DLC and UHMWPE as hard/soft composite film on Si for improved tribological performance

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Abstract

The main purpose of this study is to explore the advantages of using a composite thin film of ultra high molecular weight polyethylene (UHMWPE) on a hard diamond like carbon (DLC) coating deposited on Si, for high wear life and low coefficient of friction. The experiments are carried out using a ball-on-disc tribometer at a constant linear speed of 0.052 m/s. A 4 mm diameter silicon nitride ball with a normal load of 40 mN is used as the counterface. The tribological results are discussed on the basis of hardness, elastic modulus, contact area, contact pressure and optical images of surface films. As a result of higher load carrying capacity (high hardness and elastic modulus), the wear life of Si/DLC/UHMWPE coated layer is approximately five times greater than that of Si/UHMWPE. Looking at the film thickness effect, UHMWPE film shows maximum wear resistance when the film is of optimum thickness (6.2 μm–12.3 μm) on DLC. Wear mechanisms of different UHMWPE thicknesses for Si/DLC/UHMWPE film are explained using optical microscopy of worn surfaces. Further, the use of perfluoropolyether (PFPE) ultra-thin film as the top layer on the composite coatings reduces the coefficient of friction to very low values (0.06–0.07) and increases the wear life of the films by several folds.

1   Introduction

The important tribological advantage of soft films is low shear strength; however, soft films lead to large contact area (ultimately high friction force) and have low load carrying capacity. Therefore, their usages in applications requiring high surface load bearing capacity are limited. The contact area can be reduced by introducing a hard film in between the substrate and a soft film thus making a composite of bi-layer film. The hard film alone usually leads to high shear stress and high friction. By combining thin soft and hard films together as one composite film, friction is controlled by the low shear strength of the soft film while intermediate hard film provides mechanical support against premature wear failure. Many researchers have shown the effects of solid lubricants on hard substrates [1–3], however, the concept of hard/soft composite film for tribological benefits is new and requires thorough investigation. Gadow and Scherer [4] have demonstrated that a composite layer of hard coating (Al_2O_3 or TiO_2) topped with a polymeric soft coating on light metals such as Al and Mg alloys provides long wear life with low and consistent coefficient of friction in a pin-on-disk type of test.

Polymers are used increasingly as a protective coating film in engineering applications due to their self-lubricating properties, low production cost, easy to coat onto complex shapes, excellent wear and corrosion resistance [5] and can be used as a soft and easily shearing film because of their low strength and hardness values. Ultra high molecular weight polyethylene (UHMWPE) has been used in highly stressed parts, total joint replacement and bearings, because it has low coefficient of friction coupled with high wear resistance and good strength/ductility in comparison to many other thermoplastics such as PEEK, PS and PMMA [6]. As a hard coating, diamond like carbon films (DLC) have great attraction for tribological applications because of their high hardness, high wear resistance [7], chemical inertness, corrosion resistance [8,9] and low surface energy [10]. The range of the coefficient of friction of DLC films reported is 0.001–0.7which is probably the widest among the coated films [11]. The friction and wear behaviors of DLC depend not only on the chemical and structural properties of carbon but also the test conditions such as the substrate, counterface material, rotational speed, applied load, chemistry of the environment etc [12]. The coefficient of friction for UHMWPE is in the range of 0.1–0.2 [13].

In this study, Si was used as a substrate and tetrahedral amorphous carbon, (ta-C), was deposited as a hard film followed by a soft film of UHMWPE (28 μm thickness). In order to compare the results obtained from composite film, UHMWPE (28 μm thickness) was applied also onto the bare Si substrate and tested. Perfluoropolyethylene (PFPE) was applied onto the UHMWPE film to further extend the wear life because of its superior physical and tribological properties such as low vapour pressure, low surface tension, high thermal stability and good lubricity [14]. Further, in order to study the effect of soft film thickness, UHMWPE films of different thicknesses were coated onto Si/DLC (DLC thickness was kept fixed) and, friction and wear tests were conducted.

The primary objectives of this study are, firstly, to investigate the tribological advantages of DLC/UHMWPE composite film and secondly, to understand the effects of soft film thickness on the friction and wear properties using various tribological results including nanoscratching, nanoindentation and optical image analysis of the worn surfaces.

Table 1. *Physical properties of UHMWPE, as provided by the supplier.*

Property	Units	Value
Melt index MFR 190/15	G/10 min	1.8 ± 0.5
Bulk density	g/cm^3	0.33 ± 0.03
Average particle size d_{50}	μm	20 ± 5

2   Experiment procedures

2.1   Materials

Polished n-type Si (100) wafers (obtained from Engage Electronics (Singapore) Pte Ltd), about 455–575 µm in thickness and hardness of 12.4 GPa, were used as the substrate. Tetrahedral amorphous carbon, ta-C, (non-hydrogenated DLC) film was deposited onto Si substrate by Filtered Cathodic Vacuum Arc (FCVA) technology (Nanofilm Technologies International Pte. Ltd, Singapore). The detailed procedure of deposition is mentioned in Ref. [15]. The thickness of DLC is in the range of 50 nm and hardness is 57 GPa, as provided by the supplier. Ultra high molecular weight polyethylene (UHMWPE) polymer powder (Grade: GUR X143) was supplied by Ticona Engineering Polymers, Germany, through a local Singapore supplier. The physical properties of UHMWPE used in this study are provided in Table 1. Decahydronapthalin (decalin) was selected as the solvent to dissolve UHMWPE. To extend the wear life of the film, a commercial perfluoropolyether (PFPE) Z-dol 4000 of 0.2 wt.% (dissolved into H-Galden ZV60 purchased from Ausimont INC) was overcoated onto UHMWPE film. Chemical formulae of Zdol and H-Galden ZV60 are $HOCH_2CF_2O–(CF_2CF_2O)_p–(CF_2O)_q–CF_2CH_2OH$ and $HCF_2O–(CF_2O)_p–(CF_2CF_2O)_q–CF_2H$, respectively, where the ratio p/q is 2/3.

2.2   Preparation of different layers on Si substrate

Si substrates were rinsed for 1 min and sonicated for 15 min in soapy water followed by same procedure in distilled water and then in acetone. The final cleaning with acetone ensured that the samples were free from any contaminant or unwanted chemical due to handling. The cleaned substrates were blow-dried with pure nitrogen gas and immersed into a piranha solution (70 vol.% H_2SO_4 and 30 vol.% H_2O_2) at a temperature of 120 °C for an hour to remove any contaminants. After that, the substrates were rinsed again with distilled water and acetone for 1 min each. Si/DLC samples were ultrasonically cleaned in ethanol for 30 min before polymer film coating.

