Published in Tribology Letters 2013 (DOI : 10.1007/s11249-013-0112-3)

A tribological study of Multiply-Alkylated Cyclopentanes and Perfluoropolyether lubricants for application to Si-MEMS devices

Jonathan Y. Leong[1], N. Satyanarayana[1] and Sujeet K. Sinha[2,#]

[1]Department of Mechanical Engineering, National University of Singapore, Singapore 117576, SINGAPORE
[2]Department of Mechanical Engineering, Indian Institute of Technology, Kanpur 208016, INDIA

[#]Corresponding author: Email: sujeet@iitk.ac.in; Tel: +91-512 2596679;
Fax: +91-512 2597408

Abstract
Lubrication of Micro-Electro-Mechanical Systems (MEMS) is a major constraint in MEMS applications, restricting the designs and practical usages of such devices. Possible lubricants and methods have been investigated in this paper, comparing perfluoropolyether (PFPE) lubricant with Multiply-Alkylated Cyclopentanes (MACs). The effectiveness of both the lubricants in reducing friction and enhancing the wear life was investigated in a new method of MEMS lubrication known as Localized-Lubrication or "Loc-Lub". Friction and wear tests were conducted in a flat-on-flat test geometry under a normal load of 50 g and a sliding velocity of 5 mm s^{-1} in reciprocation, with Si as the substrate. Further tests were conducted at higher loads, to compare wear durability between lubricants and methods. It was found that MACs have a propensity to remain cohesive during the tests due to higher surface tension and provide better friction and wear properties when tested under reciprocating sliding conditions, as a complete film is present between the two surfaces. The results show that MAC lubricant is more effective in extending the wear life and reducing friction under the tested conditions compared to PFPE.

Keywords: MEMS Devices; Boundary Lubrication, Friction

1 Introduction
Friction and wear have always been a concern in engineering designs and applications when dealing with surfaces in contact. The issues of friction, adhesion and wear are predominant in Micro-Electro-Mechanical Systems (MEMS) and are currently some of the limiting factors for the design and fabrication of reliable complex MEMS devices [1]. Issues of stiction in MEMS devices due to the reduced scale and increased surface to volume ratio are well documented. The levels of stiction observed in MEMS devices also affect the running friction and wear during use. [1]. Current lubrication techniques such as hermetic packaging and vapour phase lubrication are often expensive as they require advanced equipment, specialized packaging and storage of devices [2], making mass application and production of such devices impractical. Methods such as vapour phase lubrication and dip-coating are also known to affect the entire plane or exposed surfaces of MEMS, with effects on sidewall surfaces unknown due to the inaccessibility and small gaps [3]. As a result, they may also affect the functionality of certain portions of the device such as the electrical contact points and pads.

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

Perfluoropolyether (PFPE) lubricants have been used in the magnetic hard disk industry and are well-known as an effective thin film lubricant coating [4] due to low surface tension, hydrophobicity and high thermal and chemical stability [5],[6]. Our previous work was conducted on a novel technique of lubricating MEMS ("Loc-Lub") and was found to be effective in reducing friction, adhesion and wear of contacting surfaces both at the macro- and micro-scale [7-9]. Application of PFPE (Z-dol 4000) onto surfaces and MEMs sidewalls has been investigated using this method, and found to be extremely effective [8]. However, PFPE lubricant has been found to be susceptible to catalytic degradation in the presence of metal surfaces, and have a propensity to cause corrosion due to the presence of fluorine, as investigated and reported in the literature [10-14].

Multiply-Alkylated Cyclopentanes (MACs) have been used largely in the aerospace industry [15],[16] and have been found to reduce wear on surfaces at the nano-scale. MACs have also been found to induce a hydrophobic property when coated on a surface - this hydrophobic property has been linked to a reduction in adhesion and friction between sliding surfaces, particularly for MEMS [17]. MACs also have good thermal and chemical stability and are thought to be good alternative lubricants for MEMS compared to PFPE lubricants. The use of MAC lubricant in particular was investigated in this study, as the products of the decomposition process of MACs are relatively less harmful or corrosive in comparison to those from PFPEs. It has also been reported that the thermal stability of MACs is superior to that of PFPE [18, 19]. MAC lubricants have been studied as an overcoat lubricant layer onto SAM surfaces to improve the load-carrying ability and wear life of the SAMs [20, 21]. Nanoparticle additives (such as Ag) for MAC lubricants have also been investigated [22].

This study seeks to investigate and compare the tribological properties between PFPE (Z-dol 4000) and MAC lubricant (Nye Synthetic Oil 2001A) under reciprocating sliding wear on Si surfaces, as well as testing the feasibility of MAC lubricant on MEMS devices using the "Loc-Lub" method [7, 8], and comparing its effectiveness with the traditional dip-coating method.

2 Materials

2.1 Si Wafers

Polished n-type silicon (100) wafers of 525 µm thickness and 12.4 GPa hardness, purchased from Engage Electronics (Singapore) Pte. Ltd., were used as substrate. Both polished and unpolished sides (roughness *Ra* = 16 nm and 616 nm, respectively) were used in separate tests, with the unpolished Si surfaces representing the unmodified MEMS surfaces such as sidewalls. The wafers were cut into base pieces of approximately 2 cm by 2 cm, and smaller upper pieces of 2 mm by 2 mm for the reciprocating sliding wear test as per previous research [8]. The Si wafers were cleaned firstly by washing in ethanol for 1 min, followed by ultrasonic cleaning in ethanol for 1 hour subsequently drying with N_2 gas, and finally cleaned with air plasma, using a Harrick Plasma Cleaner/Sterilizer. In the final step of the plasma cleaning, the surfaces were exposed to air plasma under vacuum for approximately 5 minutes using a RF power of 30 W [23]. Samples were stored in a desiccator overnight after the entire cleaning process, prior to any further coating or testing.

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

2.2 Lubricants

Z-dol 4000 (molecular weight = 4000 g/mol, monodispersed) was used as the PFPE lubricant, allowing for comparison with our previous research [8]. PFPE molecules have terminal -OH groups at their ends, and the chemical formula of PFPE is as follows (where p/q ratio is 2/3):

HO-CH2-CF2-(O-CF2-CF2)p-(O-CF2)q-O-CF2-CH2-OH

In this study, a concentration of 4.0 wt% of PFPE was used, by dissolving Z-dol 4000 in H-Galden as the solvent, both obtained from Solvay Solexis.

A Multiply-Alkylated Cyclopentane (MAC) lubricant, Nye Synthetic Oil 2001, was purchased from Dulub Lubricants, and dissolved to the same concentration (i.e. 4.0 wt%) using n-hexane as the solvent. A table of the physical properties of the MAC lubricant has been given by Dube *et al* [24].

Different solvents are used for the two lubricants, as the lubricants are found to dissolve only in their respective solvents and do not share a common solvent. The used solvents evaporate rapidly upon application and exposure to air, and therefore do not influence the actual lubrication mechanism during testing. The lubricant film in such a case would therefore operate in the boundary regime under the current experimental conditions, as an extremely thin fluid film for MACs and as a film of nano-scale thickness for PFPEs. As tests were started immediately after lubrication, it is believed that there is minimal interaction and bonding, if at all, between the PFPE lubricant and Si surface. The chemical composition of MAC lubricant also suggests that there is no bonding between MACs and Si surfaces. Such a film would rely primarily on adequate separation of the surfaces' asperities, as well as sufficient replenishment at the onset of starvation. Replenishment in turn depends on the availability of the lubricant molecules in the immediate vicinity of the region of starvation and the optimization of the spreading behavior; these will be briefly discussed in this study.

