Tribological properties of ultra-thin functionalized polyethylene film chemisorbed on Si with an intermediate benzophenone layer

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Abstract

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References

Abstract

An ultra-thin (approximately 20 nm) functionalized polyethylene (fPE) film is successfully attached to Si substrate via a reactive benzophenone (Ph_2CO) layer. The presence of fPE promotes wear durability of Si/ Ph_2CO /fPE to 1000 cycles compared with 100 cycles for Si/ Ph_2CO and nearly zero wear life for bare Si in a ball-on-disc (4 mm diameter Si_3N_4 ball) wear test under 40 mN applied normal load and 500 rpm sliding speed. As an enhancement to the wear life, perfluoropolyether (PFPE) is applied as a top mobile lubricant layer coated onto Si/Ph_2CO and Si/Ph_2CO/fPE. A significant improvement in the wear durability is observed as Si/Ph_2CO/PFPE fails at 250,000 cycles and Si/Ph_2CO/fPE/PFPE does not fail until one million cycles. Si/Ph_2CO/fPE/PFPE can withstand a minimum applied load of 150 mN at a sliding speed of 0.052 ms^{-1} without failure, providing a PV (pressure x velocity) limit of greater than 106.6 MPa ms^{-1}.

Keywords   Boundary lubrication, Functionalized PE, PFPE, Polymer film,

1   Introduction

A thin solid or liquid film is required to protect the sliding surfaces in micro/nano devices in which silicon is still widely used as the substrate material [1-6]. A small amount of surface tension or energy from the protective film can increase adhesion, stiction, friction and wear as a result of pull-off force and menisci formation [7-8]. In reducing adhesion, stiction and friction, organic thin films have been practically applied. Though many organic thin films can reduce stiction and friction effectively, it is observed that their long-term wear resistance does not improve significantly [9-11]. It is necessary to explore new films that can provide reliability of devices in terms of low friction and long wear durability. In recent studies, many polymer films on Si substrate have shown low friction and high wear performance [12-15]. In our previous studies, we have applied different surface modification techniques to ultra high molecular weight polyethylene (UHMWPE) film and extended the wear durability by several orders [16-18], showing that polymer films are very promising coating materials in lowering friction and improving wear durability of Si substrate. However, for application of such coatings in micro/nano devices such as MEMS (micro-electro-mechanical systems), it is also important that the thickness of the coating is controlled and brought down to only few nanometers.

Therefore, in the current study, we have proposed an ultra-thin polymer film (in nanometer range) on Si substrate and investigated its friction and wear properties in combination with other layers. The functionalized polyethylene (fPE), polyethylene-graft-maleic anhydride, was chosen as a polymer film due to its excellent tribological performance in bulk form and its terminal groups that can chemically attach to a substrate. Chemical attachments are important as they can firmly bond to the substrate and provide better wear resistance. In this case, as bare Si substrate has no functional groups, it is required to modify bare Si substrate with a benzophenone (abbreviated as Ph_2CO) layer in order to attach with fPE. Benzophenone was chosen because it can easily attach to C-H bonds of fPE in different chemical environments [19-25].

The chemisorption of fPE film onto Si/Ph_2CO can enhance the wear resistance to some extent. However, as the thickness of the fPE film used in this study is very thin, it is difficult to obtain long-term lubrication effects. If there is no replenishment layer, wear can easily initiate from the contact area despite excellent bond strength. The importance of using a mobile layer of perfluoropolyether (PFPE) in replenishing process for longer wear durability has been well studied [26]. As far as wear durability is concerned, PFPE coated self-assemble monolayers (SAMs) have shown higher durability than either SAMs or PFPE layer alone [27-28]. Hence, in this study, we have applied PFPE as the top mobile layer for effective lubrication.

This paper studies the tribological performance of chemically-bonded functionalized polyethylene on Si surface with the help of reactive benzophenone. The effects of a top mobile layer of PFPE on friction and wear performance are also investigated and compared with similar tribological coatings investigated in the past.

2   Experimental procedures

2.1   *Materials*

Polished n-type silicon (100) wafer was used as the substrate. 4-hydroxybenzophenone, allyl bromide and potassium carbonate were obtained from Alfa Aesar and used as received. Polyethylene-graft-maleic anhydride (PE-g-MAH) was obtained from Aldrich Inc. and perfluoropolyether (PFPE, Z-dol 4000) was obtained from Solvay Solexis.

2.2   *Sample preparation*

2.2.1   *Synthesis of benzophenone monolayer on Si substrate*

Si substrates (1 cm x 1 cm) were rinsed for 1 min and sonicated for 1 hr in acetone. The substrates were blow-dried with pure nitrogen gas and given plasma treatment under an air environment in order to remove any contaminants from the substrates. For the air-plasma treatment, a Harrick Plasma cleaner/steriliser was used with an exposure time of 15 min and a RF power of 30 W under vacuum.

4-hydroxybenzophenone (19.8 g) and allyl bromide liquid (13.3 g) were dissolved in acetone (60 mL). After that, 14 g of potassium carbonate was added into the solution. The extraction of 4-allyloxybenzophenone crystals from the solution was performed as described in Ref [29]. The extracted crystals (2 g) were added to dimethyl chlorosilane (20 mL) in the presence of Pt-C (10 mg, (10%)) catalyst and the mixture was then refluxed at about 75 °C for 4 hr. After removing the catalyst by filtration of the mixture in toluene, 4-(3'-chlorodimethylsilyl) propyloxybenzophenone solution was obtained.

The cleaned Si substrates were immersed in the obtained solution with triethylamine (Et$_3$N) catalyst for 24 hr. The samples coated with benzophenone layer were obtained after rinsing with chloroform and then drying with pure nitrogen gas.