Table 2. *Mechanical properties and other parameters for different samples.*

Sample	Thickness of UHMWPE (µm)	Hardness (GPa)	Elastic Modulus (GPa)	Theoretical contact area ($10^{-10}m^2$)	Theoretical contact pressure (MPa)	Nanoindentation penetration depth (µm)
Bulk UHMWPE	-	0.038	0.993	80	7.7	7.25
Si/UHMWPE	28	0.06	6.51	23.5	26	5.3
Si/DLC/UHMWPE	3.4	11.9	171.87	3.7	165	0.45
	6.2	0.86	43.74	7.3	85	1.52
	12.3	0.12	18.65	12	51.6	3.81
	28	0.09	8.81	19.4	31.8	4.5

UHMWPE (in powder form) was dissolved in decahydronapthalin (decalin) by heating them together to a temperature of 150 °C for half an hour and 250 °C for the next half an hour with a magnetic stirrer. 5 wt.% UHMWPE (that gave film thickness of 28 µm) was selected to compare the tribological

results for films with and without DLC intermediate layer. To explore the effect of UHMWPE thickness on the tribological properties of Si/DLC/UHMWPE films, Si/DLC samples were dipped into 0.5 wt.%, 1 wt.%, 3 wt.% and 5 wt.% UHMWPE solutions at dipping and withdrawal speeds of 2.4 mm/s with a fixed dipping duration of 30 s. The UHMWPE film thicknesses after dip coating with respect to weight percentages of UHMWPE in the solution are mentioned in Table 2. The samples coated with UHMWPE were given heat treatment in a clean air oven at 100 °C for 15 h. After heat treatment, the samples were cooled down to room temperature in the oven. In order to understand the effect of residue solvent in polymer film on the final properties, both bulk UHMWPE powder and coated UHMWPE polymer film were tested using differential scanning calorimetry (DSC60, Shimadzu) under an argon gas flow with a heating rate of 20 °C/min. The results showed no additional peak of the solvent in the final polymer film. This proved that the solvent had evaporated completely from the UHMWPE film during the long heat treatment and there was no residue solvent effect on the mechanical and tribological properties of polymer film. The UHMWPE coatings on DLC or Si substrates were of uniform thicknesses without any sign of uncoated area or pinholes in the film. However, when the thickness was brought down to below 3 μm, the film became patchy and of non-uniform thickness. For some samples, PFPE (0.2 wt.% in H-Galden ZV60) was dip-coated onto UHMWPE film at dipping and withdrawal speeds of 2.4 mm/s with a fixed dipping duration of 30 s. This coating condition of PFPE is expected to give PFPE film thickness of few nanometers. After coating, the samples were kept in a clean room for 24 h before any test was carried out. The schematic of the coating layers on the Si substrate is shown in Fig. 1.
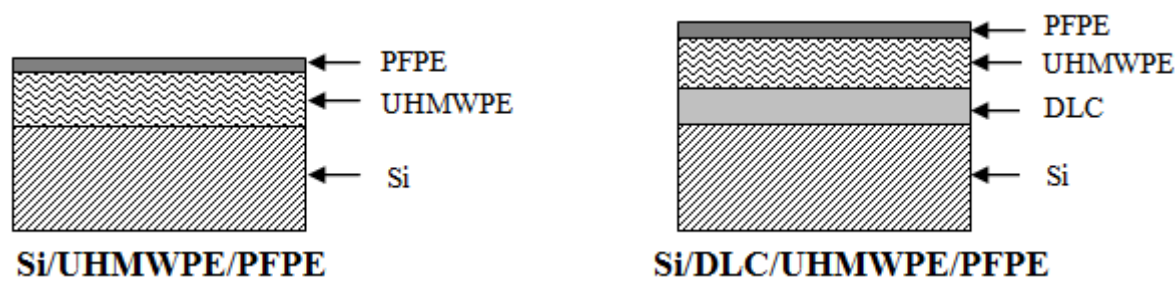

Fig. 1   *Schematic diagram (not to scale) of different layers coated on Si substrate.*

2.3   Contact angle measurement and surface analysis

The UHMWPE and PFPE coatings on Si and Si/DLC were verified by contact angle measurement. VCA Optima Contact Angle System (AST product, Inc., USA) was used for the measurement of contact angles with distilled water droplets. A water droplet of 0.5 μl was used for 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°.

Measured RMS roughnesses of Si and Si/DLC are 0.41 nm and 34.8 nm respectively and that of UHMWPE films coated on both Si and Si/DLC are 0.56 μm, all measured within a scan area of 10 μm × 10 μm using AFM. The roughness values for UHMWPE films measured within the 10 μm×10 μm scan area did not change for different film thicknesses. However, the macroscopic morphology of the film surface differs for different thicknesses of the film. These morphological differences did not affect the tribological performance in any observable way as this polymer film is the softer layer sliding against a Si_3N_4 ball counterface which is much harder than UHMWPE. The surface of the polymer film is modified easily upon initial few cycles of sliding.

The thickness of UHMWPE films was measured using field emission scanning electron microscopy (FESEM, Hitachi S4300). The samples were cut and mounted with their cross sections horizontal under FESEM to measure the polymer thickness. Ten independent measurements are carried out for each film and an average value is reported. The thickness variation is within ± 1 μm.

2.4   Nanoscratching and nanoindentation

Nanoscratching and nanoindentation tests were performed using an MTS Nano Indenter XP machine on Si/UHMWPE (28 μm thickness) and Si/DLC/UHMWPE with different UHMWPE thicknesses to obtain the values of hardness, elastic modulus and indentation depth of the films. The indenter for nanoscratching was a conical shape diamond tip with 90° cone angle and a tip radius of 5 μm. The surface morphologies of the nano scratches were observed with a JEOL JSM-5600 LV scanning electron microscope (SEM). For nanoindentation, the samples were indented using a constant load of 40 mN with a standard Berkovich diamond tip. A total of five repeats of indentation were carried out and the reported values are an average of the five data. Each indentation test consisted of the following steps: loading time duration of 100 s followed by 10 s of holding time at the final depth of indentation, and, unloading (retracting of the tip).

2.5   Friction and wear tests

Friction and wear tests were carried out on a custom built ball-on-disc tribometer. A silicon nitride ball of 4 mm diameter with a surface roughness of 5 nm (as provided by the supplier) was used as the counterface. Prior to the test, Si_3N_4 ceramic balls were cleaned with acetone. The test radius was ~1 mm with a fixed disc rotational speed of 500 rpm (linear relative speed at the sliding contact = 0.052 m/s). The normal load applied was 40 mN. The friction coefficient data were recorded at a sampling rate of 5 Hz. The initial coefficient of friction was taken as an average of the first 4 s of sliding. In this work, wear life of every sample is defined as the number of cycles when the coefficient of friction exceeds 0.3 or large fluctuations of the coefficient of friction (indicative of film failure) occur continuously, whichever happens first. Wear life is reported as the number of cycles because here we are evaluating the wear life of the coated disc surface. Therefore, how many times the counterface ball passes through any particular point on the disc is more important than the total distance of sliding. This is because the ball comes in contact with a point on the disk only once every cycle. It may be noted that when the wear of the pin or the ball is to be evaluated in a pin-on-disc type of tribometer, then, the total sliding distance is more appropriate than the number of cycles of the disc revolution. Energy dispersive spectroscopy (EDS) (Hitachi S4300 FESEM/EDS system) tests were conducted inside wear tracks to find out whether or not the film had worn by checking the presence of Si peak. Three repeats of the sliding tests were conducted for every sample and averages were calculated for final friction and wear values. All experiments were carried out in a clean booth environment at a temperature of 25 ± 2 °C and relative humidity of 55 ± 5%. The counterface and sample surfaces were studied under an optical microscope for the wear mechanisms.

Table 2 provides contact area and contact pressure values for every sample as calculated using Hertzian contact model. Mechanical properties of Si_3N_4 ball (Young's modulus: 310 GPa and Poisson's ratio: 0.22, as provided by the supplier) and UHMWPE (Poisson's ratio: 0.46 [16]) were used for the calculation of the contact area and the contact pressure.

