett.* **10** 133–42
- [3] Ma X, Tang H, Stirniman M and Gui J 2002 Lubricant thickness modulation induced by head-disk dynamic interactions *IEEE Trans. Magn.* **38** 112–17
- [4] Sundararajan S and Bhushan B 2001 Static friction and surface roughness studies of surface micromachined electrostatic micromotors using an atomic force/friction microscope *J. Vac. Sci. Technol. A* **19** 1777–85

- [5] Kato T, Mayeed M S, Kawaguchi M and Choi J 2003 Monte Carlo simulation of PFPE molecular confirmation in the ultrathin liquid films *J. Japan. Soc. Tribol.* **48** 679–86
- [6] Becker T and Mugele F 2003 Nanofluidics: viscous dissipation in layered liquid films *Phys. Rev. Lett.* **91** 166104-1
- [7] Choi J and Kato T 2003 Static and dynamic behavior of liquid nano-meniscus bridge *STLE Tribol. Trans.* **44** 19–26
Also see: Choi J and Kato T 2003 Nanorheological properties of the PFPE nanomeniscus bridge in the separation range of 10–1000 nm *Langmuir* **19** 7933–40
- [8] Israelachvili J N and Tabor D 1972 The measurement of van der Waals dispersion forces in the range 1.5–130 nm *Proc. R. Soc. Lond. A* **331** 19–38
- [9] Luckham P F and Manimaaran S 1997 A nanorheological study of adsorbed polymer layers *Macromolecules* **30** 5025–33
- [10] Koinkar V N and Bhushan B 1996 Micro/nanoscale studies of boundary layers of liquid lubricants for magnetic disks *J. Appl. Phys.* **79** 8071–5
- [11] Sinha S K, Kawaguchi M, Kato T and Kennedy F E 2003 Wear durability studies of ultra-thin perfluoropolyether lubricant on magnetic hard disks *Tribol. Int.* **36** 217–25
- [12] Tian X and Bhushan B 1996 The micro-meniscus effect of a thin liquid film on the static friction of rough surface contact *J. Phys. D: Appl. Phys.* **29** 163–78
- [13] Gellman A J, Paserba K R and Vaidyanathan N 2002 Desorption kinetics of polyether lubricants from surfaces *Tribol. Lett.* **12** 111–15
- [14] Rühle J, Novotny V, Clarke T and Street G B 1996 Ultrathin perfluoropolyether films—influence of anchoring and mobility of polymers on the tribological properties *ASME J. Tribol.* **118** 663–8
- [15] Kawaguchi M, Choi J, Kato T and Tanaka K 2003 A study of friction properties of Zdol on magnetic disk surface *IEEE Trans. Magn.* **39** 2483–5
- [16] Sinha S K, Choi J and Kato T 2003 Topographical and tribo-chemical studies of contact sliding on ultrathin perfluoropolyether film *IEEE Trans. Magn.* **39** 875–80
- [17] Schallamach A 1971 How does rubber slide? *Wear* **17** 301–12
- [18] Reiter G, Levent Demirel A, Peanasky J, Cai L L and Granick S 1994 Stick to slip transition and adhesion of lubricated surfaces in moving contact *J. Chem. Phys.* **101** 2606–15
- [19] Denn M M 2001 Extrusion instability and wall slip *Annu. Rev. Fluid Mech.* **33** 265–87
- [20] Waltman R J, Khurshudov A and Tyndall G W 2002 Autophobic dewetting of perfluoropolyether films on amorphous-nitrogenated carbon surface *Tribol. Lett.* **12** 163–9
- [21] Koudine A A and Barquins M 1997 On the influence of rubber thickness on the existence of Schallamach waves *Int. J. Adhesion Adhesives* **17** 107–10
- [22] Schmidt R H, Haugstad G and Gladfelter W L 2003 Scan-induced patterning in glassy polymer films: using scanning force microscopy to study plastic deformation at the nanometer length scale *Langmuir* **19** 898–909
- [23] Ma X, Gui J, Grannen K J, Smoliar L A, Marchon B, Jhon M S and Bauer C L 1999 Spreading of PFPE lubricants on carbon surfaces: effect of hydrogen and nitrogen content *Tribol. Lett.* **6** 9–14
- [24] Tyndall G W, Waltman R J and Pocker D J 1998 Concerning the interactions between Zdol perfluoropolyether lubricant and an amorphous-nitrogenated carbon surface *Langmuir* **14** 7527–36