Molecular orientation, crystallinity, and topographical changes in sliding and their frictional effects for UHMWPE film

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Abstract

This paper presents a study on the frictional anisotropy of semi-crystalline UHMWPE polymer film deposited on DLC-overcoated Si substrate. For UHMWPE film slid against a silicon nitride ball, there is a remarkable difference in the coefficient of friction between the forward and reverse directions after the slider has been initially slid against the film for certain number of cycles. The changes in the friction are greatly influenced by the initial number of sliding cycles. This frictional behavior is explained in terms of crystallinity change and molecular orientational effects on UHMWPE and micro-topographical effects due to the initial sliding. Nanoscratch test is conducted to understand the friction of the polymer film in the sliding track and the data are compared with the macroscale friction data. The results show that the friction in the reverse of the initial sliding direction is high in comparison to that in the forward direction and this behavior mainly depends upon the number of initial sliding cycles. The initial sliding cycles affect the crystallinity and molecular orientation of the film, as well as the film topography. This combined effect on the polymer film results in an anisotropic frictional behavior of the film.

1 Introduction

Ultra high molecular weight polyethylene (UHMWPE) has been widely used as a bearing material in total knee and hip joint replacement [1] and as solid lubricant coatings [2, 3]. Despite its extensive use, the tribological and mechanical properties of this polymer limit the lifespan of such load bearing applications. Many researchers have tried to improve the wear resistance of UHMWPE. It is well known that cross-link density is one of the factor that has a strong influence on the wear resistance of UHMWPE [4]. Cross-link density enhances the resistance to plastic flow and lamellae alignment [5, 6]. The degree of cross-linking can be increased using methods such as radiation [4, 7, 8] and ion implantation [9, 10]. Another method used to modify the mechanical properties of UHMWPE is by subjecting the polymer to a high pressure and thus inducing orthorhombic crystal structure formation that can provide highly crystalline phase [11–13]. Simis et al. [14] established the link between the mechanical properties and the microstructure in terms of crystalline mass fraction, lamellae size, and distribution. Sperling [15] has also proved that the wear resistance of a polymer is affected by its mechanical properties which are related to the crystallinity of the polymer. From these studies, we now understand that the crystallinity is one of the most important factors in determining the wear life of the polymer by means of enhanced mechanical properties such as yield stress, elastic modulus, and impact resistance [13].

Various modifications were applied such as, controlling annealing temperature [16–18] and cooling rate [19], using less entangled reactor powders which could give high crystalline film [20–22], and monitoring the level of radiation absorbed [23], in order to increase the crystallinity. However, it should be noted that the crystallinity of the film can be changed during the course of sliding process which in turn affects the friction and wear properties, especially in continuous sliding tests. The relationship between the changes in the crystallinity as a result of sliding and friction remains unclear. Another factor that affects friction is the orientation of the polymer molecules. The molecular orientation of PTFE has been widely studied by Tabor's and Tanaka's groups [24, 25] in 1970s in which they showed the polymer molecule orientation along the sliding direction. Recently, we have studied UHMWPE as a thin film and investigated its friction and wear properties on different substrates, different thicknesses, and different surface energies using continuous sliding tests [2, 3, 26]. Our studies have shown that the crystallinity and molecular orientation of the polymer changes as the sliding progresses in one direction. This leads to a phenomenon of low and high coefficient of friction along the initial sliding (forward) and reverse directions, respectively. This paper will explore a deeper study of the friction of UHMWPE films in terms of changes in the crystallinity, molecular orientation, and micro-topography due to the sliding cycles and directions.