As mentioned before, in this work, we focus on two comparisons for tribological performances. First, the comparison of different (Si/DLC versus Si/DLC/UHMWPE) coated layers with a fixed 28 μm UHMWPE thickness and the second is the comparison of different UHMWPE thicknesses (3.4 μm, 6.2 μm, 12.3 μm and 28 μm) on Si/DLC/UHMWPE films.

3   Results

3.1   Contact angle results

The water contact angles of bare Si, Si/UHMWPE, Si/UHMWPE/PFPE, Si/DLC, Si/DLC/UHMWPE and Si/DLC/UHMWPE/PFPE (28 μm UHMWPE thickness) are shown in Table 3. Bare Si substrate showed a water contact angle of 21° which was more hydrophilic than all other samples. Hydroxyl group is formed on bare Si after the piranha treatment which can react with water molecules to form hydrogen bonds. The hydrogen bonds tend to be hydrophilic surface [17]. After coating DLC onto Si, the value increased to 81°. The possible reason is, DLC film used in this study is non-hydrogenated and has only sp³ hybridized carbons, which are less reactive with water molecules. When UHMWPE was applied on bare Si and Si/DLC, the surfaces became more hydrophobic with water

contact angle of 93° and 91° respectively. After PFPE coating, the contact angles rose further to 95° and 102° for Si/UHMWPE and Si/DLC/UHMWPE, respectively. It is well known that the hydrocarbons in UHMWPE and the fluorocarbons in PFPE do not form hydrogen bonds and their surface tensions are low, in other words, their water contact angles are high [17]. The differences in the contact angles for UHMWPE and PFPE are nearly the same and the variations are within the measurement error. This means that there is no effect of intermediate layer on the contact angle of the top layer.

Table 3. *Water contact angles of different coated layers.*

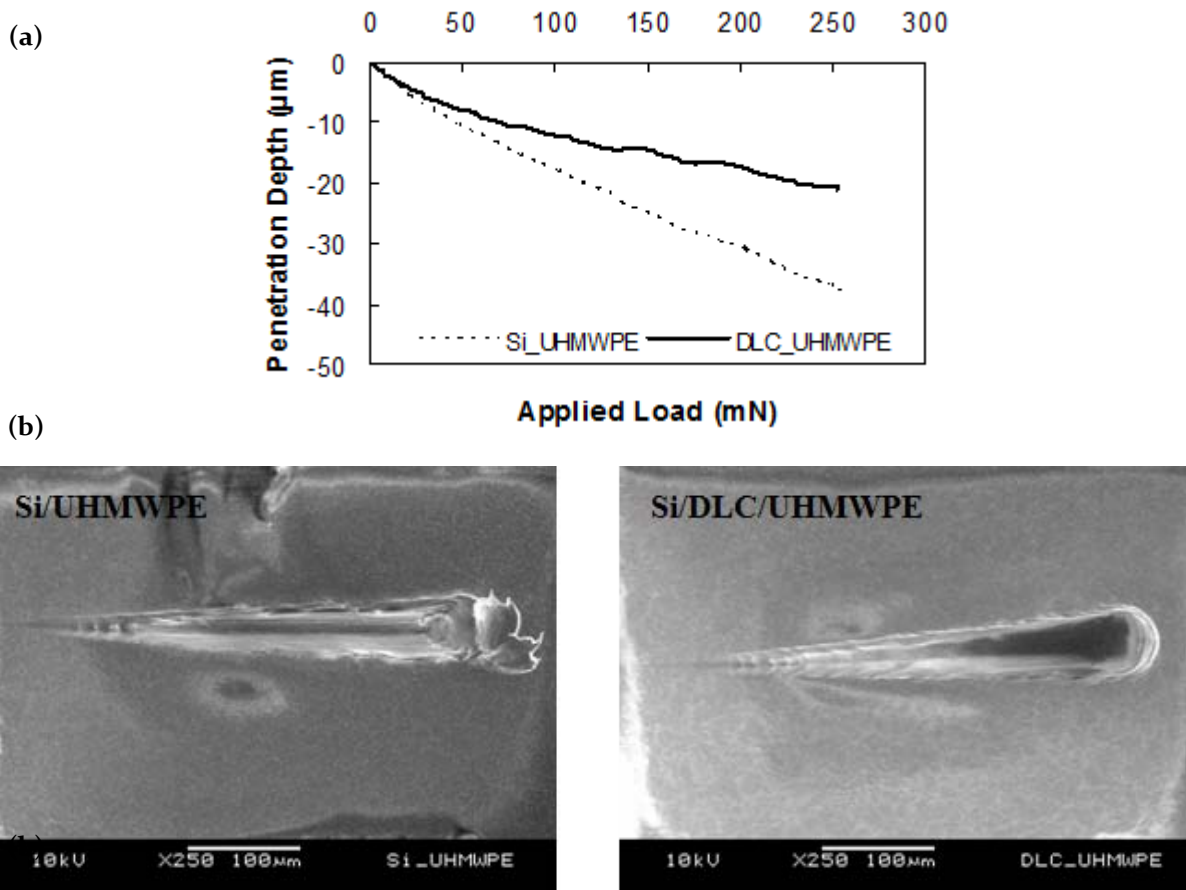| Sample	Layers	Contact Angle (°)
A1	Si	21
A2	Si/UHMWPE	93
A3	Si/UHMWPE/PFPE	95
A4	Si/DLC	81
A5	Si/DLC/UHMWPE	91
A6	Si/DLC/UHMWPE/PFPE	102

(a)

(b)

Fig. 2 *(a) Scratch penetration depth as a function of progressively applied normal load and (b) SEM images of the scratch deformation for Si/UHMWPE and Si/DLC/UHMWPE films. The thickness of UHMWPE is 28 µm for both cases. The progressive scratch tests were conducted using a 5 µm-radius 90°-conical shape diamond tip with scratch velocity of 10 µm/s for a scratch distance of 500 µm. Normal load varied from 0 to 250 mN and the scratching direction is from left to right.*

3.2 Nanoscratching and nanoindentation analysis

Fig. 2(a) shows nanoscratching results of Si/UHMWPE and Si/DLC/UHMWPE (28 μm thickness). The scratch tests were conducted using a ramp loading setup from 0 to 250 mN at a constant scratch velocity of 10 μm/s using a 90° conical shaped diamond tip with 5 μm tip radius. It is observed that there is a difference in the penetration depths for the two films as the load increases. It is noted that the load carrying capacity or the hardness of Si/UHMWPE is much inferior to that of Si/DLC/UHMWPE. Fig. 2(b) shows the SEM images after nanoscratching for the two films. In Fig. 2(b) we can see that Si/UHMWPE film was easier to penetrate and it peeled off the substrate as can be seen at the end of the scratch. Si/UHMWPE film shows a clear damage of polymer along both sides of the scratch and a pile of polymer at the end of the scratch by a process of plastic deformation and partial delamination [18]. In contrast, there were no wear debris along the scratch for Si/DLC/UHMWPE film and the scratch resembled plastic deformation of the polymer by ploughing without any visible detachment or delamination of the film.