3 Experimental Techniques

3.1 Lubrication Methods

Two main application methods were used in the comparison of the lubricants – the first method was dip-coating, a well-known method of lubricating surfaces with a thin film. A recently developed method of lubrication, "Loc-Lub", was used as the second method [7, 8]. Dip-coating was carried out with dipping/withdrawal speeds of 2.1 mm s^{-1} and a dipping duration of 1 min, as per previous research [8, 25]. In the current study, only the larger bottom Si pieces were dip-coated due to handling and coating issues on the smaller pieces. The "Loc-Lub" method was described in detail in our previous work and has been found to be a successful technique in lubricating flat-on-flat reciprocating surfaces as well as MEMS devices, particularly sidewalls [8],[7].

3.2 Contact Angles

Static water contact angles were measured using a VCA Optima Contact Angle System (AST Products Inc., USA) and deionized water. The size of the droplet used for this measurement was 0.5 µl, with 5 – 6 repeated measurements on each surface.

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

For all contact angle measurements, an average was taken from at least 5 consistent values, with the variation under ±2 ˚ unless stated. The error of measurement was within ± 1 ˚.

3.3 Spreading rates

The qualitative spreading rates of the lubricants were investigated as a measure of the self-replenishing ability [5, 26]. A similar test as that used by Guo *et al* [26] was fashioned for comparative analysis between PFPE and MAC lubricants. A drop of approximately 100 nl of the lubricant solution was dispensed on a cleaned Si surface, and the change in the droplet size was observed over a period of 24 hours.

The spreading behavior between surfaces with no load applied was also investigated. This was carried out by applying lubricant via "Loc-Lub" between a glass slide of 1 cm by 1 cm resting on a cleaned Si wafer of at least 2 cm by 2 cm size. The behavior of the applied lubricant was observed with an optical microscope. The same surfaces were investigated again after the glass and silicon slides were separated. The glass slides were cleaned in the same manner as the Si wafers prior to testing to ensure that no contaminant interfered with the behavior of the lubricant droplets or film on the surface. Water contact angles were measured for the glass surfaces to ensure that the surface properties and hydrophobicity after cleaning were close to those of Si wafers. This would ensure that the lubricant behavior is similar to that under normal test conditions.

Spreading rates are used in this study for understanding the behavior of the lubricant solution, explaining the differences in properties under reciprocating sliding wear.

3.4 Reciprocating Sliding Wear Tests

Reciprocating sliding wear tests (RSW) were conducted on a custom made wear tester, as per our previous work [8]. The normal loads used were 50 g, 70 g and 100 g, with a sliding speed of 5 mm s^{-1} at a frequency of 2.5 Hz and at an amplitude of 1 mm. Data sampling was taken at a frequency of 10 Hz.

The initial coefficient of friction (CoF) was taken as the measured average CoF in the first 4 seconds of the test, equivalent to the duration of the first 10 cycles. Samples were considered to have failed if the measured CoF exceeded 0.3 for a sustained period of time, great fluctuations were observed in the measured CoF, or if wear scratches were visible with the naked eye on the test surface, whichever happened first. Wear tests were carried out in a controlled environment at a temperature of 25 ± 2 ˚C, and a relative humidity of 55 ± 5 % for 6 hours test duration. Surfaces that did not fail after 6 hours were tested for a longer duration of 60 hours. Further tests were also carried out under heavier loads to compare wear resistance of the surfaces. The surfaces were kept parallel throughout the duration of the tests.

3.5 Optical Microscopy, FESEM and EDS analysis

Optical Microscopy was carried out to obtain images of the coated surfaces after various forms of lubrication for the two lubricants, and to observe the conditions of the wear tracks on the tested Si surfaces. Further investigation was carried out on a Field Emission Scanning Electron Microscope (FESEM), using a Hitachi S4300 machine coupled with an Energy Dispersive Spectrometer (EDS). EDS mapping and scanning of elements were used to investigate the distribution density both prior to

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

and after wear tests to investigate the sliding effects and provide insight into the mechanism of lubrication, discussed in tandem with the other analytical techniques.

4 Results and Discussion

4.1 Contact Angles

The water contact angles of the MAC-coated samples were generally higher than those on PFPE samples, the data are summarized in Table 1. Bare Si (after air plasma cleaning) had a water contact angle of 5.5˚ and 5.7˚ for polished and unpolished surfaces respectively. The water contact angle data for PFPE was taken from previous research [8].

Table 1: Water Contact Angles for Polished and Unpolished Si surfaces under different lubricants and methods of lubricant application

Water Contact Angles (˚)	MAC lubricant	PFPE lubricant
Polished, Dip-coated	46.3	38.5
Unpolished, Dip-coated	56.0	30.4
Polished, Loc-Lub	-	55.0
Unpolished, Loc-Lub	-	38.8

Contact angles for the samples under Loc-Lub of MAC lubricant could not be carried out as the MAC lubricant remained as a stable droplet when the upper Si piece was removed. The main point of comparison for the surface modifications is therefore from the dip-coated samples. The water contact angles are found to be higher with MAC lubricant than PFPE lubricant under dip-coating, implying that a more hydrophobic surface is induced upon coating with MAC lubricant.

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

4.2 Spreading rates

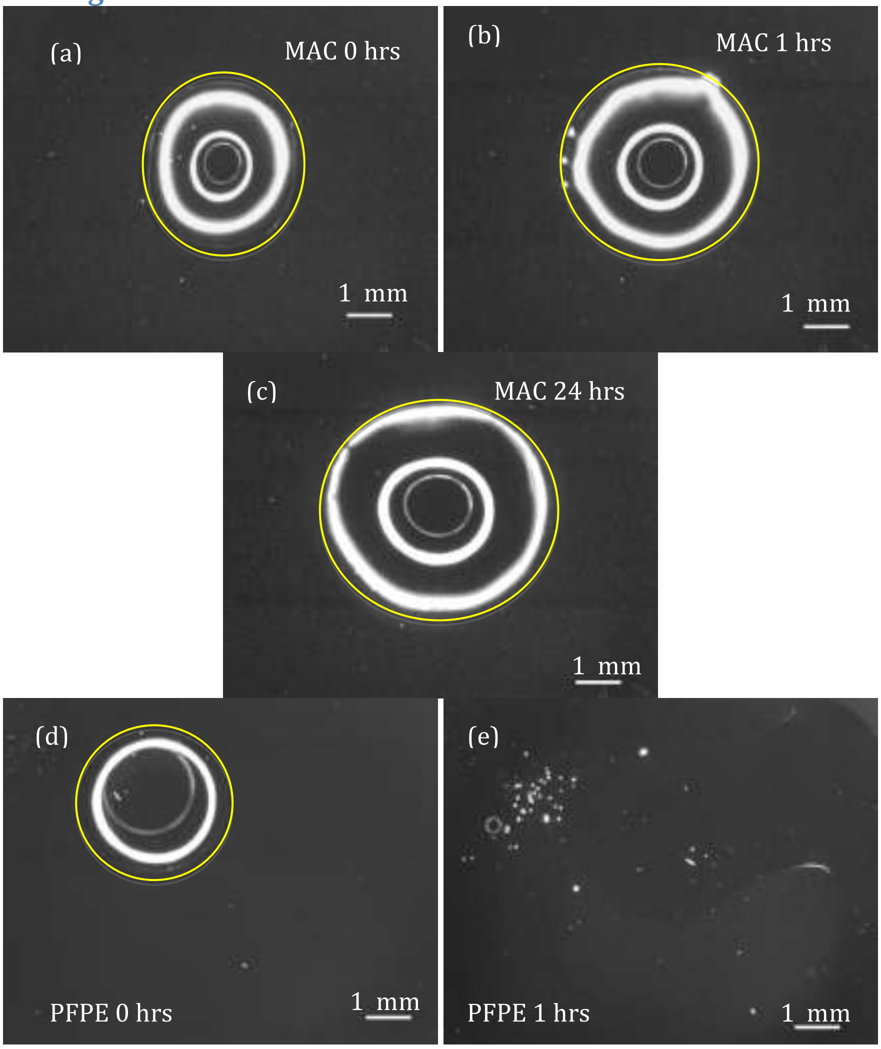


Figure 1: Spreading rate images of MAC lubricant a) after dispense, b) 1 hour after dispense, c) 24 hours after dispense, and of PFPE lubricant d) after dispense, e) 1 hr after dispense, on cleaned Si surfaces. PFPE droplet had no visible shape after 1 hr and had spread over the Si surface.