2.2.2 Preparation of functionalized polyethylene (fPE) on benzophenone coated Si (Si/Ph$_2$CO) samples

The fPE solution was prepared by dissolving polyethylene-graft-maleic anhydride, PE-g-MAH (1 wt%) in toluene at a temperature of 75 °C for 15 min. A magnetic stirrer was used to increase the dissolution rate. The chemical structures of benzophenone and PE-g-MAH (fPE) are provided in Fig. 1. The benzophenone coated Si samples (Si/Ph$_2$CO) were immersed into the fPE solution for 5 hr. The samples were then ultrasonically cleaned with toluene and methanol for 10 min each in order to remove fPE not chemically attached to the samples. After blow-drying with pure nitrogen at room temperature, the chemically attached fPE layer was formed on Si/Ph$_2$CO as Si/Ph$_2$CO/fPE.
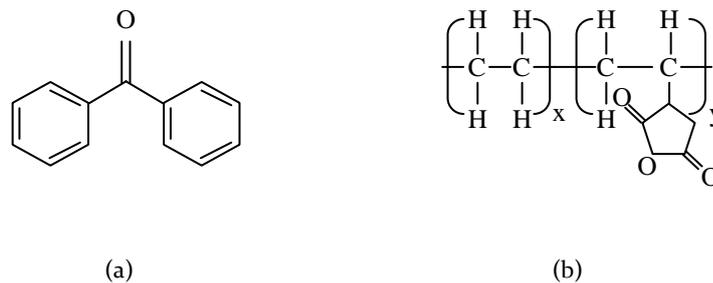

(a)   (b)

Fig. 1.   *The chemical structures of (a) benzophenone and (b) polyethylene-graft-maleic anhydride (fPE).*

2.2.3 Preparation of PFPE mobile layer on Si/Ph$_2$CO and Si/Ph$_2$CO/fPE samples

Perfluoropolyether (PFPE, Zdol 4000) was dip-coated from a solution of 0.2 wt% PFPE in H-Galden ZV60 solvent onto Si/Ph$_2$CO and Si/Ph$_2$CO/fPE samples at dipping and withdrawal speeds of 2.4 mm/s with a fixed dipping duration of 30 s. The chemical structures of PFPE and H-Galden ZV60 are HOCH$_2$CF$_2$O-(CF$_2$CF$_2$O)$_p$-(CF$_2$O)$_q$-CF$_2$CH$_2$OH and HCF$_2$O-(CF$_2$O)$_p$-(CF$_2$CF$_2$O)$_q$-CF$_2$H, respectively, where the ratio p/q is quoted as 2/3. A simple schematic diagram of Si substrate with different modified layers is provided in Fig. 2.
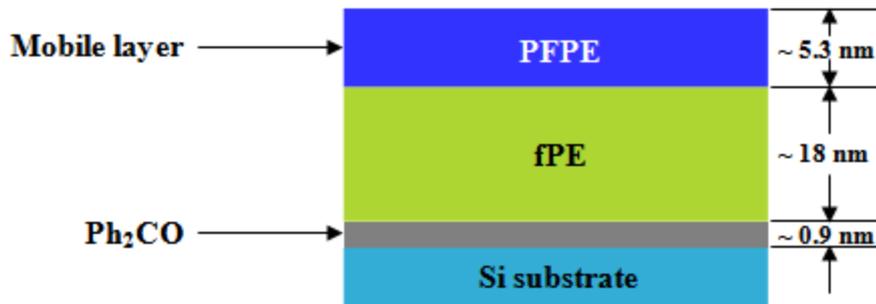
Fig. 2. *A schematic diagram of Si substrate with different modified layers (not to scale).*

2.3   Surface characterizations

2.3.1   Contact angle and surface energy measurements

The presence of different surface layers on Si substrate was first verified by contact angle measurement. VCA Optima Contact Angle System (AST product, Inc., USA) was used for the measurement of contact angles with deionized water, ethylene glycol and hexadecane droplets. A droplet of 0.5 µl was used for each contact angle measurements. A total of five independent measurements were performed randomly on the samples and an average value was taken for every sample. The measurement error was within ± 3°. After measuring the contact angle with different liquids, the surface energies were calculated using the equipment software. The relationship between the contact angle and the surface free energy was first demonstrated by Young in the form,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

where θ is the contact angle, γ is the surface energy and the subscripts SV, SL and LV represent surface-vapor, surface-liquid and liquid-vapor interfaces, respectively. We used the acid-base approach in which at least three liquids are required; two have known acid and base fractions larger than zero and at least one must be equal basic and polar parts.

2.3.2   Roughness and thickness measurements

The average roughness of the samples was measured using dynamic optical profilers (Veeco Wyko NT1100) (a non-contact profiling device). The scanning area for the measurement was 124 µm x 93 µm in VSI (vertical scan interferometry) mode. As the total film thickness was less than 25 nm, the reflectivity of the Si substrate was not affected by the coated polymer films as the film appeared transparent to naked eyes. Nevertheless, roughness measurement of the coated films was carried out without any additional gold sputtering for optical reflectivity, as any additional process could damage the film itself because of heating effect. Interestingly, we did observe a change in the roughness values after each successive film deposition as presented in the results section.

The thickness of each coated layer was determined using a variable-angle-spectroscopic ellipsometry (VASE, J. A. Woollam. Co., USA) at wavelengths from 400 to 1,000 nm at 10 nm intervals and at incident angles of 65°, 70°, and 75°. The refractive indices were assumed as 1.46 for SiO₂ [30], 1.5 for benzophenone [29], 1.54 for fPE [31] and 1.296 for PEPE [32].

2.3.3   XPS analysis

The chemical state of the layers was observed by XPS (x-ray photoelectron microscopy) (Kratos Analytical AXIS His). XPS (Al Kα source) tests were performed with an X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and pass energy of 40 eV. The core level signals were obtained at a photoelectron take-off angle of 90° (with respect to the sample surface). All binding energies (BE) were

referenced to the C1s hydrocarbon peak at 284.6 eV. In peak combination, the line width (full width at half-maximum or FWHM) for the Gaussian peaks was maintained constant for all components in a particular spectrum. The curve de-convolution of the XP spectra was performed by using XPS Peak Fitting Program XPSPEAK41 (Freeware for XPS Community, Chemistry, CUHK).

2.4 *Friction and wear tests*

Friction and wear tests were carried out on a custom built ball-on-disc tribometer which can measure the normal and frictional displacements of the cantilever with laser sensors. The displacements were converted to the respective forces with the calibration chart. The sensitivity of the laser sensor was 0.5 μm which was equivalent to 0.125 mN force. A silicon nitride (Si_3N_4) ball of 4 mm diameter with a surface roughness of 5 nm (supplier's data) was used as the counterface. The normal load used was 40 mN. The static friction was measured at a sliding track radius of 1 mm with a fixed disc rotational speed of 2 rpm (relative linear speed 0.21 mm/s). The sampling rate used in recording of the data was set at 10 Hz. The wear durability was determined at a fixed disc rotational speed of 500 rpm (relative linear speed was 0.052 m/s) and recorded at a sampling rate of 5 Hz. The wear durability was defined as the number of cycles completed when either the coefficient of friction exceeded 0.3 or large fluctuations in the coefficient of friction (indicative of film failure) occurred. The ambient temperature and the relative humidity were fixed at 25 °C and 65 %, respectively.