2 Experiment

2.1 Materials

Tetrahedral amorphous carbon, ta-C (non-hydrogenated DLC) was deposited on polished n-type Si (100) wafers (obtained from Engage Electronics (Singapore) Pte Ltd), about 455–575 lm in thickness and hardness of 12.4 GPa. A detailed procedure of deposition is mentioned in Ref. [27]. The thickness of the DLC film is in the range of 50 nm and hardness is 57 GPa, as provided by the supplier. UHMWPE film was coated onto a cleaned Si/DLC substrate by simple dip-coating. The cleaning and coating procedures are provided in Ref. [3, 26]. The thickness of the UHMWPE film used in this study was 12.3 μm and its initial roughness (Ra) was 0.56 μm, measured within a scan area of 10 μm x 10 μm using an AFM.

2.2 Friction measurements

The friction measurements were conducted on a custom-built tribometer. The setup has been described in detail elsewhere [3, 26]. A cleaned silicon nitride ball 4 mm in diameter with a surface roughness of 5 nm (as provided by the supplier) was used as the stationary counterface. The normal load of 4 mN was applied which gave a normal contact pressure in the range of 51.6 MPa calculated using Hertzian contact model. The test track radius and rotational speed were fixed at 1 mm and 500 rpm (0.052 m/s), respectively. In order to study the effects of the number of initial sliding cycles and the

sliding directions on the frictional behavior of the polymer film, we have selected 10,000, 30,000, 50,000, and 100,000 as different initial test cycles. After running different cycles, we stopped the experiments and replaced the counter-surface with a new ball in order to eliminate the effects of the transfer film deposited on the ball during the initial sliding. Then, the friction tests were continued precisely on the same track in the forward (same as the initial sliding direction) or in the reverse direction. All experiments were carried out in a clean booth environment at a temperature of 25 ± 2 °C and relative humidity of 55 ± 5%. The optical microscopy was used to analyze the surface morphologies of the samples and the balls. All experiments were repeated at least three times and the average of the data is reported.

2.3   Nanoscratching and nanoindentation

Nanoscratching and nanoindentation tests were carried out using an MTS Nano Indenter XP machine. The indenter for nanoscratching was a conical shape diamond tip with 90° cone angle and a tip radius of 5 μm. The applied load, the scratch velocity, and the scratch distance were 5 mN, 10 lm/s, and 50 μm, respectively. The scratching was performed on the sliding track in the forward and reverse directions. The main purpose of conducting nanoscratching is to investigate the friction in micrometer range and to compare it with the ball-on-disc test data. A constant load of 40 mN with a standard Berkovich diamond tip was used for nanoindentation. For each indentation, 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) was set. Fifteen independent indentations were conducted and averages of their hardness are reported in this paper.

2.4   Measurement of molecular crystallinity of UHMWPE on the track

The percent crystallinity of UHMWPE on the tracks was determined using Fourier Transform Infrared Spectroscopy (FTIR, Spectrum 1000, Perkin Elmer Life and Analytical Sciences, Boston, MA, USA). The spectra were obtained with an accumulation of 16 scans on transmission mode with a spot size of 100 μm diameter. The crystalline peaks were found at 729 cm^{-1} [28] and 719 cm^{-1} [29, 30], respectively. The relative percentage crystallinity was calculated as the total area under the crystalline peaks (A and B) divided by the overall area (A, B, and C) [31], as shown in Fig. 1. Five independent measurements were conducted on the track for each sample and the average values are reported in this paper.
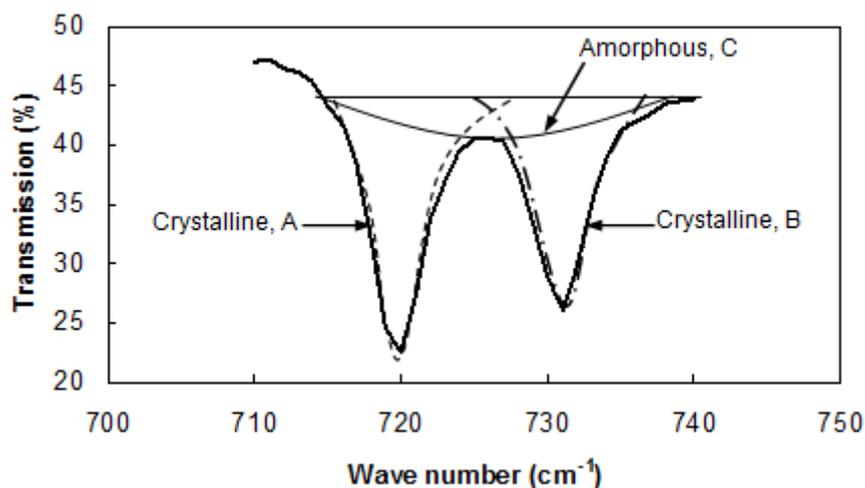