The hardness, elastic modulus and penetration depth data for UHMWPE with different thicknesses using nanoindentation test are shown in Table 2. It is clear that DLC intermediate layer provides higher hardness, and elastic modulus, and, shallower penetration depth than those of Si/UHMWPE (at 28 μm UHMWPE thickness). The hardness and the elastic modulus increased whereas the penetration depth decreased as the thickness of UHMWPE film was reduced in the composite film. Comparing with the bulk values, the hardness and elastic modulus of the bulk UHMWPE is approximately one order of magnitude lower than those of the 28 μm thick film indicating that there is considerable amount of substrate effect. It is noted that the contact area decreases gradually but the contact pressure increases significantly with a decrease in the thickness of the polymer film below 6.2 μm due to the effect of hard DLC.

3.3 Friction and wear of composite films (UHMWPE film thickness fixed as 28 μm)

Fig. 3 shows friction and wear life data for samples with differently coated layers; UHMWPE film thickness in all cases was 28 μm. Bare Si and Si/DLC surfaces show high coefficients of friction (0.65 for bare Si and 0.25 for Si/DLC). After coating UHMWPE onto Si and Si/DLC, the coefficient of friction reduces to 0.18 and 0.13, respectively, due to the self-lubricating properties of UHMWPE. Furthermore, UHMWPE film is soft enough to reduce shear stress in comparison with bare Si or Si/DLC. After applying PFPE layer, the coefficient of friction further reduces to 0.06 and 0.07 for Si/UHMWPE/PFPE and Si/DLC/UHMWPE/PFPE, respectively. Because PFPE molecules serve as liquid lubricant that can reduce shear stress and as a result friction is very low. The effect of PFPE overcoating onto UHMWPE film in reducing the coefficient of friction is well studied [19].

As can be seen in Fig. 3(b), an intermediate hard layer of DLC has provided approximately five times improvement in wear life in comparison with Si/UHMWPE. This indicates that the underlying DLC provides high load carrying capacity to the UHMWPE film and thus a better tribological result of Si/DLC/UHMWPE film. The coefficient of friction of Si/DLC is 0.25 but it has very low wear life under the same sliding conditions. It is obvious that a composite film of hard (DLC) and soft (UHMWPE) layers can give excellent tribological performances. Moreover, PFPE overcoating can slightly reduce the coefficient of friction even further and the wear life is improved by several times to a few orders of magnitude. In the case of Si/DLC/UHMWPE/PFPE, the composite film did not show any sign of failure when the experiment was stopped due to long test duration. The coefficient of friction remained low for the entire sliding process and no wear debris was found on the wear track after 300,000 cycles of sliding. In order to detect film failure, we conducted EDS test on each track to check for the Si peak. As we did not observe Si peak on the wear track in EDS result, it was concluded that the film had not failed even at 300,000 sliding cycles. Fig. 3(c) shows the coefficient of friction trace versus sliding cycles for some films.

The optical microscopic surface images of Si/UHMWPE/PFPE and Si/DLC/UHMWPE/PFPE before and after the sliding tests, and, the counterface balls after the sliding tests, are shown in Fig. 4. It is clearly seen from the wear track picture of Si/UHMWPE/PFPE that the film is worn severely after the sliding test (100,000 cycles). From counterface ball image, we can say that much polymer is transferred from the film to the ball for Si/UHMWPE/PFPE whereas Si/DLC/UHMWPE/PFPE composite film shows very little polymer transfer. This transferred polymer has greatly influenced the coefficient of friction by roughening the interface and by increasing the adhesion between the film and the