3 Results

3.1 *Surface energy and roughness*

Table 1 presents the water contact angle, the surface energy, the surface roughness and the coating thickness data for bare Si and modified Si. The bare Si surface without modification is the most hydrophilic with highest surface energy among all the surfaces. After modifying with benzophenone, the water contact angle of Si/Ph_2CO is hydrophobic at 86°. This value correlates with the measurement of Shen *et al.* [33]. fPE layer on Si/Ph_2CO sample has a contact angle of 80° which is slightly less than the reported values for the bulk polyethylene (91°-97°) [34-35]. This difference appears to be because of the effect of under layer of benzophenone. After coating PFPE film on Si/Ph_2CO and $Si/Ph_2CO/fPE$ samples, the water contact angles further reduce to 82° and 71°, respectively. The noticeable changes in the water contact angle after modifying with different layers confirm the successful formation of the layers on the Si substrate. The formation of different layers will also be verified by chemical analysis using XPS in the next section.

Table 1. *Water contact angle, surface energy, surface average roughness and thickness data for bare Si and coated Si.*

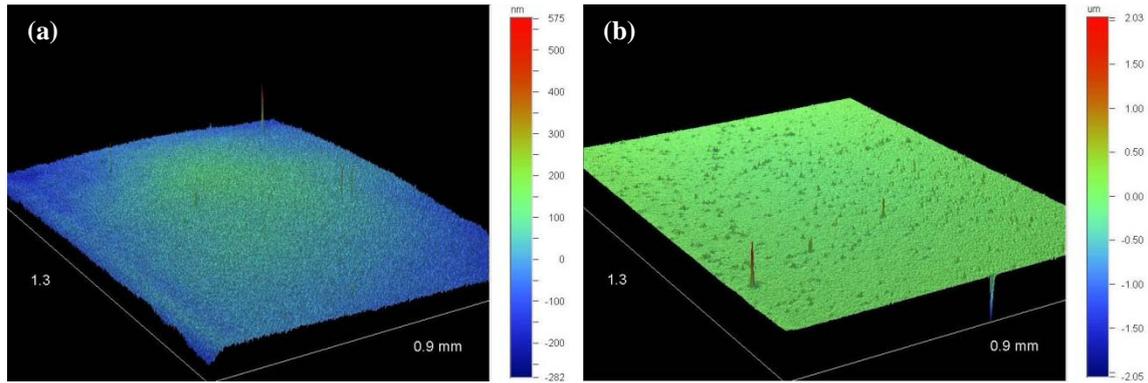| Sample	Water contact angle (°)	Surface energy (mJ/m²)	Surface average roughness, R_a (nm)	Thickness of top layer (nm)
Si	6	42.9	0.4	-
Si/Ph_2CO	86	25.6	0.86	0.7 ± 0.2
$Si/Ph_2CO/fPE$	80	28.9	6.7	15 ± 3
$Si/Ph_2CO/PFPE$	82	31.8	3.59	4.3 ± 1
$Si/Ph_2CO/fPE/PFPE$	71	24.5	4.09	4.3 ± 1

Fig. 3. *Surface imaging on (a) Si/Ph2CO and (b) Si/Ph2CO/fPE/PFPE using DMEMS (dynamic MEMS) where the scan size is 124 μm × 93 μm.*

3.2   Roughness and thickness

The surface roughness (R_a) of bare Si is about 0.4 nm whereas roughness values of the modified layers are much higher in the range of 0.86-6.7 nm. All of the layers have shown very similar roughness values except that fPE makes the surface slightly rougher because of large molecules whereas PFPE smoothens the surface by filling original valleys. The roughness data also confirm successful formation and coverage of the layers on the Si substrate. Some images of surface topography are shown in Fig. 3.

The thickness of the modified benzophenone layer on Si is 0.7 ± 0.2 nm which is slightly lower than the value reported in [29]. The fPE and PFPE films have thickness values of 15 ± 3 nm and 4.3 ± 1 nm respectively.

3.3   XPS results

The chemical analysis of the formation of different layers such as benzophenone, fPE and PFPE was studied by XPS and their C1s spectra are shown in Fig. 3. The two C1s peaks are observed in the spectrum of Si/Ph$_2$CO (Fig. 4 (a)). The peak at 285 eV formed due to the presence of C-C/C-H bonds from the benzophenone film [36] is not found in the C1s spectrum of bare Si. The C1s peak (O-C=O) in Fig. 4 (b) represents the functional group of anhydride from the fPE film [37]. The existence of the O-C=O peak confirms the successful formation of fPE onto Si/Ph$_2$CO. After a PFPE film is coated onto Si/Ph$_2$CO/fPE, three extra C1s peaks (O-C-F2, F-C-F and O-C-F) are observed in Fig. 4 (c) which verifies the formation of the PFPE film.
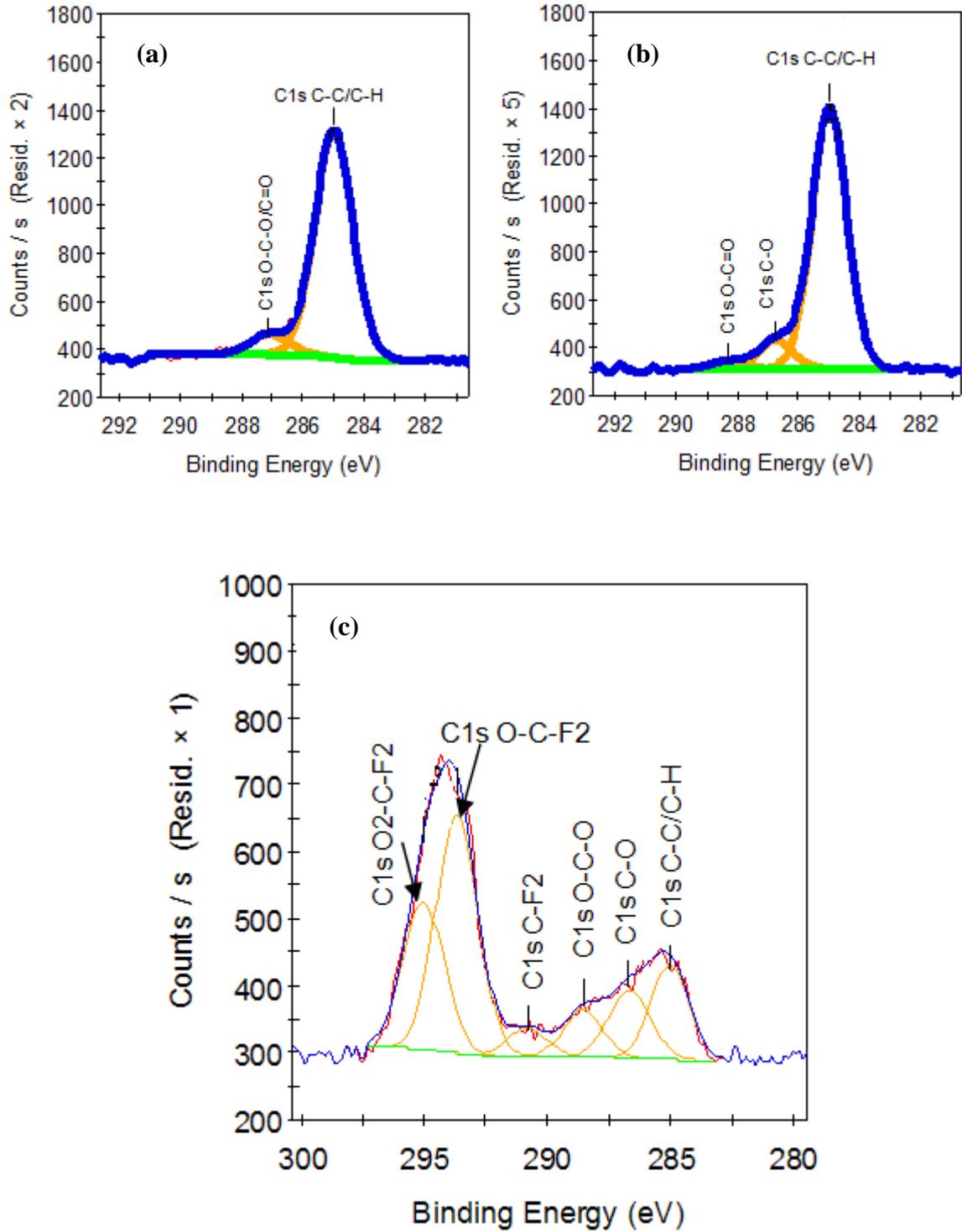
Fig. 4. *High-resolution C1s X-ray photoelectron spectrum (XPS) of (a) Si/Ph₂CO (b) Si/Ph₂CO/fPE and (c) Si/Ph₂CO/fPE/PFPE.*