Fig. 1   *UHMWPE curve with amorphous and crystalline peaks using FTIR.*

2.5 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM, Hitachi S4300) was used to image the wear tracks in order to distinguish the different surface morphologies for different number of cycles. Gold coating was performed on the tested polymer films at 10 mA for 40 s (JEOL, JFC- 1200 Fine Coater) prior to FESEM imaging.

2.6 Wear Track Profilometry

Surface roughness was measured by Tencor P-10 alphastep profiler using a diamond tip (2 lm radius) with a load of 0.2 mg. The scanning speed was 5 µm/s and the sampling rate was 100 Hz. The RMS roughness (Rrms) reported in this paper was taken from a scan length of 50 µm along the sliding track.

3 Results

A prior test was performed on the original film for the purpose of comparing the coefficients of friction between before and after sliding. After sliding for different numbers of cycles, we replaced the counter-surface with a new ball in order to prevent the influence of the transfer films on the friction. During replacing the ball, we carefully removed the old ball without moving the test location in order to obtain the friction precisely on the same track. As an additional confirmation of the exact location, we examined the tracks under an optical microscope after every test. There were no extra track or fresh sliding mark and our observation suggested that all the friction data reported in this paper were recorded on the same track for different initial sliding cycles and in different sliding directions.

3.1 Friction of UHMWPE as a function of sliding cycles in the forward direction

The coefficients of friction of UHMWPE as a function of cycles for different number of sliding cycles in the forward direction are shown in Fig. 2. The sliding speed was fixed at 0.052 ms-1 with a constant normal load of 40 mN. The initial coefficient of friction (FD) was generally observed as less than 0.05. The coefficients of friction in the forward direction after 10,000 cycles and 30,000 initial sliding cycles were approximately in the range of 0.07–0.08. However, if the ball was slid over the surface for higher number of cycles such as 50,000 cycles and 100,000 cycles, it is seen that the friction coefficient drops to 0.05 or less in the forward direction when the ball was replaced with a new one.