counterface. Thus, the best tribological performances of Si/DLC/UHMWPE/PFPE depend on many factors. First, hard DLC has high load carrying capacity and provides better penetration resistance. Second, the linear UHMWPE has self-lubricating property that helps reduce shear stress. In other words, although the hard DLC alone has high shear stress, the overcoating of soft UHMWPE layer onto DLC can reduce the shear stress drastically. Third, the higher thermal stability and lubricating properties of PFPE can provide further reduction in the coefficient of friction and increase in the resistance to frictional heating.
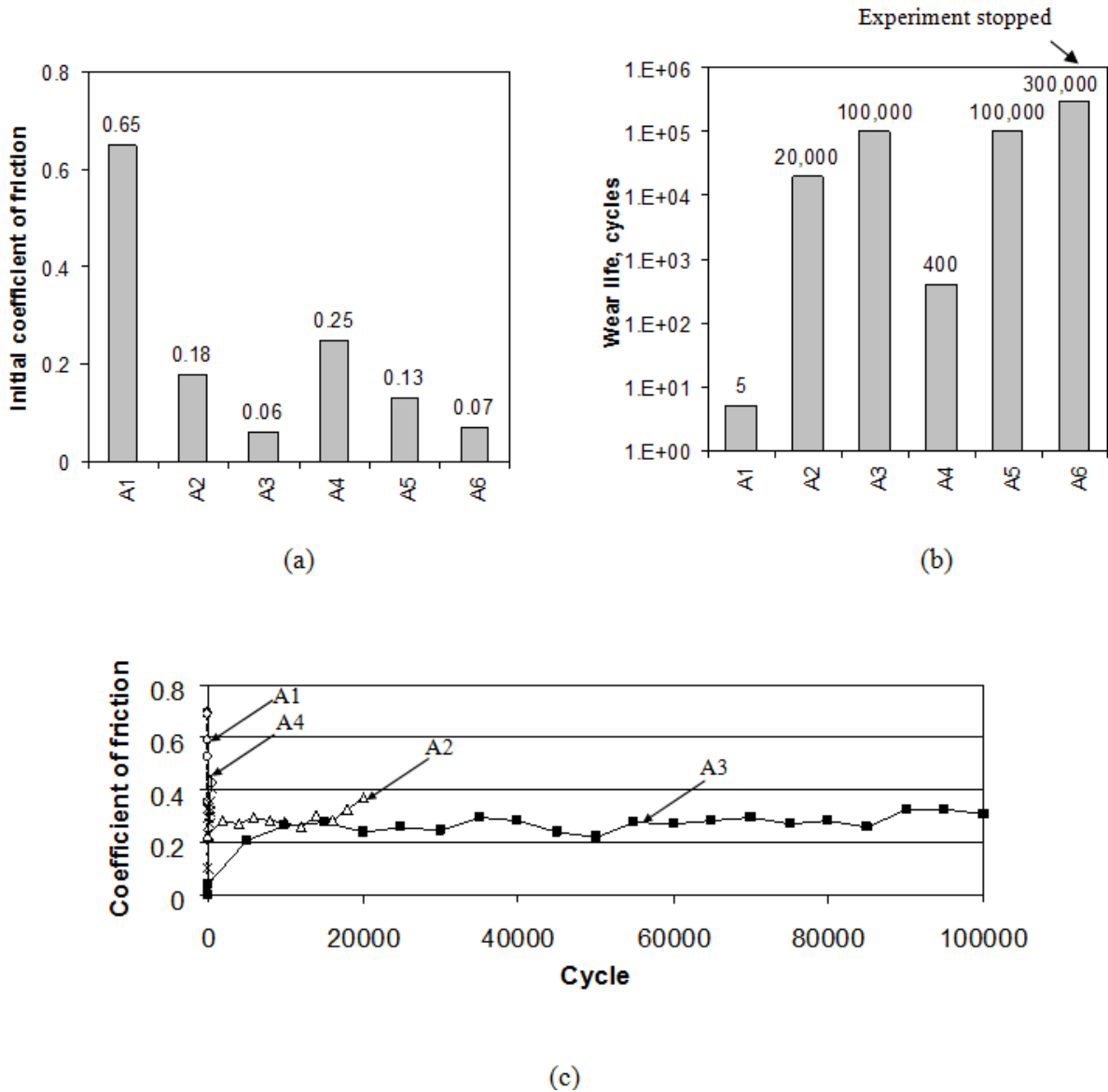
Fig. 3   (a) Coefficient of friction, (b) wear life (logarithmic scale) of bare Si and Si coated with different single and composite films and (c) coefficient of friction versus sliding cycles of some films at a normal load of 40 mN and at a rotational speed of 500 rpm (linear speed is 5.2 cm/s) where UHMWPE thickness is fixed as 28 μm for all coated samples. (A1 = bare Si, A2 = Si/UHMWPE, A3 = Si/UHMWPE/PFPE, A4 = Si/DLC, A5 = Si/DLC/UHMWPE, A6 = Si/DLC/UHMWPE/PFPE).
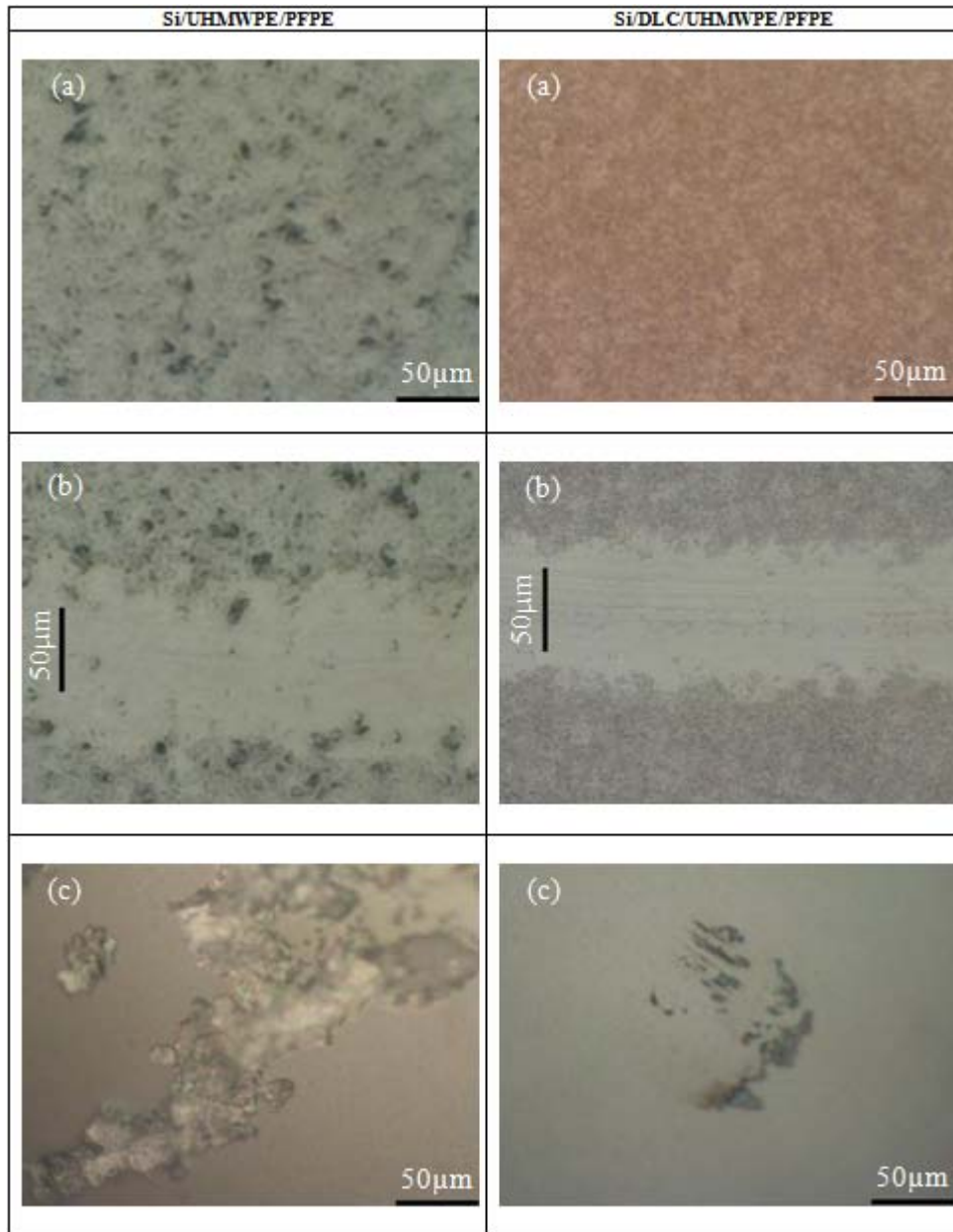
Fig. 4 *Optical images of Si/UHMWPE/PFPE (column 1) and Si/DLC/UHMWPE/PFPE (column 2) surfaces (a) before the test, (b) after sliding 100,000 cycles and (c) counterface ball after 100,000 cycles.*

3.4   Effect of UHMWPE thickness on the friction and wear

The effect of UHMWPE thickness on the friction and wear properties of Si/DLC/UHMWPE is shown in Fig. 5. At the initial stage of sliding cycles, the coefficients of friction are the same and variations are within the measurement errors for all thicknesses. However, the effects of thickness are observed on friction and wear at higher sliding cycles. The coefficient of friction of thin film (3.4 µm) increases with increasing number of cycles and the role of underlying hard DLC is dominant which causes high shear stress and film fails at ~100,000 cycles. For the 6.2 µm film, the friction shows the same trend as thinner film (3.4 µm), but the shear stress on 6.2 µm film is lower (lower coefficient of friction) in comparison with that on 3.4 µm film and the wear life extends to 200,000 cycles. The coefficient of friction for 12.3 µm film is stable at 0.14±0.02 for the entire 300,000 cycles when experiments are stopped. For 28 µm film, although its coefficient of friction is low until 20,000 cycles, it shows large fluctuations in friction characteristics and fails at 100,000 cycles. These large fluctuations