3.4   Micro-tribological properties

3.4.1   *Static friction*

For better understanding of the effect of the changes of surface energy on the frictional properties of modified Si, static friction (the initial high friction at the start of the sliding) is studied and summarized in Fig. 5. Bare Si which has the highest surface energy (see Table 1) among all surfaces used shows much higher static friction than any modified film. The reason is the strong adhesion between bare Si and the silicon nitride ball due to high surface energy of bare Si. The lower coefficients of friction are observed for other modified layers as their surface energies are also low.
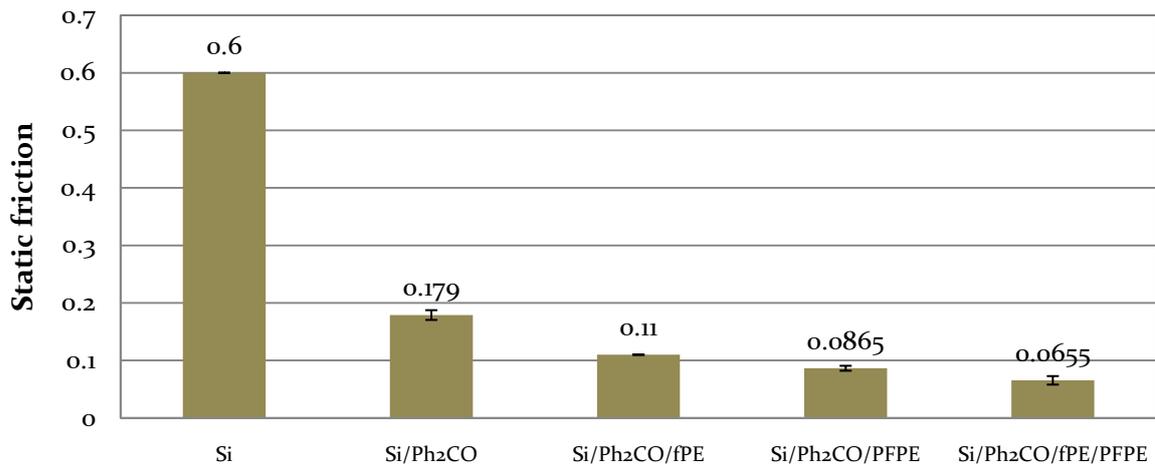

Fig. 5.   *The static coefficient of friction of Si with different modified layers under the application of 40 mN applied load and 2 rpm rotational speed.*

Though the surface energy of Si/Ph$_2$CO is lower than that of Si/Ph$_2$CO/fPE and Si/Ph$_2$CO/PFPE, its friction is higher. The possible reason is the benzene structure in Si/Ph$_2$CO could obstruct the sliding and increase the friction. Branched or complex molecular chains tend to provide a higher barrier to sliding and thus high friction. Si/Ph$_2$CO/fPE has lower coefficient of friction at 0.11 and further reduction in friction is observed for Si/Ph$_2$CO/PFPE and Si/Ph$_2$CO/fPE/PFPE due to the presence of the mobile fraction of PFPE which provides a low shear stress material. It is consistent with our previous study where the friction of PFPE was in the range of 0.06-0.07 [16].

3.4.2   **Wear durability**

Fig. 6 shows the wear durability of different modified Si samples. Bare Si fails within a few number of sliding cycles. This is because of the high friction experienced and the brittle nature of Si and the top SiO$_2$ layer. The wear durability of Si/Ph$_2$CO increases to 100 cycles whereas that of Si/Ph$_2$CO/fPE extends to 1,000 cycles. For comparison, the wear life of Si/fPE without benzophenone (Ph$_2$CO) intermediate layer is also presented and the wear life is approximately 150 cycles. Though the wear life of either Si/Ph$_2$CO or Si/fPE film is around 100 cycles, the application of a dual Si/Ph$_2$CO/fPE film promotes the wear resistance to 1,000 cycles. PFPE over-coated as ultra-thin (2-4 nm) lubricant increased the wear life of Si/Ph$_2$CO/fPE by more than three orders of magnitude. The optical images of Si/Ph$_2$CO, Si/Ph$_2$CO/fPE and Si/Ph$_2$CO/PFPE on failure at 100 cycles, 1,000 cycles and 250,000 cycles, respectively are shown in Fig. 7. Some debris particles are clearly observed on the image of Si/Ph$_2$CO after 100 cycles of sliding and these debris particles were examined with EDS (energy dispersive spectroscopy) and confirmed as Si. A clear wear track is also observed on the image of Si/Ph$_2$CO/fPE