The spreading rates of the two lubricants differed greatly and are shown in Figure 1. PFPE was found to spread so rapidly on cleaned Si wafers that no discernible shape could be made of the droplet after 1 hour, as seen in Figure 1(e). The PFPE lubricant, having lost any notable shape as a droplet, spread to form a thin film layer on the surface within the first hour after dispensing on the surface.

MAC lubricant on the other hand, kept its uniform shape over the timeframe, and retained a near perfect circular shape even after 24 hours. A small amount of spreading was observed, and a stable state reached after approximately 6 hours. PFPE is thus found to have a higher spreading rate than MAC. A higher spreading rate assists in self-replenishment, but also implies that the lubricant layer can be easily swept away from the interface (and effectively lost) due to the reciprocating sliding movement of the flat on flat wafers.

The cohesiveness of the MAC lubricant, believed to be due to the high surface tension of the liquid (approximately 32 dynes/cm for neat Nye Synthetic Oil 2001A,

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

compared to 23 dynes/cm for neat Fomblin Z-dol 4000), shows that it is not likely to break apart into smaller droplets or form a thin film, which would be easily removed from the Si surface without a self-replenishing effect. Conversely, PFPE is known to form an extremely thin film on a surface [27, 28], as opposed to remaining as a cohesive droplet. The effect of these phenomena on the tribological properties will be examined in the wear tests and discussed further on.

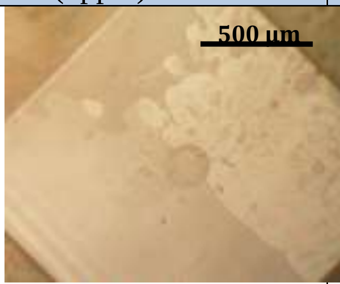
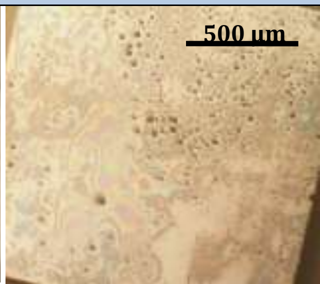
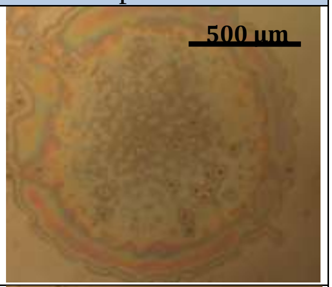
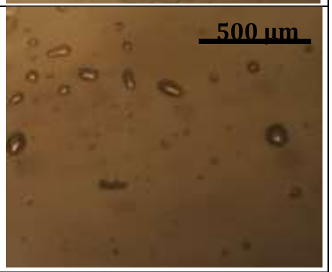
	During contact between Si (lower) and glass (upper) surfaces	Si surface (lower) after contact and separation	Glass surface (upper) after contact and separation
4 wt% PFPE			
4 wt% MAC			

Figure 2: Spreading of lubricants observed under contact through a cleaned glass slide

The application of both lubricant solutions with glass slides (Figure 2) showed a remarkable difference in solution behavior at the interface. PFPE formed a thin continuous film under contact, and only changed its spreading slightly when the glass slide was removed, due to the meniscus and surface tension forces. MAC lubricant remained in discrete droplets even under contact, preferring to de-wet the glass and silicon surfaces rather than forming a film. This difference in behavior is due to the high surface tension of the MAC lubricant compared to that of PFPE, and is useful in preventing the lubricant from spreading into the surrounding environment.

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

4.3 Reciprocating Sliding Wear Tests

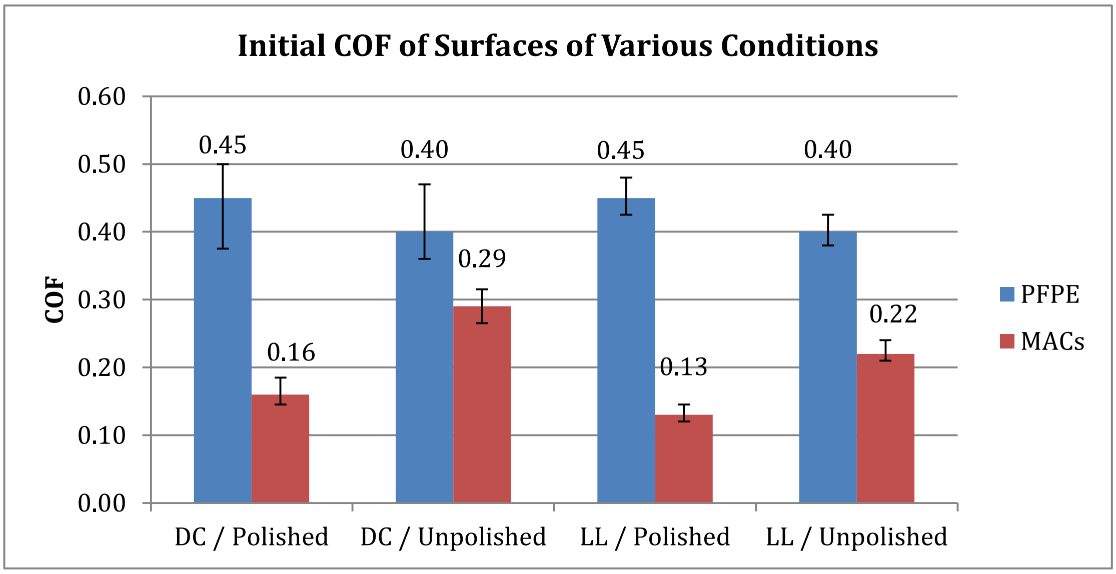


Figure 3: Initial coefficient of friction for various lubricated Si Surfaces under dip-coating (DC) and Loc-Lub (LL), at reciprocating speed of 5 mm s^{-1} and 50 g load