happen due to the different removal rates of polymer from the sliding track that increases roughness. Further explanations on this aspect are provided in the Discussion section.
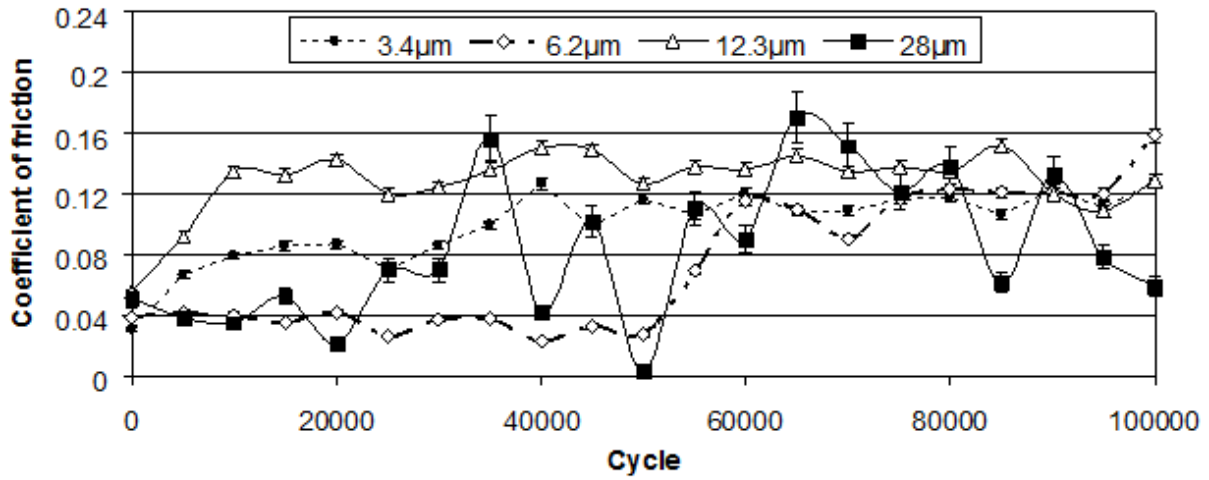
(a)
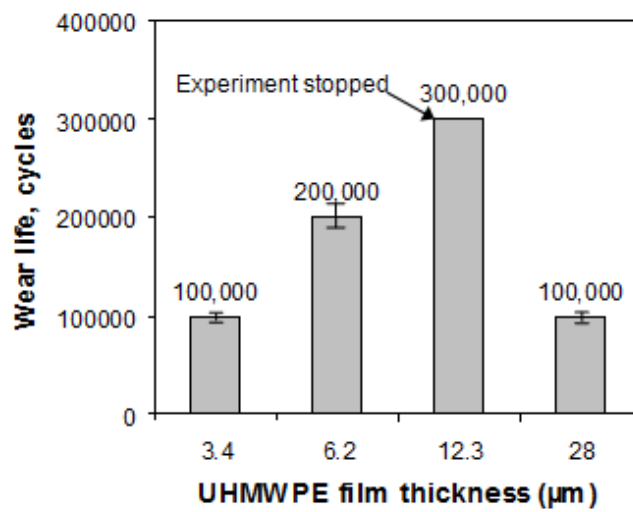
(b)

Fig. 5 *(a) Coefficient of friction with respect to sliding cycles in typical runs for different thicknesses of UHMWPE in composites films of Si/DLC/UHMWPE, (b) Wear life for different UHMWPE thicknesses for Si/DLC/UHMWPE. Data are averages of three repeated tests. For 12.3 μm thick film there was no failure at 300,000 cycles of sliding when the experiments were stopped due to long test duration.*

3.5   *Wear mechanisms for different UHMWPE thicknesses*

The optical images of the wear tracks for Si/DLC/UHMWPE film of different thicknesses with respect to the number of cycles are shown in Fig. 6. The widths of the wear tracks increase with

increasing cycles for all films. This increase in the width of the contact area leads to high friction as sliding progresses. It can be seen from the optical images that the contact stress is a major factor contributing to friction and wear of 3.4 μm thick film. It agrees well with the nanoindentation results (Table 2) where the contact pressure of 3.4 μm film is highest and contact area is lowest. As a result, the surface image shows some kind of polymer degradation possibly due to high frictional heat generated within a small contact area.
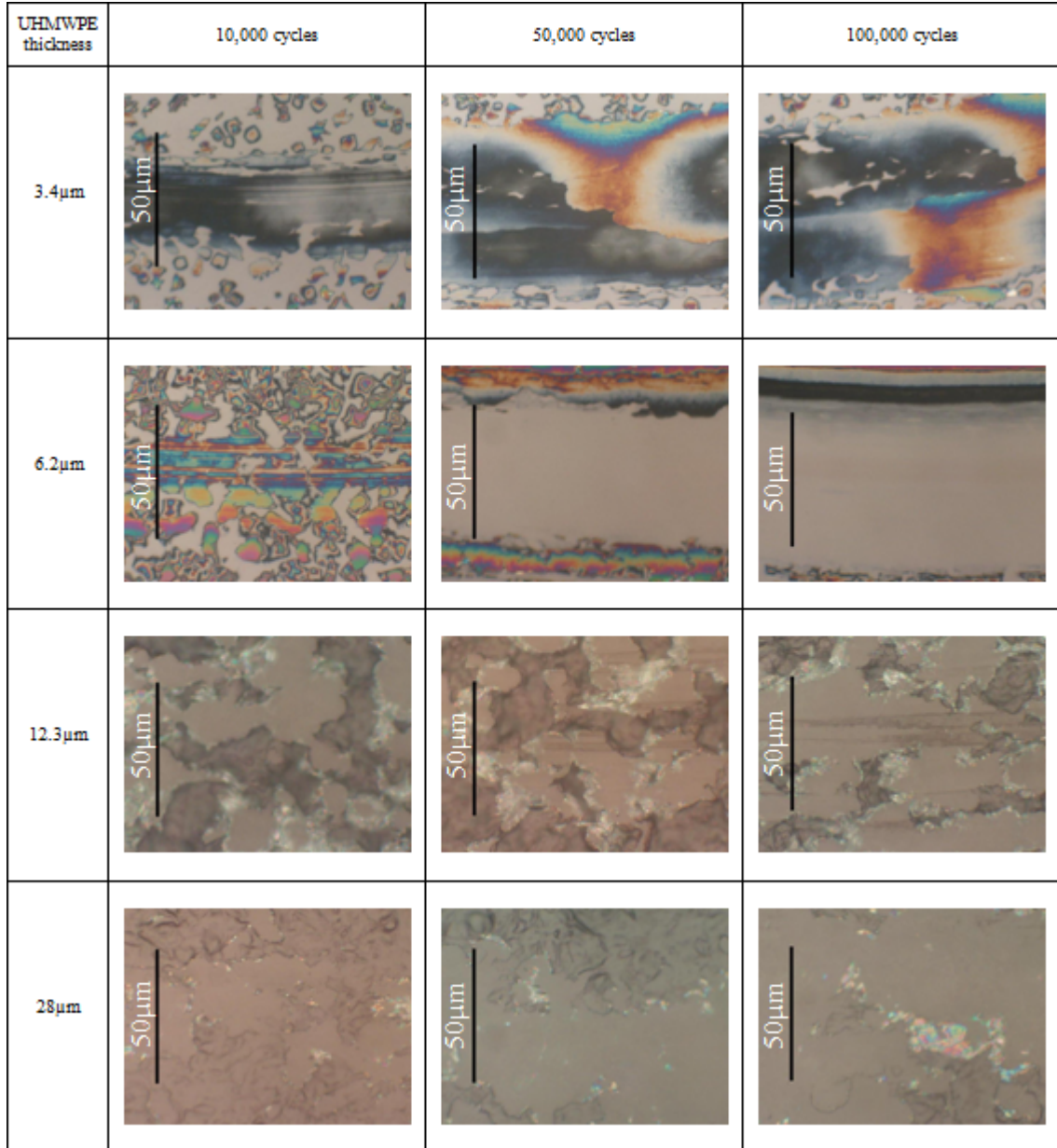

Fig. 6 *Wear track optical images of 3.4 μm, 6.2 μm, 12.3 μm and 28 μm UHMWPE thicknesses for Si/DLC/UHMWPE (at a normal load of 40 mN, at a linear speed of 5.2 cm/s (500 rpm) and test radius 1 mm) against Si3N4 counterface ball after 10,000, 50,000 and 100,000 sliding cycles.*