after 1,000 cycles of sliding. Satyanarayana *et al.* [39] have studied the wear resistance of Si/APTMS/fPE film and observed a wear life under similar contact condition of 4,000 cycles. The results show that though Si/Ph_2CO and $Si/Ph_2CO/fPE$ can increase the wear resistance of Si, neither Ph_2CO nor Ph_2CO/fPE alone is adequate to protect Si substrate for extended use.
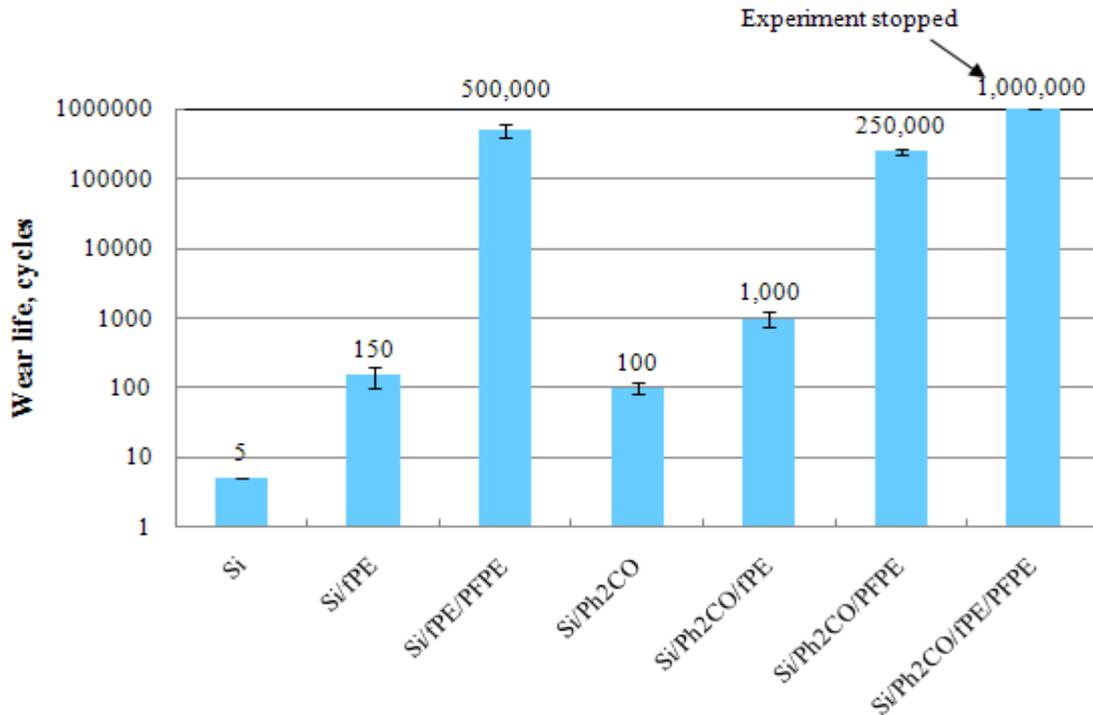

Fig. 6. *The wear durability of Si with different modifications under the application of 40 mN applied normal load and 500 rpm rotational speed.*

A significant improvement in wear durability is revealed for $Si/Ph_2CO/PFPE$ film. It fails after 250,000 cycles of sliding (Fig. 7c). It is found that wear debris from the substrate was transferred to the ball surface (Fig. 7e) but no damage or scratching on the ball surface was observed as seen on the image taken after cleaning the ball with acetone (Fig. 7f). A much greater improvement is observed for $Si/Ph_2CO/fPE/PFPE$ film as it does not fail until one million cycles, when the experiment was stopped. The image of the ball slid against this film is shown in Fig. 7g. The ball image had a small patch which was transferred lubricant of the counterface surface but no wear debris was observed (the ball surface after cleaning with acetone is shown in Fig. 7h). Thus, it is confirmed that for $Si/Ph_2CO/fPE/PFPE$ film neither the ball nor the film was damaged for the entire 1 million cycles of sliding. As a study of the role of substrate modifications on the wear performance of PFPE, the wear durability of PFPE alone on bare Si (without any intermediate layer) was also measured and it failed in less than 1,000 cycles, showing that Ph_2CO and fPE films provide better chemical attachment of PFPE to Si/Ph_2CO and $Si/Ph_2CO/fPE$.
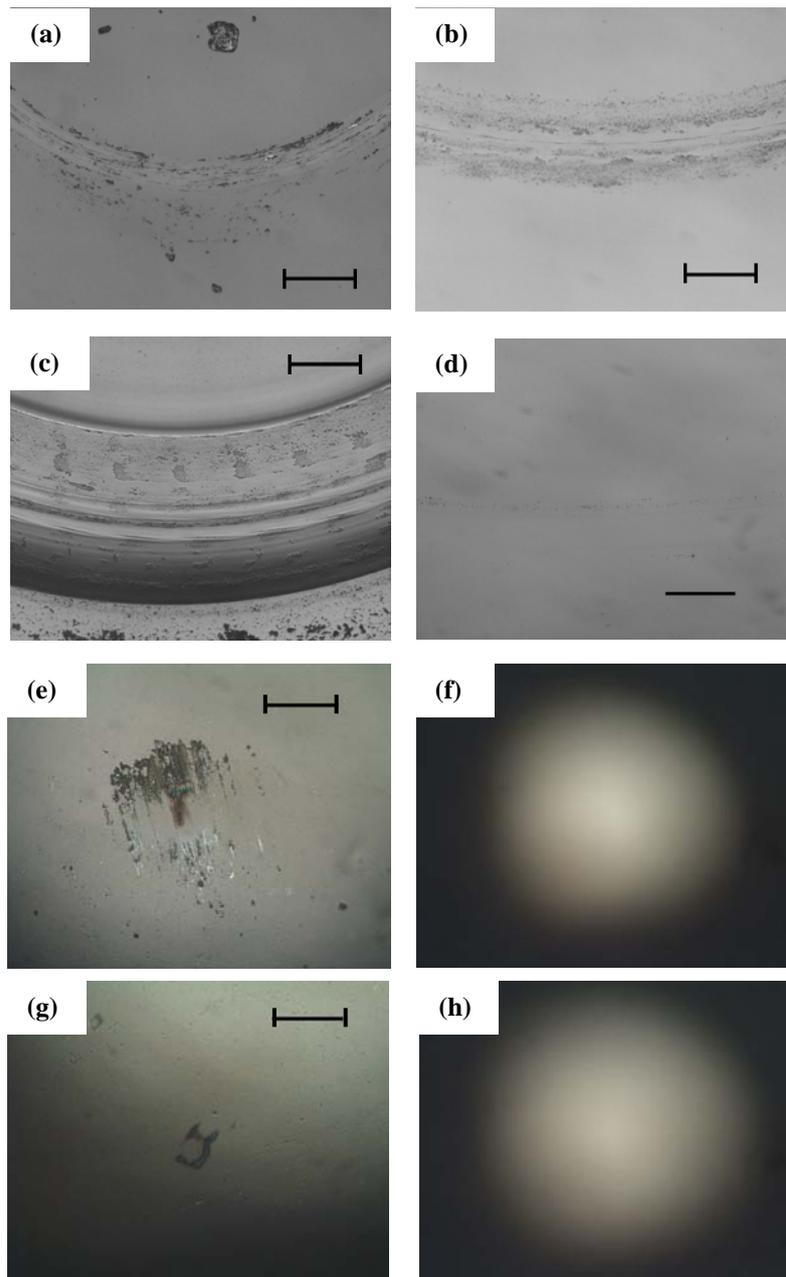
Fig. 7. *The optical images of (a) Si/Ph₂CO, (b) Si/Ph₂CO/fPE, (c) Si/Ph₂CO/PFPE when they had failed, and (d) Si/Ph₂CO/fPE/PFPE after the experiment was stopped. The optical images of Si_3N_4 ball (e) slid against (c) and (f) after cleaning with acetone, (g) slid against (d) and (h) after cleaning with acetone. The applied load was 40 mN and the scale bars shown are 100 μm.*