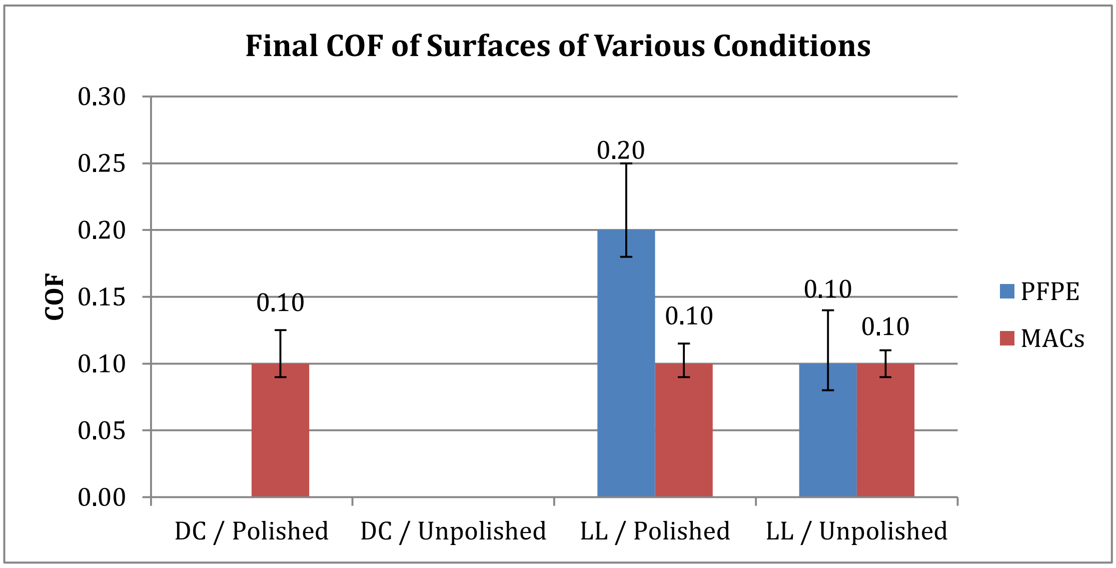


Figure 4: Final CoF for various Si samples that did not fail after 54,000 cycles, under dip-coating (DC) and Loc-Lub (LL) method, at reciprocating speed of 5 mm s^{-1} and 50 g load

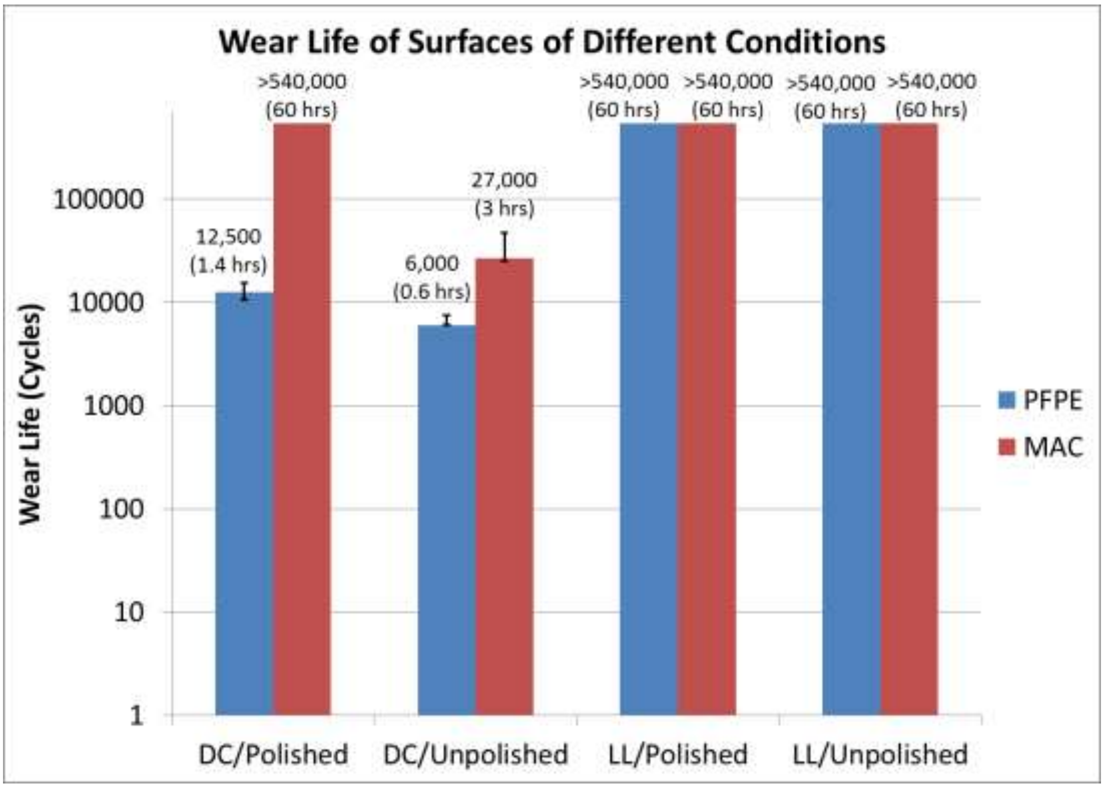


Figure 5: Wear life (on a vertical log scale) of various Si samples lubricated via dip-coating (DC) and Loc-Lub (LL) method, at reciprocating speed of 5 mm s^{-1} and 50 g load

As the lubricant forms a layer on the surface when applied (either discontinuous or continuous) and the solvent evaporates rapidly after application, the surfaces are considered to operate in the boundary regime. Such type of nano-scale films may behave more as a solid than a liquid, tendency for which is even greater when sliding speed is increased [29, 30]. Moreover, the sliding in the present case was between two parallel plates without any convergence and hence lubrication regime will not be that of hydrodynamic lubrication. A summary of the results from the wear and friction tests are presented as follows: the initial CoF (Figure 3), the stable CoF at the end of the test for samples which did not fail within the first 54,000 cycles of wear testing (Figure 4), and the wear lives of the various samples (Figure 5). Final CoF measurements for dip-coated PFPE polished Si surfaces and dip-coated unpolished surfaces for both lubricants were not reported as a stable CoF could not be observed – the wear tests showed continuous increase or fluctuation of measured friction. MAC lubricant was shown to give an overall improvement in wear life and friction properties when compared to PFPE lubricant. It was noted that the samples lubricated with MAC lubricant had no visible running-in time and lower initial CoF. However, samples lubricated with PFPE experienced significant amount of running-in time with higher initial friction, before stabilizing at a lower level.

The difference in spreading behaviour observed in the previous section provides an explanation on the wear lives and the friction trends between the two lubricants applied via the same method: low initial coefficient of friction was observed for MAC and not for PFPE, as there were sufficient MAC molecules between the contacting surfaces to provide adequate lubrication by reducing asperity contact between the

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

surfaces. The propensity of the MAC lubricant to remain in a cohesive droplet also assures a layer of lubricant in between the surfaces and minimizes the need for self-replenishment within the parameters of this study. It is thought that this cohesiveness assists to provide a lower stable coefficient of friction for samples lasting beyond the span of the extended test (540,000 cycles) as the lubricant layer is not depleted as easily and thus prevents direct contact between the surfaces.

Table 2: Initial and final coefficients of friction for wear tests conducted at higher loads, lubricated via "Loc-Lub"

Lubricant	Load	Initial COF	Final COF
PFPE 4 wt%	70g	0.147	0.075
PFPE 4 wt%	100g	0.125	0.073
PFPE 0.4 wt%	70g	0.195	0.10
MAC 4 wt%	70g	0.23	0.09
MAC 4 wt%	100g	0.155	0.075
MAC 0.4 wt%	70g	0.19	0.11

Surfaces lubricated via Loc-Lub method using PFPE and MAC continued to show low coefficients of friction at higher loads (70 g and 100 g) after 540,000 cycles (Table 2). Further observation using optical microscopy was done to study the surface morphology in order to investigate if failure of the lubricant films occurred, resulting in wear on Si surfaces.