3.2 Friction of UHMWPE as a function of sliding cycles in the reverse direction

The coefficients of friction of UHMWPE as a function of cycles in the reverse direction after different numbers of initial sliding cycles are shown in Fig. 3. For comparison purpose, we have provided the coefficient of friction of the original run as FD which is the same as in Fig. 2. When the sliding is reversed, the most significant observation is that all the friction data in the reverse direction are higher than that of the original film as well as that in the forward direction for the same number of sliding cycles. Reversing the sliding direction remarkably affected friction for all number of initial cycles. Generally, if the number of initial sliding cycles increases, the friction in the reverse direction also increases. It is seen that up to 30,000 cycles, the friction in the reverse direction increases gradually to 0.15. However, above 30,000 initial sliding cycles the friction falls again. This behavior suggests that the frictional property of UHMWPE film is influenced by the number of initial sliding cycles which probably changes some features of the polymer film such as the crystallinity, the molecular orientation, and the topography, as explained below. Those changes are major factors on friction when the sliding direction is reversed after initial number of sliding cycles. Therefore, it is important to understand the frictional behavior of UHMWPE film in order to make a clear distinction between two sliding directions for different numbers of initial sliding cycles. The changes in friction in the reverse direction are re-examined by conducting nanoscratching test on the track. The results are described in the following section.
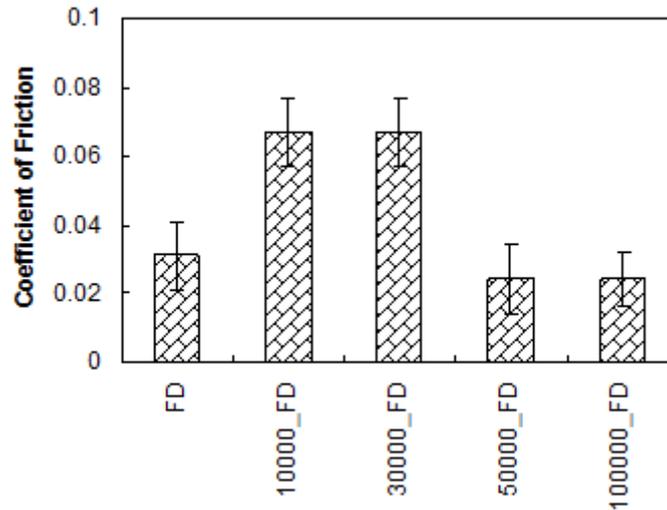
Fig. 2   *Averages coefficient of friction of UHMWPE film for first 200 cycles in forward direction. FD refers to forward direction. 10000_FD means after sliding 10,000 cycles in forward direction, the counterface has been replaced with a new ball and sliding continued on the same track in forward direction.*
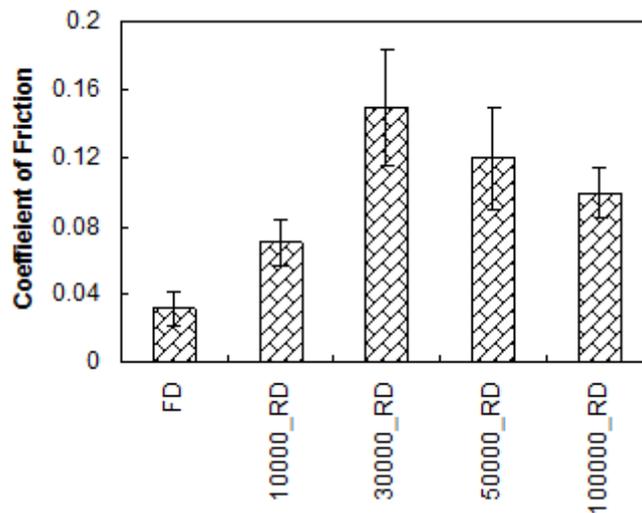

Fig. 3   *Averages coefficient of friction of UHMWPE film for the first 200 cycles in reverse direction. RD refers to reverse direction. 10000_RD means after sliding 10,000 cycles in the forward direction, the counterface has been replaced with a new ball and continued onthe same track in the reverse direction.*

3.3   *Friction of UHMWPE as a function of scratch distance in nanoscratching*

The coefficients of friction of UHMWPE from the nanoscratching tests are shown in Fig. 4. The initial friction is below 0.05 up to 20 μm scratching distance and then increases to approximately 0.08. The sudden change in friction is because of the polymer debris that adhered to the tip by abrading the asperities while scratching. Except for this sudden change, both the initial frictions from ball-on-disc and nanoscratch tests were the same (less than 0.05). The coefficients of friction with different number of cycles using nanoscratching in forward direction has shown similar results as for ball-on-disc. However, when the coefficient of friction in the reverse direction is studied, as we mentioned in the previous section, we have observed that the coefficient of friction increases with increasing number of sliding cycles. The nanoscratching data re-confirms what we have shown in the ball sliding tests. The