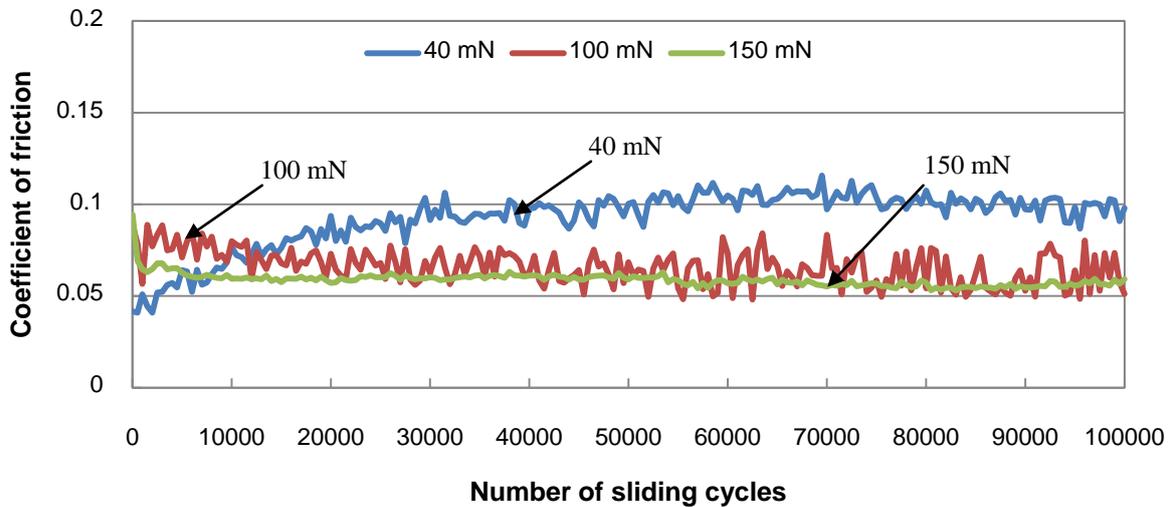### 3.4.3 Effect of applied loads on the tribological behaviors of Si/Ph$_2$CO/fPE/PFPE

Fig. 8. *Variation of the coefficient of friction and applied load with respect to the number of sliding cycles for Si/Ph$_2$CO/fPE/PFPE.*

The applied load is an important factor in determining the wear durability of a film. Fig. 8 shows results of the effect of applied load on the coefficient of friction of a Si/Ph$_2$CO/fPE/PFPE film for 100,000 cycles. The coefficient of friction does not change much throughout the tests for all applied loads. However, the coefficient of friction decreases (from 0.1 to 0.06) with an increase in applied load from (40 mN to 100 mN or 150 mN). The wear durability shows that Si/Ph$_2$CO/fPE/PFPE withstands a maximum applied load of 150 mN and sliding speed of 0.104 ms^{-1} for one million cycles or more with no sign of failure. A minimum PV (pressure x velocity) limit for the film is obtained as 106.6 MPa ms^{-1} by multiplying the contact pressure and the sliding speed. The theoretical contact pressure was calculated using the Hertzian contact theory with the elastic modulii of 190 GPa and 310 GPa for Si substrate and Si$_3$N$_4$ ball, respectively.

4 Discussion

This study is mainly focused on the tribological advantages of fPE and fPE/PFPE when Si is modified with benzophenone for the subsequent chemisorption of fPE on Si. It is observed that the static friction depends on both the surface energy and the chemical structure of the modified layers. Generally, higher surface energy gives stronger adhesion and higher friction [38]. In a comparison between the lower surface energy of Si/Ph$_2$CO and Si/Ph$_2$CO/fPE, the presence of bulky and rigid benzene structures restrict the sliding movement and hence increase the friction, whereas the linear and flexible backbone structure of fPE provides the "smooth molecular profile" and low friction. Our earlier study has shown that polymer with benzene side groups such as polystyrene would give high coefficient of friction despite high water contact angle [39]. Further reduction in friction was observed as PFPE was applied as the top layer due to its low surface energy and superior lubricating properties.

On the wear durability, although the presence of Si/Ph$_2$CO or Si/Ph$_2$CO/fPE could slightly extend the wear performance, the application of PFPE film on both Si/Ph$_2$CO and Si/Ph$_2$CO/fPE films increases the wear resistance by more than three orders. One reason for the enhancement in the wear durability is that PFPE molecules can chemically attach to either Si/Ph$_2$CO or Si/Ph$_2$CO/fPE. The bonded and mobile PFPE combination provides efficient lubrication on the Si/Ph$_2$CO/fPE surface. The chemical interaction between PFPE and Si/Ph$_2$CO or Si/Ph$_2$CO/fPE studied with XPS and the O1s peaks are provided in Fig. 9. Peak A represents the oxygen of O-F groups and Peak B reveals that of O-C groups. The number of O1s counts for Peak A is invariant for both films, showing the O-F groups not