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

4.4 Optical Microscopy

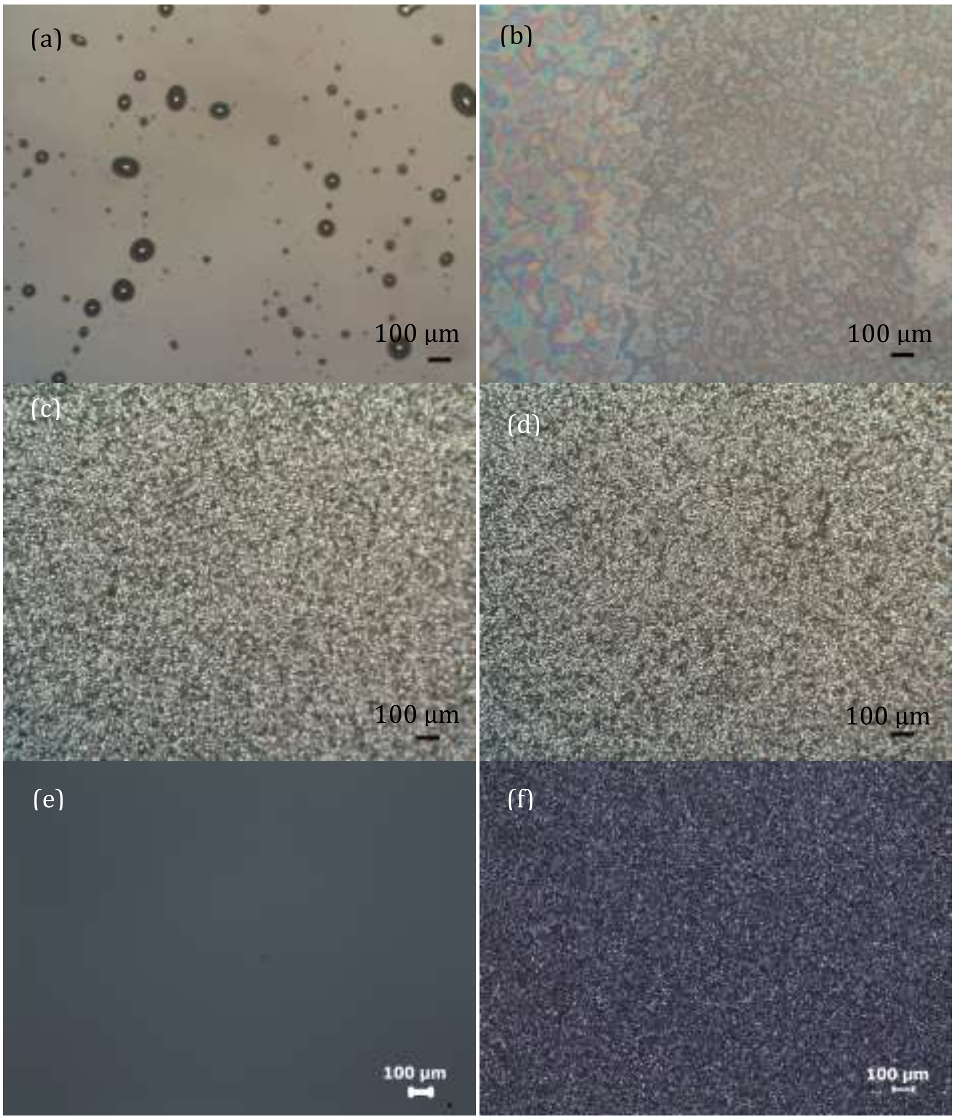


Figure 6: Si Surfaces lubricated via dip-coating before wear test; (a) Polished Si with MAC, (b) Polished Si with PFPE, (c) Unpolished Si with MAC, (d) Unpolished Si with PFPE, (e) Bare polished Si and (f) Bare unpolished Si.

Observation of the polished Si surface prior to wear testing shows that dip-coating with MAC lubricant forms a spread of micro-droplets, while dip-coating with PFPE produces a more uniform film (Figure 6), similar to that observed in Figure 2. The cohesive property of MAC and the lack of propensity to spread on the Si surface as earlier noted in Figure 1 support this observation.

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

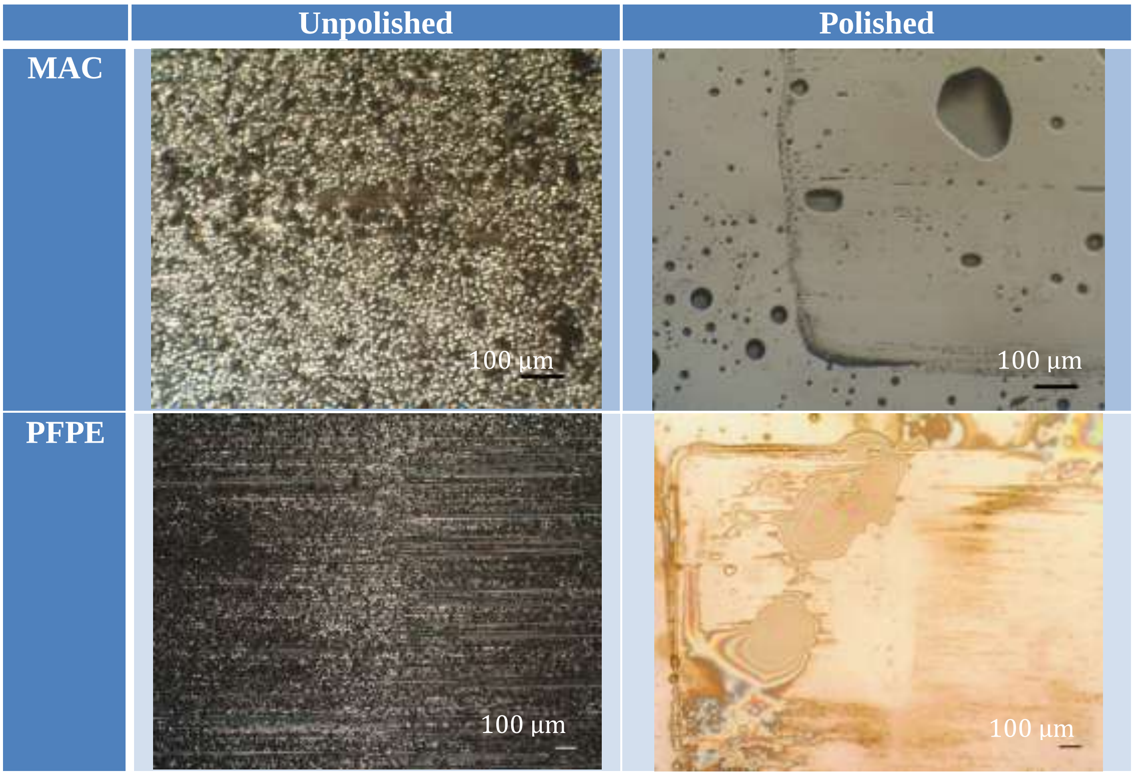


Figure 7: Optical images of Si samples dip-coated with MAC and PFPE lubricant at 4.0 wt%, after 6 hrs (54,000 cycles) of reciprocating sliding wear tests at reciprocating speed of 5 mm s^{-1} and 50 g load