polymer films show high friction if slid against the initial sliding direction. The coefficient of friction drops when the number of initial sliding cycles is high enough (see data for 100,000 RD in Fig. 4).
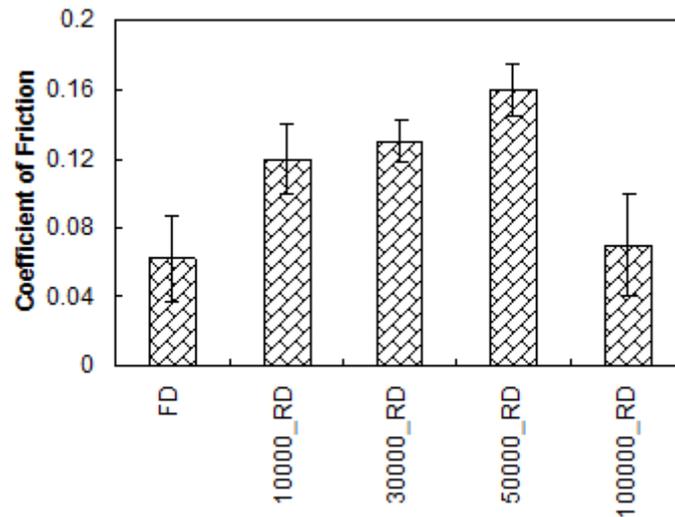

Fig. 4 *Averages coefficient of friction of UHMWPE film for 50 μm scratching distance in the reverse direction. RD refers to reverse direction. 10000_RD means after sliding 10,000 cycles in the forward direction, the nanoscratching has been done on the same track in the reverse direction.*

The FESEM images of the nanoscratches obtained from the above tests, for example with initial sliding of 10,000 cycles and 100,000 cycles, are shown in Fig. 5. The wear track width for 10,000 cycles is approximately 22 μm and that for 100,000 cycles is in the range of 50 μm. The image of 10,000 cycles (Fig. 5a) has debris and curled marks along the scratch whereas the image of 100,000 cycles (Fig. 5b) does not have these marks. It is found that there is not much amount of debris on the scratch conducted on 100,000 cycles. In nanoscratching, we have taken into account the role of the debris which can come out from the polymer film. The sizes of the debris were comparatively small for 4 mm diameter Si_3N_4 ball and their effects could be neglected in ball-on-disc test. However, their sizes could not be negligible in nanoscratching where the tip radius was 5 μm. The debris that is pulled out from the film can also block the scratching. As a result, the coefficients of friction increased in nanoscratching. Except this small difference, we have confirmed that the coefficient of friction is strongly affected by the number of initial sliding cycles and sliding directions.
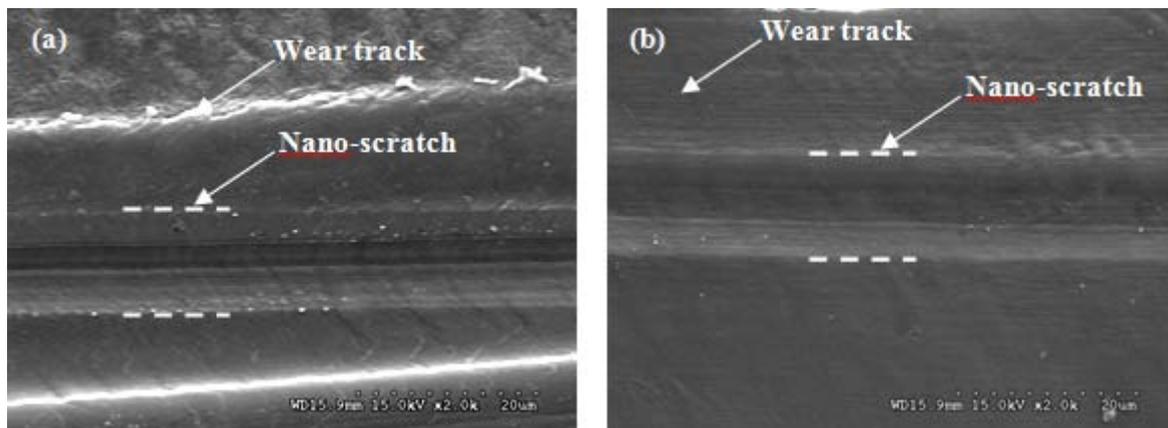