The optical image of 6.2 μm film after 50,000 cycles shows smooth surface after removal of the asperities and the effect of roughness on friction is less after 50,000 cycles. It is indicative of a very smooth track that suggests softening of the sliding surface [20]; soft polymer surface can help maintain low coefficient of friction. It is clear from the optical images of 12.3 μm and 28 μm films that the rates of material removal from the sliding track are not uniform. The asperities of the films are removed non-uniformly at an early stage and as a result the surface becomes roughened. Despite uneven removal of the polymer, for 12.3 μm film, the surface becomes as smooth as 6.2 μm film with increasing cycles and the effect of surface roughness on friction and wear is not much. However for 28 μm film, the early

failure of the film is due to the large amount of polymer being transferred to the ball that causes large fluctuations in the coefficient of friction. The optical images of Si_3N_4 balls after the sliding tests against different UHMWPE thicknesses at a normal load of 40 mN, are shown in Fig. 7. The amount of polymer transferred from the thickest film (Fig. 7(d)) is much greater than that from film of any other thickness.
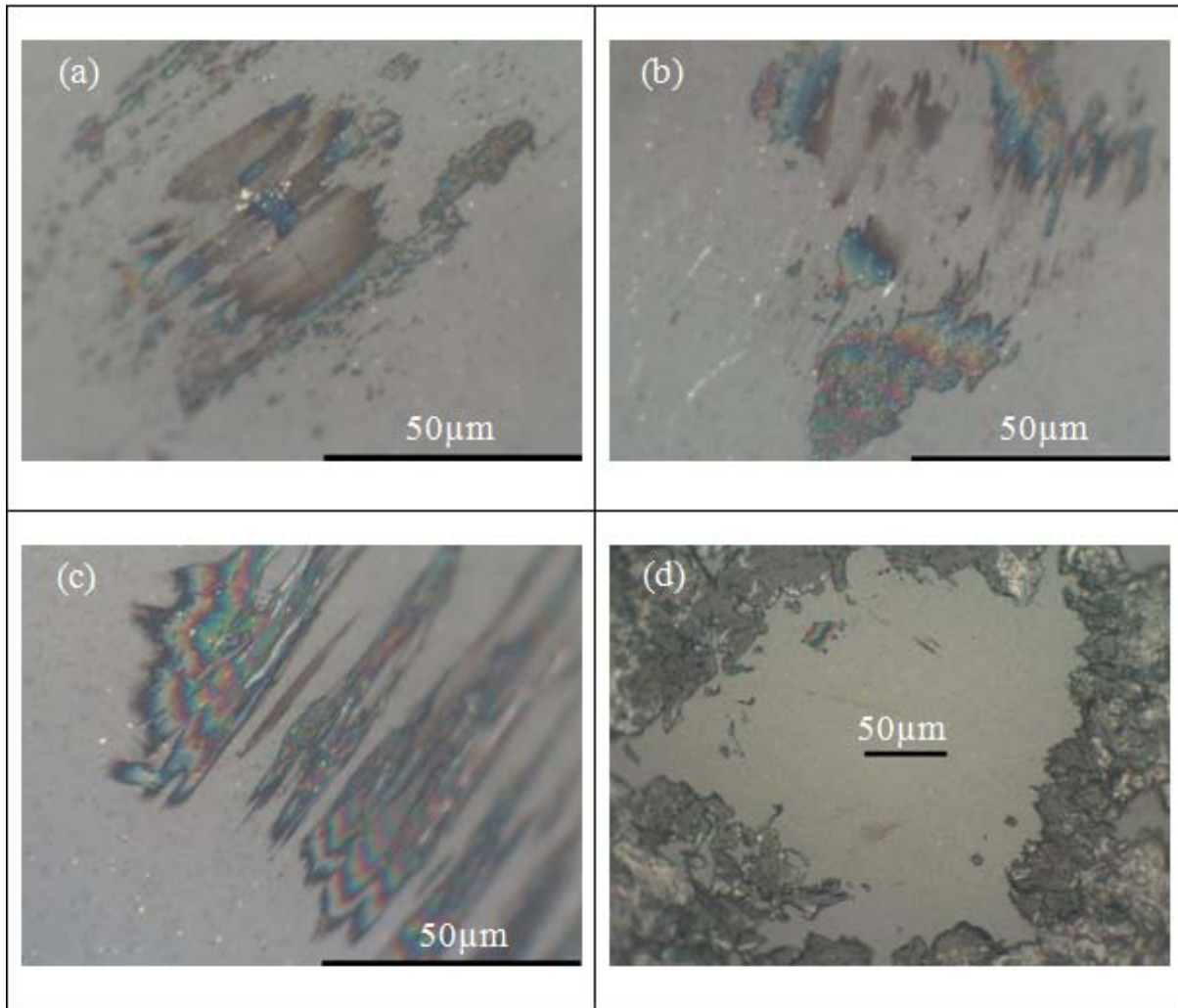

Fig. 7 *Optical images of Si3N4 counterface ball against Si/DLC/UHMWPE with different polymer film thicknesses (a) 3.4 μm (b) 6.2 μm (c) 12.3 μm and (d) 28 μm after sliding 100,000 cycles. Subpanels (a, b, c) are magnified 500 times and subpanel (d) is magnified 200 times.*

4   Discussion

Bare Si shows hydrophilic property that attracts water molecules and the presence of these water molecules effectively weakens the adhesion strength between substrate and UHMWPE [21,22]. When DLC coated onto bare Si, the film surface became hydrophobic. In contrast with bare Si, Si/DLC film repels water. The adhesion between Si/DLC and UHMWPE is stronger than the adhesion between bare Si and UHMWPE. Consequently, the polymer from Si/UHMWPE is easily removed during contact sliding test in comparison with that from Si/DLC/UHMWPE as shown in Fig. 3(b). Moreover, nanoscratching curve also shows a large difference in penetration resistance between Si/UHMWPE and Si/DLC/UHMWPE for 28 μm UHMWPE thickness films. The slope of load penetration depth of Si/UHMWPE is steeper than that of Si/DLC/UHMWPE, which means the penetration resistance of the latter is stronger because of the higher load carrying capacity provided by hard DLC intermediate film. In other words, the contact area of Si/UHMWPE is larger than that of Si/DLC/UHMWPE and as a result the friction of former is higher than that of the latter.

The hardness data from nanoindentation (Table 2) also show the same trends as nanoscratching. At the early stage, the initial penetration depth (5.3 µm for Si/UHMWPE) is shallower than the whole film thickness (28 µm). However, as the sliding proceeds, the transferred film on the ball surface is continuously renewed by wearing out of the polymer from the contact point on the film and the ball reaches the Si substrate after about 20,000 cycles due to weak penetration (low hardness) resistance and large contact area. For Si/DLC/UHMWPE, we did not see any sign of film failure until 100,000 cycles because of strong penetration resistance and small contact area in comparison with Si/UHMWPE.

The elastic modulus of Si/DLC/UHMWPE is higher than that of Si/UHMWPE, which means greater relaxation time for Si/DLC/UHMWPE layer for any change in the elastic property due to interface temperature or creep. This is because, the lower the elastic modulus, the higher is the mobility of the molecules to flow in viscous manner due to less strong inter-molecular bonding. Thus, the relaxation time for larger contact area decreases with decreasing elastic modulus [23] and hence the film is prone to damage because of thermal effect. As a result, the polymer is easily removed from the sliding track due to thermal and time dependent changes in the modulus of the film and the wear life of Si/UHMWPE is shorter than that of Si/DLC/UHMWPE. Thus, better bonding of the UHMWPE molecules with DLC and better mechanical properties of DLC with self-lubricating property of UHMWPE are the main reasons for higher tribological performance of the composite film.