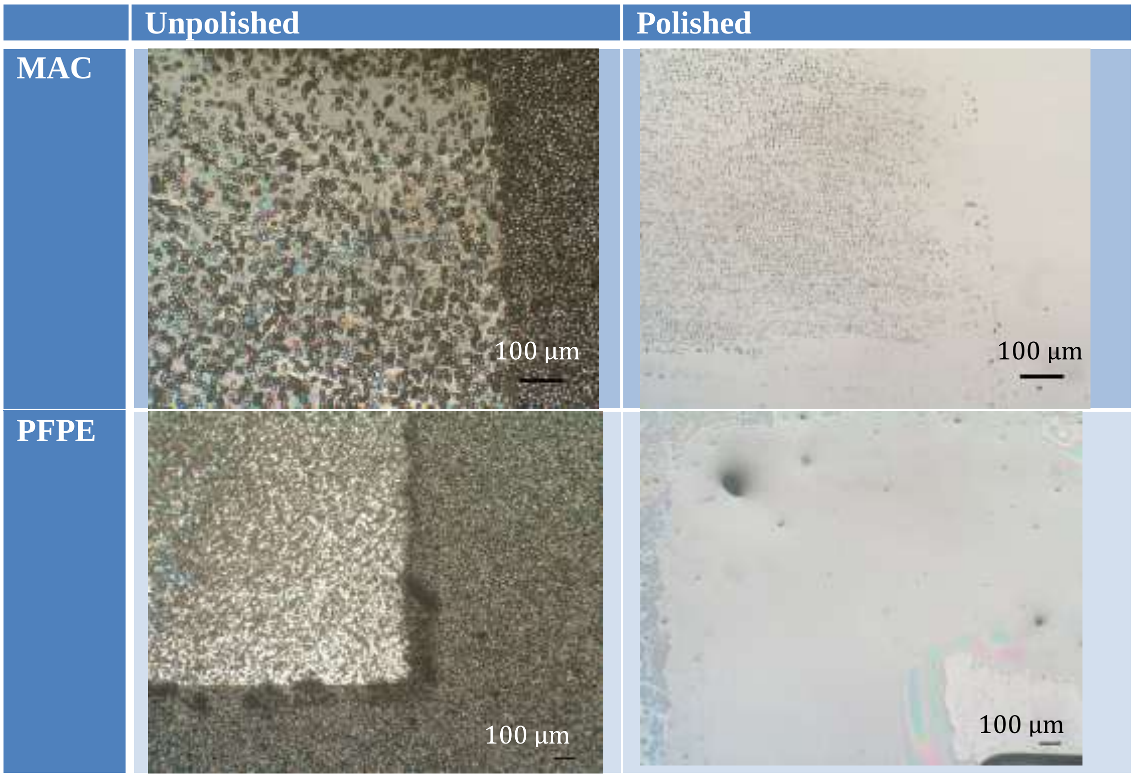


Figure 8: Optical images of Si surfaces under Loc-Lub of MAC and PFPE lubricant at 4.0 wt%, after 60 hrs (540,000 cycles) of reciprocating sliding wear tests, at reciprocating speed of 5 mm s^{-1} and 50 g load

Optical microscopy of the tested surfaces (Figure 7 & 8) showed no scratches on polished Si samples under both dip-coating and "Loc-Lub" MAC lubrication, indicating that no visible wear has taken place on the contact surface. Both lubrication methods using MAC lubricant showed low coefficient of friction lasting beyond the duration of the test. Scratches were found on unpolished dip-coated samples for both PFPE and MAC lubrication, indicating failure. A polishing effect was observed on "Loc-Lub" unpolished samples, similar to that for the same tests using PFPE in previous research [8]. No scratches were observed on all samples lubricated via the "Loc-Lub" method, indicating successful prevention of wear.

This cohesive behavior of MAC lubricant (Figures 1, 2, 6), and the capillary forces between the surfaces, is thought to maintain the lubricant layer between the sliding interfaces, reducing the need for self-replenishment. Comparison between PFPE and MAC lubricants, in conjunction with the wear lives, shows that MAC lubricants exhibit better properties in wear prevention and lowering friction for the test conditions.

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

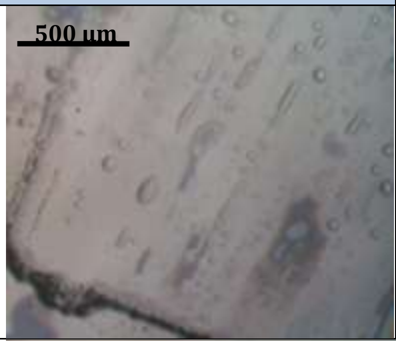
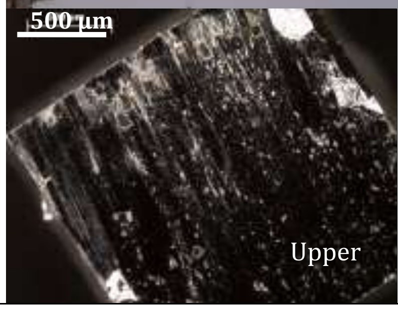
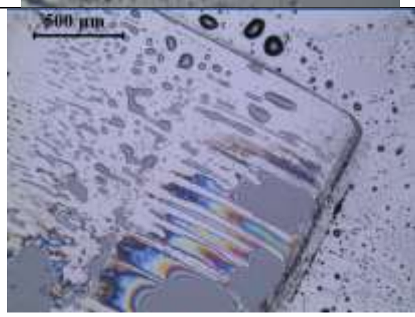
Conc. (wt%)	Load	Images PFPE	Images MAC
4%	70g		
4%	100g		
0.4%	70g	 	

Figure 9: Optical images of wear tracks on polished Si wafers for various concentrations of lubricants and load, after 540,000 cycles

Figure 9 shows a summary of the optical microscopy on the surfaces after the wear tests at higher loads (70 and 100 g). A significant amount of polymer and debris build-up along the edges of the contact region for 4 wt% PFPE and MAC lubricated surfaces were found, although visibly less build-up on MAC lubricated surfaces. Tests conducted at a lower concentration (0.4 wt%) shows extensive wear on both top and bottom surfaces when lubricated with PFPE. Small scratches and wear scars for 0.4 wt% MAC lubricated samples were noticed only under much higher magnification (Figure 10).

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

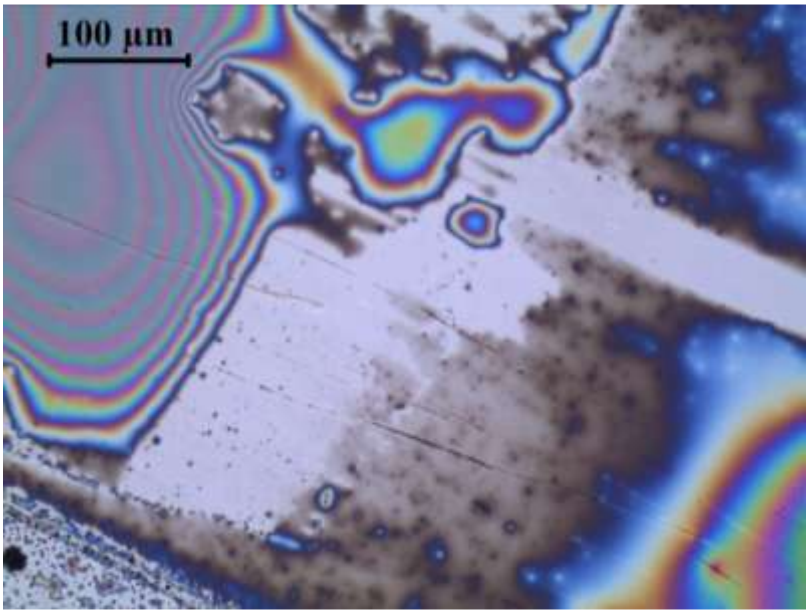


Figure 10: Optical microscopy images of wear tracks on polished Si surfaces tested at 70g load with 0.4 wt% MAC under Loc-Lub after 540,000 cycles at reciprocating speed of 5 mm s^{-1}. Wear in the form of a few scratches was only visible at higher magnification.