Fig. 5 *The FESEM images of nanoscratches which were conducted on wear tracks after sliding: **a** 10,000 cycles and **b** 100,000 cycles. The scratching was carried out from right to left that was opposite to the initial sliding direction. The width of the wear tracks are measured as *22 μm for (a) and ~50 μm for (b).*

4   Discussion

The transfer material on the Si3N4 ball was studied under an optical microscope and the images of the balls after sliding 10,000 cycles and 100,000 cycles against the films are shown in Fig. 6. It consists of lumpy polymers near the contact point and sharp-edged polymers pulled out in the sliding direction. Lumps indicate that polymer first adheres to the ball as soon as the sliding starts. And when the sliding is continuous, more polymers are attached near the contact zone and become thick. Sharp edge polymers indicate that the morphology of the polymer on the track has been changed. We believe that the changes in the surface morphology increase the roughness of the film. Those changes are critically dependent on the number of sliding cycles. The polymer transfer process between the track and the ball occurs at all times during the sliding. As the sliding cycles increase, a steady-state is achieved when all asperities are compressed and there is very little further transfer of the polymer to the ball. At the steady-state, the surface roughness is quite low and may further decrease with increase in the sliding cycles.

Table 1. *The hardness of UHMWPE film with different number of sliding cycles using nanoindentation.*

Sliding cycles	Hardness (GPa)	Roughness, R_{rms} (nm)
0	0.12 ± 0.008	118.8 ± 2.5
10,000	0.12 ± 0.008	123.8 ± 2.5
30,000	0.12 ± 0.009	135.8 ± 3.0
50,000	0.122 ± 0.023	43.0 ± 1.0
100,000	0.138 ± 0.022	32.0 ± 1.0

The last column gives data for the average roughness, Rrms (nm), of the wear track before the test (0 sliding cycles) and after different number of sliding cycles. Surface profile was taken along the wear track at the centre of the track

After different initial sliding cycles, we conducted nanoindentation tests on the track in order to measure the changes in the hardness of the film and the results are summarized in Table 1. The hardness of the 12.3 µm film at the beginning was 0.12 GPa and there was no significant variation until 30,000 cycles. It is obvious that all the frictional changes occurring in this range are not affected by the hardness of the substrate but by the surface morphology of the track. This was proved by recording the surface profiles of the wear track at different points. All measurements showed wear track depth of 0.3 ± 0.1 µm for all sliding cycles which was closer to the initial roughness of the film and much lower than the thickness of the film. Thus, we can conclude that, within the given experimental conditions, there is no deepening of the wear track due to sliding and there is only topographical changes taking place during sliding due to the plastic deformation of the asperities. Hence, high hardness for the film after sliding 50,000 and 100,000 cycles is attributed to the changes in the physical state of the film rather than due to the substrate effect. At the early stage of sliding, the material removal rate from the film by detachment of the asperities was not uniform and the film surface became roughened. This was confirmed by recording surface roughness profile on the wear tracks (Table 1). As the sliding continued with a new ball in the same forward direction (Fig. 2), the coefficient of friction for 10,000 cycles and 30,000 cycles increased because of the increased roughness of the film. When the sliding cycles were above 30,000 cycles, the surface became smooth again because of the plastic deformation in the top layer and molecular orientation and as a result the hardness has slightly increased. The high hardness of the film provides higher resistance to penetration which in turn reduces the contact area and the coefficient of friction. During the initial sliding process the molecules on the top layer of the film get plastically deformed and oriented in the direction of sliding. Such orientation of the molecules has effect on increasing the relative crystallinity and the strengthening of the film [32]. Moreover, the density of the film depends on the number of sliding cycles. As the number increases, the density will be high with longer pressing time that can reduce the friction [33].
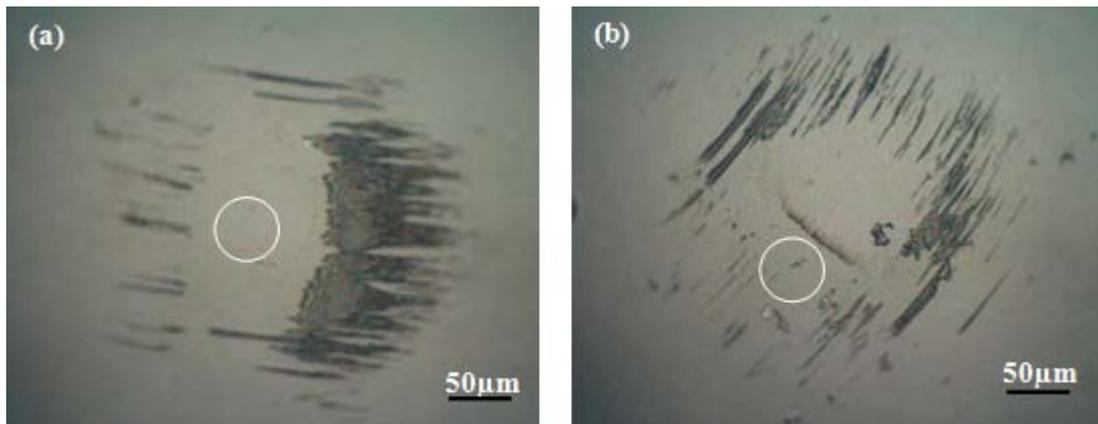
Fig. 6   *Optical images of Si3N4 ball surface after sliding (a) 10,000 cycles and (b) 100,000 cycles against UHMWPE film in forward direction.* **White cycles** *show the contact points.*