involve in reaction. However, a great difference in the number of O1s counts for Peak B is observed. As the number of O1s counts of Peak B for Si/Ph$_2$CO/PFPE film is much higher than that for Si/Ph$_2$CO/fPE/PFPE film, we can state that the reaction probability of OH groups of PFPE in the former film is higher than that of the latter film (see boxes in Fig. 9). The extra OH groups of PFPE provide higher adhesion to the film which in turn reduces the wear resistance [40]. In the case of Si/Ph$_2$CO/fPE/PFPE, the anhydride groups in fPE react extensively with hydroxyl (OH) groups in PFPE [41] and thus the intensity of O1s drops. The reaction enhanced the wear resistance due to greater bonding and it could be the main reason for higher static friction and lower wear durability of Si/Ph$_2$CO/PFPE film in comparison with Si/Ph$_2$CO/fPE/PFPE film. Hence, the presence of fPE bonded to Si with the help of benzophenone has helped increase wear performance. This would not have been possible with a polymer layer such as polystyrene because PE has linear molecular chains which provide excellent wear resistance in coated form [39]. Benzophenone acts as very effective bonding agent for the substrate Si and the fPE layer.
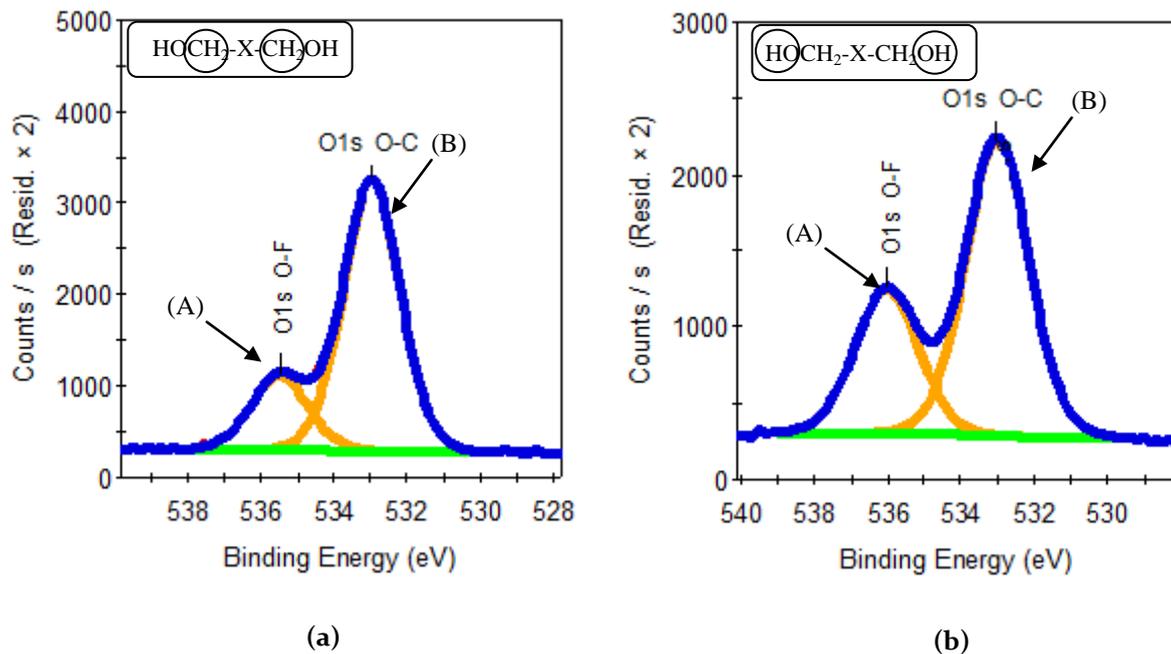

(a)   **(b)**

Fig. 9. *High-resolution O1s X-ray photoelectron spectrum (XPS) of (a) Si/Ph$_2$CO/PFPE and (b) Si/Ph$_2$CO/fPE/PFPE. HOCH$_2$-X-CH$_2$OH is the chemical structure of PFPE where X is CF$_2$O-(CF$_2$CF$_2$O)$_p$-(CF$_2$O)$_q$-CF$_2$. Circles show the elements that mostly take place in reactions.*

5   Conclusions

In the present study, functionalized polyethylene (fPE) was coated onto Si substrate by reacting with benzophenone as the intermediate layer. Perfluoropolyether (PFPE) lubricant was applied as the top mobile layer onto Si/Ph$_2$CO/fPE. The formation of each layer was confirmed by water contact angle measurement and XPS analysis. The friction and wear durability of different modified layers were measured with a ball-on-disc tribometer and the final conclusions are as follow:

1. Though there is a small deviation in contact angle between thin fPE film and bulk PE, the occurrence of C1s O-C=O confirmed that fPE attached to the silicon substrate via a benzophenone reactive group.
2. The static friction depended on both the surface energy and the molecular structure of the films. Generally, the higher surface energy of the Si substrate provided higher static friction than any other modified films. In addition, though Si/Ph$_2$CO has lower surface energy than Si/Ph$_2$CO/fPE, due to its bulky benzene structure Si/Ph$_2$CO shows higher coefficient of friction.
3. The wear durability of Si/Ph$_2$CO/fPE shows a ten times increase over that of Si/Ph$_2$CO. The existence of PFPE film on Si/Ph$_2$CO, Si/fPE and Si/Ph$_2$CO/fPE increased the wear life to

200,000 cycles, 500,000 cycles and more than one million cycles, respectively, where the applied load was 40 mN at a sliding speed of 0.052 ms^{-1}.

4. The coefficient of friction showed a minor decrease with increasing applied load (40 mN to 150 mN) for Si/Ph$_2$CO/fPE/PFPE film. The PV limit that the film could safely withstand was 106.6 MPa ms^{-1}, which is probably a minimum as the film did not fail in our tests.

Acknowledgements

References

[1] Bhushan, B., Israelachvili, J. N., Landman, U.: Nanotribology: friction, wear and lubrication at the atomic scale. Nature 374, 607-616 (1995)

[2] Bhushan, B.: Tribology and Mechanics of Magnetic Storage Devices; 2nd edn. Springer, New York, (1996)

[3] Man, K. F., Stark, B. H., Ramesham, R.: A Resource Handbook for MEMS Reliability; California Institute of Technology. Pasadena, (1998)

[4] Kayali, R. L., Stark, B. H.: MEMS reliability assurance activities at JPL, EEE Links 5, 10-13 (1999)

[5] Tanner, D. M., Smith, N. F., Irwin, L. W., et al.: MEMS Reliability: Infrastructure, Test Structure, Experiments, and Failure Modes; Sandia National Laboratories: Albuquerque (2000)

[6] Arney, S.: Designing for MEMS reliability. MRS Bull 26, 296-299 (2001)

[7] Bhushan, B.: Principles and Applications of Tribology. Wiley: New York (1999)

[8] Bhushan, B.: Introduction to Tribology. Wiley, New York (2002)

[9] Tsukruk, V.V.: Nanocomposite polymer layers for molecular tribology. Tribol. Lett. 10(1-2), 127-132 (2001)

[10] Tsukruk, V.V.: Molecular lubricants and glues for micro- and nanodevices. Adv. Mater. 13, 95-108 (2001)