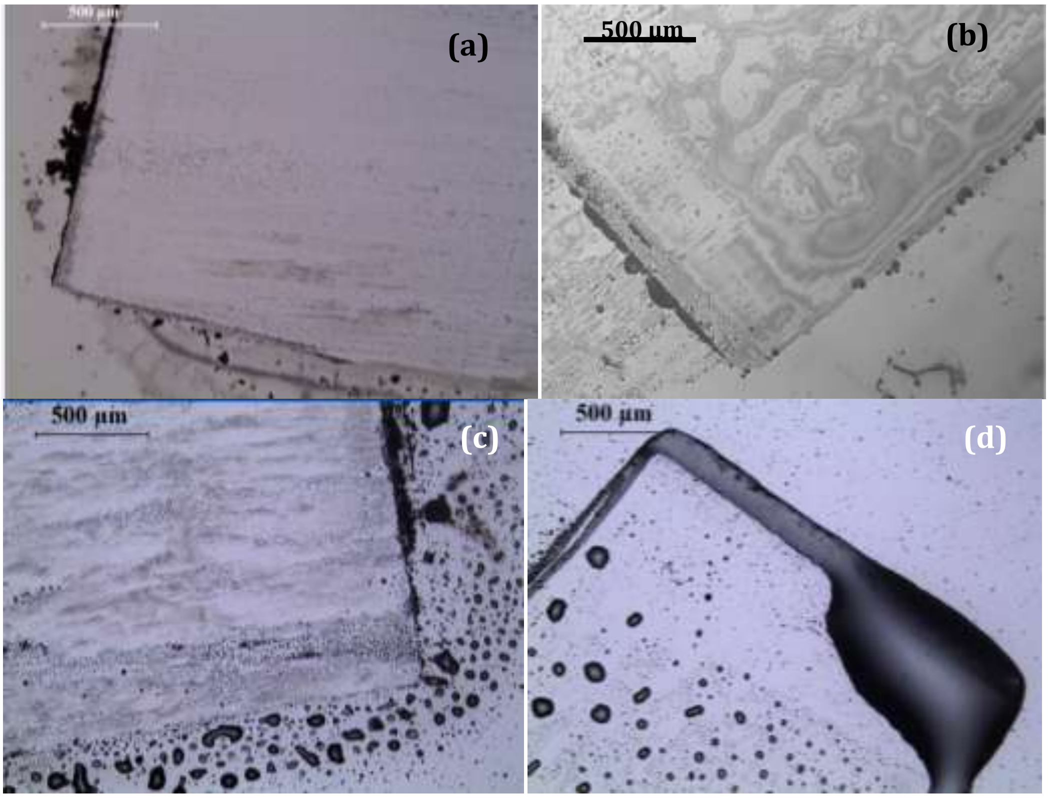


Figure 11: Optical Microscopy Images of Wear Tracks on Polished Si Surfaces, at reciprocating speed of 5 mm s^{-1} and 70g load with (a) 0.4 wt% PFPE, (b) 4 wt% PFPE, (c) 0.4 wt% MAC, (d) 4 wt% MAC, after 54,000 cycles

Optical microscopy was also used to compare the differences in wear after 54,000 cycles at 70 g between two different concentrations of the lubricants (Figure 11). When comparing between MAC and PFPE at 4 wt% concentration, a lower amount of wear was observed with MAC lubricant. The differences in lubricant spreading behaviour are also clearly visible in the optical images. This implies that MAC lubricated surfaces have a longer wear life than PFPE lubricated surfaces under the test conditions.

The improved life exhibited in MAC lubricated surfaces is due to a number of factors, one of which is believed to be the differences in the lubricant behaviour. PFPE is known to form an extremely thin film on the surface, making it suitable for magnetic hard disc lubrication where contacting surfaces move very close to each other [27, 28], while MAC has been found to de-wet on silicon surfaces instead of forming a thin film [17, 31]. The high mobility of MAC lubricant droplets enables it to replenish itself in depleted areas within the contact [21], sharing the same self-replenishing property as PFPE. MAC droplets are also believed to stay intact instead of spreading thinly on the surfaces due to the de-wetting effect and its cohesiveness, creating a constant and comparatively thicker film of lubricant between the two sliding surfaces (Figure 2). This decreases the chances of direct contact between the Si surface asperities as compared to PFPE.

Secondly, MAC lubricants are not observed to experience a loss of lubricant to outside the contact zone as a result of the sweeping action, as observed for PFPE in previous research [8]. As PFPE only forms a very thin layer, the availability for self-replenishment over a period of time is lessened as compared to that for MAC – this is also due to PFPE spreading outside the wear track. These two factors combined provide a feasible explanation why PFPE shows a lower wear life and resistance than MAC.

4.5 Discussion

The discovery of MAC lubricant being effective in providing a good wear life compared to PFPE and low coefficient of friction under these reciprocating sliding wear conditions has been presented in this study. The absence of a running-in time or a high initial CoF for the MAC lubricant strongly suggests that MAC lubricant may be of better use in lubricating MEMS devices under reciprocating sliding wear. Since a high coefficient of friction is commonly related to wear, the low initial friction observed for MAC lubricated samples also implies a reduced amount of wear at the onset of sliding, avoiding early breakage. Throughout the tests conducted with MAC lubrication at 50 g load, wear was not visible when observed under optical microscopy.

Optical microscopy prior to wear tests revealed that the surface of the sample was not evenly coated with MAC lubricant as it was with PFPE. Instead, MAC droplets were noted when viewed under high magnification – it is believed that the main reason for improved tribological properties for samples lubricated with MAC lubricant is the tendency of the MAC lubricant to conglomerate into larger droplets and their cohesive behavior. This ensures that the lubricant present at the interface is not swept aside or removed from the contacting plane surfaces, as would be expected with thin films. The lubricant then maintains a consistent film between the contacting surfaces. This phenomenon was confirmed with the analysis of the spreading rates for the individual lubricants. An examination of the wear track confirms that the lubricant layer remains mostly in the contact region. This lack of spreading can therefore be more effective than the self-replenishing mechanism attributed to other lubricants such as PFPE, as the replenishing mechanism would be redundant. As the tests were

http://link.springer.com/article/10.1007%2Fs11249-013-0112-3

conducted under boundary lubrication conditions, the continual presence of the lubricant at the interface would then reduce the amount of asperity contact between the surfaces, leading to a lower amount of friction as well as reduced wear.

Differences in the polished and unpolished Si surfaces tested between lubricants depend on the nature of the lubricant's cohesiveness. PFPE has been found to show lower friction coefficient on unpolished surfaces due to the collection of the lubricant in the valleys of the asperities, adding to the effectiveness of its self-replenishment property. PFPE has high spreading capability on a surface such as Si. This increases the lubricity of PFPE under these conditions, as there is a ready source of replenishment when the thin lubricant layer is swept away [8].

MAC lubricant, on the other hand, is extremely cohesive and provides a consistent layer between the two surfaces. This separates the surfaces from direct contact during sliding. However, in the presence of asperities, this layer is broken up, with the tips of the asperities on the Si wafers coming into contact with each other. This contact present between the unpolished surfaces cause higher friction compared to smooth polished surfaces as the lubricant layer is now interrupted. The dewetting of MAC on the surfaces, also observed in references [17, 31], suggest a lack of spreading and depletion of lubricant at the contact areas. The advantages of the cohesiveness of MAC on wear life may be reduced for unpolished surfaces as a result - this can be seen in the results for dip-coated unpolished samples lubricated with PFPE and MAC. These differences in mechanism bear further research, along with the lower coefficients of friction observed at higher load tests.

5 Conclusion

With improved wear and friction properties, as well as a slightly differing lubrication mechanism, Multiply-Alkylated Cyclopentanes or MAC lubricant has been proven to be an effective lubricant when compared to PFPE under reciprocating sliding wear conditions using "Loc-Lub". This improvement in tribological properties covers the three areas viz. running-in friction, steady state dynamic friction, and wear prevention. Given that MAC lubricants also show very high thermal stability and the ability to coat itself onto various surfaces as well as feasibility in the "Loc-Lub" method, it presents as a strong candidate for implementation in the lubrication of MEMS.

The use of MAC in MEMS can be further investigated, along with the mechanism of lubrication, in actual micro-devices, both as an additive in liquid lubrication as well as in solution as a base lubricant itself.