However, as we can see in Fig. 3, the coefficients of friction of different cycles are higher in the reverse direction than that in the forward direction. It proves that rather than the effects of the surface roughness and hardness, there are other factors such as the relative crystallinity and the molecular orientation that have influenced this change in the coefficient of friction.

The relation between the relative crystallinity on the track and the coefficient of friction in the reverse direction as a function of initial sliding cycles is shown in Fig. 7. The results show that the crystallinity of the film varies with the number of the initial sliding cycles. The film before the test had a relative crystallinity of 76%. The degree of relative crystallinity increased to 79% after 10,000 cycles of sliding. A higher degree of relative crystallinity indicates that molecules in the amorphous regions have aligned somewhat due to sliding. The degree of alignment or relative crystallinity can increase with sliding cycles but we have found that beyond 10,000 cycles the relative crystallinity fell and reached the lowest value of 66% after 50,000 cycles. One possible reason is that as sliding continued, the taller asperities of the film were flattened and plastically deformed. The plastically deformed top layer partially covered the original crystalline region. The partially covered layer has now disturbed the original crystalline region, hence bringing about a reduction in the overall relative crystallinity. The main interesting finding brought out from this FTIR study is that the degree of relative crystallinity increased again beyond 50,000 cycles and it showed a high value of 87% for 100,000 initial sliding cycles. This increase in the relative crystallinity beyond 50,000 sliding cycles could be an indication of the molecular alignment in the direction of sliding. This alignment also has strengthening effect as seen in the increase in the nanoindentation value for the film after 100,000 sliding cycles (Table 1).