In order to further extend the wear life, PFPE was coated onto Si/UHMWPE and Si/DLC/UHMWPE because of its high lubricity and thermal stability. After PFPE coating, the coefficient of friction was as low as less than 0.1 for both films, and, wear lives extended to 100,000 cycles for Si/UHMWPE and at least 300,000 cycles for Si/DLC/UHMWPE when the experiments were stopped. Since UHMWPE film does not have any reactive chemical groups, the chemical bonding between UHMWPE and PFPE films is ruled out. We assume that PFPE molecules are trapped in the initial roughness of the UHMWPE films and these molecules may serve as liquid lubricant to reduce shear stress and friction [19]. The possible reason for the great increase in the wear life is the thermal stability of PFPE, which can withstand higher (up to a range of 327–477 °C [24]) frictional heat generated at the interface without degradation. Also, lower coefficient of friction in the presence of PFPE means low frictional energy dissipation and less heating of the interface.

When the UHMWPE film thickness decreases, the load carrying capacity of the film is greatly influenced by the underlying hard DLC substrate and the effects of shear stress (in the dynamic case) and contact pressure are high which lead to the high friction and early film failure. As shown in Fig. 8, the contact area has a near linear relationship with the film thickness but the contact pressure has two trends: below 6.2 µm it increases significantly and above 6.2 µm it displays a gradual decrease. For the thin film (3.4 µm), though the contact area decreases slightly, its contact pressure increases significantly which means that the shear stress could increase significantly since the ratio of shear stress to contact pressure can be assumed as constant [25] within our experimental range. If the film thickness is too low in comparison with the contact radius, the counterface ball will penetrate into DLC film through UHMWPE; hard DLC particles may detach out and serve as third-body abrasive particles at the interface which will increase friction and initiate wear [26]. For the 6.2 µm film, the contact area is high and the shear stress is low and its wear life extends to 200,000 cycles. Under this condition, the polymer helps in the lubrication of the interface without any failure of the DLC which was seen in the case of 3.4 µm thick film.

When the film thickness increases, the contact area will increase with deeper penetration depth that leads to large friction coefficient (due to large transfer of the film polymer to the counterface) and lowwear life. This result agrees with the work of Aubert et al. [27]. At the initial stage of the test, the asperities of the film are removed by microcutting [28] and the removal rates of the polymer film vary in different parts of the sliding tracks (28 µm film in Fig. 6), which lead to non-uniform contact points. When the transferred polymer on the ball surface is of large amount and rough, the friction coefficient between non-uniform film and roughened polymer adhered ball is highly fluctuating. As a result, the thicker film (28 µm) fails earlier at about 100,000 cycles. For the 12.3 µm film, though its optical image (Fig. 6) shows similar non-uniform pattern as that of the 28 µm film, the polymer transferred amount is quantitatively low. Moreover the surface becomes smoother with increasing sliding cycles. Therefore, though the coefficient of friction for 12.3 µm film is slightly high, it shows consistent value at 0.14 ± 0.02 for at least 300,000 cycles when the experiments are stopped due to long test duration.
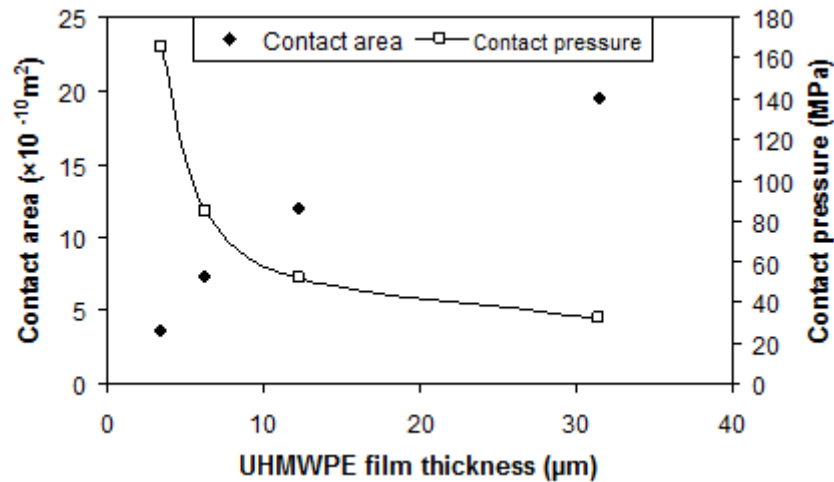
Fig. 8 *Contact area and contact pressure versus UHMWPE thickness for Si/DLC/UHMWPE where contact area and contact pressure are theoretically calculated using Hertzian equation and nanoindentation data presented in Table 2.*

In order to get higher wear life for the UHMWPE film, the film thickness should be in an optimum range to avoid factors that increase or fluctuate friction, such as high contact stress, large contact area and greater polymer transfer to the counterface. According to our present results, the range of optimum thickness to obtain higher wear life for Si/DLC/UHMWPE film is approximately within the range of 6.2 μm–12.3 μm. The benefit of high wear resistant UHMWPE film can be reaped only if the film thickness is optimum so to avoid the large interface/substrate effect on friction and wear (for low film thickness) or, the substantial polymer transfer to the counterface (for high film thickness). It should also be noted that in a composite coating such as the present one, there are some other effects that can also change the wear characteristics of the films in a drastic manner. For example, the interfacial strength and the crystallinity of the polymer in the film are two very important parameters and an investigation on their effects on the wear characteristics of the composite films is underway.

5   Conclusions

In this study, we have investigated the advantages of DLC/UHMWPE composite film (with and without PFPE as the top overcoat) and the role of UHMWPE thickness on the tribological performance when the films are coated onto Si wafer. After coating UHMWPE onto Si, the coefficient of friction reduces to 0.18 and wear durability is remarkably increased to 20,000 cycles compared to only few cycles for bare Si surface. The presence of DLC intermediate layer between the Si substrate and UHMWPE film provides higher load carrying capacity (high hardness and elastic modulus) and better adhesion between UHMWPE and DLC coated substrate and as a result, the coefficient of friction decreases to 0.13 and wear durability extends to 100,000 cycles for Si/DLC/UHMWPE. This is five times improvement over the film without DLC intermediate layer. Overcoating with PFPE as top layer gives coefficient of friction as low as 0.06 and wear durability increases to 100,000 cycles and more than 300,000 cycles (test stopped due to long duration) for Si/UHMWPE/PFPE and Si/DLC/UHMWPE/PFPE, respectively, when thickness of UHMWPE is fixed at 28 μm. For Si/DLC/UHMWPE film, the wear lives of thin film (3.4 μm) and thick film (28 μm) are approximately 100,000 cycles, which are shorter than those of moderate (optimum) thicknesses (6.2 μm and 12.3 μm). The wear lives of moderate films are 200,000 cycles and more than 300,000 cycles for 6.2 μm and 12.3 μm, respectively. The lower wear durability of 3.4 μm thick film is due to high contact stress that generates high frictional heat at the interface contributing to film failure and that of 28 μm thick film is due to larger contact area owing to soft layer and large fluctuations in the coefficient of friction with occasional high peaks due to polymer transfer to the counterface.

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