Acknowledgments

This research is supported by the Singapore National Research Foundation under its CRP (Competitive Research Program) funding (Award Number: NRF-CRP 2-2007-04). The views expressed herein are those of the authors and are not necessarily those of the Singapore National Research Foundation.

References

1. Mate, C. M., *Tribology on the Small Scale - A Bottom Up Approach To Friction, Lubrication and Wear.* Oxford: Oxford University Press, 2007.
2. Potter, C. N., *Hermetic MEMS Package and Method of Manufacture*, in *U.S. Patent No. 7,358,106 B2*2005, Stellar MicroDevices, Inc., Austin, TX: Austin, TX.
3. Ashurst, W. R., de Boer, M. P., Carraro, C., and Maboudian, R., *An investigation of sidewall adhesion in MEMS.* Applied Surface Science, 2003. **212-213**: p. 735-741.
4. Bhushan, B., *Tribology and Mechanics of Magnetic Storage Devices.* Springer-Verlag, New York, 1990.
5. Tani, H. and Matsumoto, H., *Spreading Mechanism of PFPE Lubricant on the Magnetic Disks.* Journal of Tribology, 2001. **123**(3): p. 533-540.
6. Wang, M., Miyake, S., and Matsunuma, S., *Nanowear studies of PFPE lubricant on magnetic perpendicular recording DLC-film-coated disk by lateral oscillation test.* Wear, 2005. **259**(7-12): p. 1332-1342.
7. Sinha, S. K., Jonathan, L. Y., Satyanarayana, N., Yu, H., Harikumar, V., and Zhou, G., *Method of applying a lubricant to a micromechanical device.* U.S. Provisional Patent, 61/314,627, 2010.
8. Jonathan, L. Y., Harikumar, V., Satyanarayana, N., and Sinha, S. K., *Localized lubrication of micromachines: A feasibility study on Si in reciprocating sliding with PFPE as the lubricant.* Wear, 2010. **270**(1-2): p. 19-31.
9. Hongbin, Y., Guangya, Z., Sinha, S. K., Leong, J. Y., and Fook Siong, C., *Characterization and Reduction of MEMS Sidewall Friction Using Novel Microtribometer and Localized Lubrication Method.* Journal of Microelectromechanical Systems, 2011. **20**(4): p. 991-1000.
10. Paciorek, K. J. L. and Kratzer, R. H., *Stability of perfluoroalkylethers.* Journal of Fluorine Chemistry, 1994. **67**(2): p. 169-175.
11. Kasai, P. H., *Degradation of Perfluorpolymers Catalyzed by Lewis Acids.* ASME Adv. Inf. Stor. Syst., 1992. **4**: p. 291-314.
12. Luo, J., Yang, M., Zhang, C., Pan, G., and Wen, S., *Study on the cyclotriphosphazene film on magnetic head surface.* Tribology International, 2004. **37**(7): p. 585-590.
13. Nakayama, K. and Mirza, S. M., *Verification of the Decomposition of Perfluoropolyether Fluid Due to Tribomicroplasma.* Tribology Transactions, 2006. **49**(1): p. 17 - 25.
14. Wei, J., Fong, W., Bogy, D., and Bhatia, C., *The decomposition mechanisms of a perfluoropolyether at the head/disk interface of hard disk drives.* Tribology Letters, 1998. **5**(2): p. 203-209.
15. Bair, S., Vergne, P., and Marchetti, M., *The Effect of Shear-Thinning on Film Thickness for Space Lubricants.* Tribology Transactions, 2002. **45**(3): p. 330 - 333.
16. Nelias, D., Legrand, E., Vergne, P., and Mondier, J.-B., *Traction Behavior of Some Lubricants Used for Rolling Bearings in Spacecraft Applications: Experiments and Thermal Model Based on Primary Laboratory Data.* Journal of Tribology, 2002. **124**(1): p. 72-81.

17. Wang, Y., Mo, Y., Zhu, M., and Bai, M., *Wettability and Nanotribological Property of Multiply Alkylated Cyclopentanes (MACs) on Silicon Substrates.* Tribology Transactions, 2010. **53**(2): p. 219 - 223.
18. Chun, S. W., Talke, F. E., Kang, H. J., and Kim, W. K., *Thermal Characteristics of Multiply Alkylated Cyclopentane and Perfluoropolyether.* Tribology Transactions, 2003. **46**(1): p. 70 - 75.
19. Wang, Y., Wang, L., Mo, Y., and Xue, Q., *Fabrication and Tribological Behavior of Patterned Multiply-Alkylated Cyclopentanes (MACs)–Octadecyltrichlorosilane (OTS) Dual-Component Film by a Soft Lithographic Approach.* Tribology Letters, 2011. **41**(1): p. 163-170.
20. Ma, J. Q., Pang, C. J., Mo, Y. F., and Bai, M. W., *Preparation and tribological properties of multiply-alkylated cyclopentane (MAC),Äìoctadecyltrichlorosilane (OTS) double-layer film on silicon.* Wear, 2007. **263**(7,Äì12): p. 1000-1007.
21. Ma, J., Liu, J., Mo, Y., and Bai, M., *Effect of multiply-alkylated cyclopentane (MAC) on durability and load-carrying capacity of self-assembled monolayers on silicon wafer* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2007. **301**(1-3): p. 481-489.
22. Ma, J., Mo, Y., and Bai, M., *Effect of Ag nanoparticles additive on the tribological behavior of multialkylated cyclopentanes (MACs).* Wear, 2009. **266**(7,Äì8): p. 627-631.
23. Abdul Samad, M., Satyanarayana, N., and Sinha, S. K., *Tribology of UHMWPE film on air-plasma treated tool steel and the effect of PFPE overcoat.* Surface and Coatings Technology, 2010. **204**(9-10): p. 1330-1338.
24. Dube, M. J., Bollea, D., Jones, W. R., Marchetti, M., and Jansen, M. J., *A New Synthetic Hydrocarbon Liquid Lubricant for Space Applications.* Tribology Letters, 2003. **15**(1): p. 3-8.
25. Myo, M., Jonathan, L. Y., and Sinha, S. K., *Effects of interfacial energy modifications on the tribology of UHMWPE coated Si.* Journal of Physics D: Applied Physics, 2008. **41**(5): p. 055307.
26. Xiao-Yan, G., Xin, L., Yuan-Zhong, H., and Hui, W., *The spreading behaviour of perfluoropolyether droplets on solid surfaces.* Chinese Physics B, 2008. **17**(3): p. 1094.
27. Li, N., Meng, Y., and Bogy, D., *Effects of PFPE Lubricant Properties on the Critical Clearance and Rate of the Lubricant Transfer from Disk Surface to Slider.* Tribology Letters, 2011: p. 1-12.
28. Sinha, S. K., Kawaguchi, M., Kato, T., and Kennedy, F. E., *Wear durability studies of ultra-thin perfluoropolyether lubricant on magnetic hard disks.* Tribology International, 2003. **36**(4-6): p. 217-225.
29. Briscoe, B. J. and Evans, D. C. B., *The Shear Properties of Langmuir-Blodgett Layers.* Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences, 1982. **380**(1779): p. 389-407.
30. Demirel, A. L. and Granick, S., *Glasslike Transition of a Confined Simple Fluid.* Physical Review Letters, 1996. **77**(11): p. 2261-2264.
31. Wang, Y. and Baia, M., *Wettability Study of Multiply-Alkylated Cyclopentanes (MACs) on Silicon Substrates*, in *Advanced Tribology*, Luo, Jianbin, Meng, Yonggang, Shao, Tianmin, and Zhao, Qian, Editors. 2010, Springer Berlin Heidelberg. p. 102-103.