[11] Satyanarayana, N., Sinha, S. K.: Tribology of self assembled monolayers on silicon surfaces. J. Phys. D: Appl. Phys. 38, 3512-3522 (2005)

[12] Sidorenko, A., Ahn, H. S., Kim, D. I., Yang, H., Tsukruk, V.V.: Wear stability of polymer nanocomposite coatings with trilayer architecture. Wear 252(11-12), 946-955 (2002)

[13] Satyanarayana, N., Sinha, S. K., Ong, B. H.: Tribology of a novel UHMWPE/PFPE dual-film on Si surface. Sens. Actua. A-Phys. 128(1), 98-108 (2006)

[14] Morgan, S. E., Misra, R., Jones, P.: Nanomechanical and surface frictional characteristics of a copolymer based on benzoyl-1,4-phenylene and 1,3-phenylene. Polym. 47, 2865-2873 (2006)

[15] Sun, C., Zhou, F., Shi, L., Yu, B., Gao, P., Zhang, J., Liu, W.: Tribological properties of chemically bonded polyimide films on silicon with polyglycidyl methacrylate brush as adhesive layer. Appl. Surf. Sci. 253, 1729-1735 (2006)

[16] Minn, M., Sinha, S. K.: DLC and UHMWPE as hard/soft composite film on Si for improved tribological performance. Surf. & Coat. Tech. 202, 3698-3708 (2008)

[17] Minn, M., Leong, Y. H., Sinha, S. K.: Effects of interfacial energy modification on the tribology of UHMWPE coated Si. J. Phys. D: Appl. Phys. 41, 055307 (2008)

[18] Minn, M., Sinha, S. K.: Tribology of ultra high molecular weight polyethylene film on Si substrate with chromium nitride, titanium nitride and diamond like carbon as intermediate layers. Thin Solid Films 518, 3830-3836 (2010)

[19] Horie, K., Ando, H., Mita, I.: Photochemistry in polymer solids. 8. Mechanism of photoreaction of benzophenone in poly(vinyl alcohol). Macromolecules 20(1), 54-58 (1987)

[20] Smets, G. J., Hamouly, S., Oh, T. J.: Photochemical reactions on polymers. Pure Appl. Chem. 56(3), 439-446 (1984)

[21] Horie, K., Morishita, K., Mita, I.: Photochemistry in polymer solids. 3. Kinetics for nonexponential decay of benzophenone phosphorescence in acrylic and methacrylic polymers. Macromolecules 17(9), 1746-1750 (1984)

[22] Horie, K., Mita, I.: Photochemistry in polymer solids-4. On the intensity dependence of non-exponential decay of benzophenone phosphorescence in poly(methyl methacrylate). Eur. Polym. J. 20, 1037-1039 (1984)

[23] Bra¨uchle, C., Burland, D. M., Bjorklund, G. C.: Hydrogen abstraction by benzophenone studied by holographic photochemistry. J. Phys. Chem. 85, 123-127 (1981)

[24] Dorma´n, G., Prestwich, G. D.: Benzophenone photophores in biochemistry. Biochemistry 33(19), 5661-5673 (1994)

[25] Turro, N. J.: Modern Molecular Photochemistry. University Science Books: Mill Valley (1991)

[26]   Ahn, H-S., Julthongpiput, D., Kim, D-I., Tsukruk, V. V.: Dramatic enhancement of wear stability in oil-enriched polymer gel nanolayers. Wear 255(7-12), 801-807 (2003)

[27]   Eapen, K. C., Patton, S. T., Zabinski, J. S.: Lubrication of microelectromechanical systems (MEMS) using bound and mobile phases of Fomblin Zdol®. Tribol. Lett. 12(1), 35-41 (2002)

[28]   Choi, J., Morishita, H., Kato, T.: Frictional properties of bilayered mixed lubricant films on an amorphous carbon surface: effect of alkyl chain length and SAM/PFPE portion. Appl. Surf. Sci. 228(1-4), 191-200 (2004)

[29]   Prucker, O., Naumann, C. A., Ruhe, J., Knoll, W., Frank, C. W.: Photochemical attachment of polymer films to solid surfaces via monolayers of benzophenone derivatives. J. Am. Chem. Soc. 121, 8766-8770 (1999)

[30]   Julthongpiput, D., LeMieux, M., Tsukruk, V.V.: Micromechanical properties of glassy and rubbery polymer brush layers as probed by atomic force microscopy. Polymer 44(16), 4557-4562 (2003)

[31]   Handbook of chemicals and laboratory equipment: Aldrich® (2006)

[32]   Website: http://www.solvaysolexis.com/static//wma/pdf/5/4/3/4/fom thin.pdf, last accessed in May (2010)

[33]   Shen, W. W.; Boxer, S. G.; Knoll, W.; Frank, C. W. Polymer-supported lipid bilayers on benzophenone-modified substrates. Biomacromolecules 2(1), 70-79 (2001)

[34]   Price, G. J., Clifton, A. A., Keen, F.: Ultrasonically enhanced persulfate oxidation of polyethylene surfaces. Polymer 37(26), 5825-5829 (1996)

[35]   Sira, M., Trunec, D., Stahel, P., Bursikova, V., Navratil, Z., Bursik, J.: Surface modification of polyethylene and polypropylene in atmospheric pressure glow discharge. J. Phys. D: Appl. Phys. 38(4), 621-627 (2005)

[36]   Kiguchi, M., Eva, P. D.: Photostabilisation of wood surfaces using a grafted benzophenone UV absorber. Polym. Degrad. Stabil. 61(1), 33-45 (1998)

[37]   Freudenberg, U., Zschoche, S., Simon, F., Janke, A., Schmidt, K., Behrens, S. H., Auweter, H., Werner, C.: Covalent immobilization of cellulose layers onto maleic anhydride copolymer thin films. Biomacromolecules 6(3), 1628-1634 (2005)

[38]   Miyoshi, K.: Surface design and engineering toward wear-resistant, self-lubricating diamond films and coatings. NASA-TM, 208905 (1999)

[39]   Satyanarayana, N., Sinha, S. K., Shen, L.: Effect of molecular structure on friction and wear of polymer thin films deposited on Si surface. Tribol. Lett. 28(1), 71-80 (2007)

[40]   Bhushan, B.: Self-assembled monolayers for controlling adhesion, friction and wear, in Springer handbook of nanotechnology; 2nd edn. Springer-Verlag GmbH, New York (2007), p. 831-860

[41]   Buchholz, V., Adler, P., Ba¨cker, M., Ho¨lle, W., Simon, A., Wegner, G.: Regeneration and hydroxyl accessibility of cellulose in ultrathin films. Langmuir 13, 3206-3209 (1997)