The results in Fig. 7 show that the coefficient of friction in the reverse direction increased with increasing number of cycles up to a point and then decreased with higher number of cycles. The friction was inversely proportional to the crystallinity of the film. The presence of the amorphous region in lower relative crystallinity region is high which can extend and align during the sliding that can increase friction. In contrast, high relative crystallinity somewhat hardens the polymer film and as a result, reduces the contact area and the coefficient of friction. As soon as sliding starts, the polymer molecules are oriented along the sliding direction which in turn affects the relative crystallinity of the film. Moreover, as mentioned above, polymer asperities on the film are unevenly deformed and the remaining roughness features are inclined in the direction of sliding, similar to the shape of the 'hair cuticles' (as seen in Fig. 8d). This change in surface morphology is coupled with the initial increase in the film roughness when measured along the wear track. When the sliding direction is reversed, the oriented polymers are against the new sliding direction. This is another important reason for the increase in the friction upon changing the sliding direction. Complete orientation of the polymer molecules may take many initial sliding cycles. However, Pooley et al. [24] also showed on PTFE film that if the molecules were highly oriented in the sliding direction, the coefficients of friction were not much different in both directions. When the initial sliding cycles were 100,000, the coefficient of friction in the reverse direction somewhat decreased because of: (a) nearly complete orientation of the molecules by plastic deformation, (b) higher relative crystallinity that increased the load carrying capacity of the film and reduced the contact area, and (c) smoothness of the film.
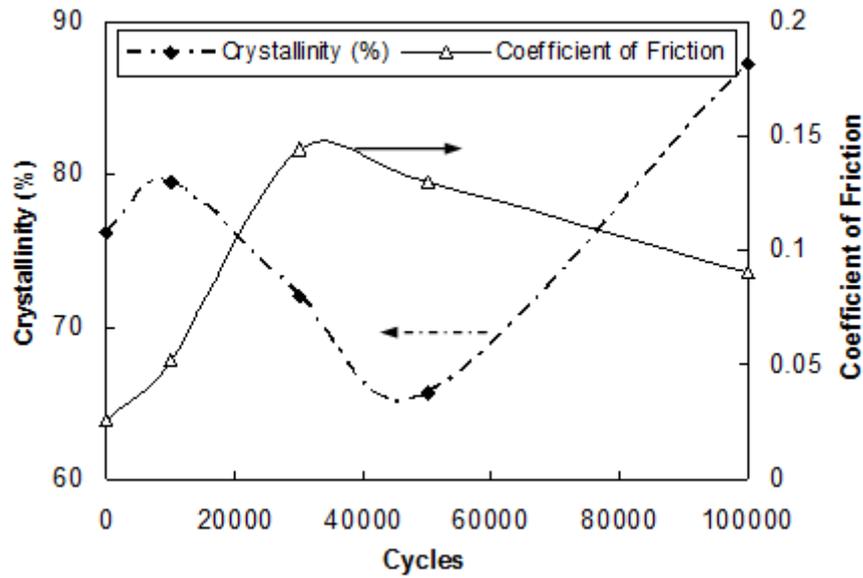
Fig. 7 *The relation between the film crystallinity and the coefficient of friction (in the reverse direction) as a function of sliding cycles.*

A better understanding of the relative crystallinity and surface morphology on the track is studied by FESEM. Their topography images are shown in Fig. 8. A distinct type of lamellae structure, that is a sign of crystalline region [34], is clearly seen in Fig. 8a (before sliding). The images of the tracks after sliding 10,000 cycles and 50,000 cycles (Fig. 8b, c) consist of covered and uncovered areas. The covered areas are due to the plastically deformed layers which were formed by flattening the taller asperities of the crystalline zone. As the sliding cycles are increased, the coverage by the deformed polymers on the track appears more and as a result the relative crystallinity of the original film surface drops. We have also found that there are sharp corners with steps at the leading edges of the covered layers that increase with the number of cycles (Fig. 8b, c). In the case of the reverse direction sliding, these steps and corners may obstruct the sliding process and increase the friction, similar to the case of hair cuticle. It can be seen in Fig. 8d that the coverage by deformed and oriented molecules is near complete with probably majority of the polymer molecules oriented in the initial sliding direction. Thus, for very high number of initial sliding cycles, the early roughness effect (hair cuticle type) in the reverse direction is eliminated and the molecular orientation is increased with proportional increase in the relative crystallinity and hardness of the film. It is also possible that the relative crystallinity of the layers below the top plastically deformed layer can increase for the long sliding period [35, 36]. The high crystallinity due to molecular orientation and smoothness of the wear track for 100,000 initial sliding cycle case, therefore, reduced the frictional resistance in the reverse direction.
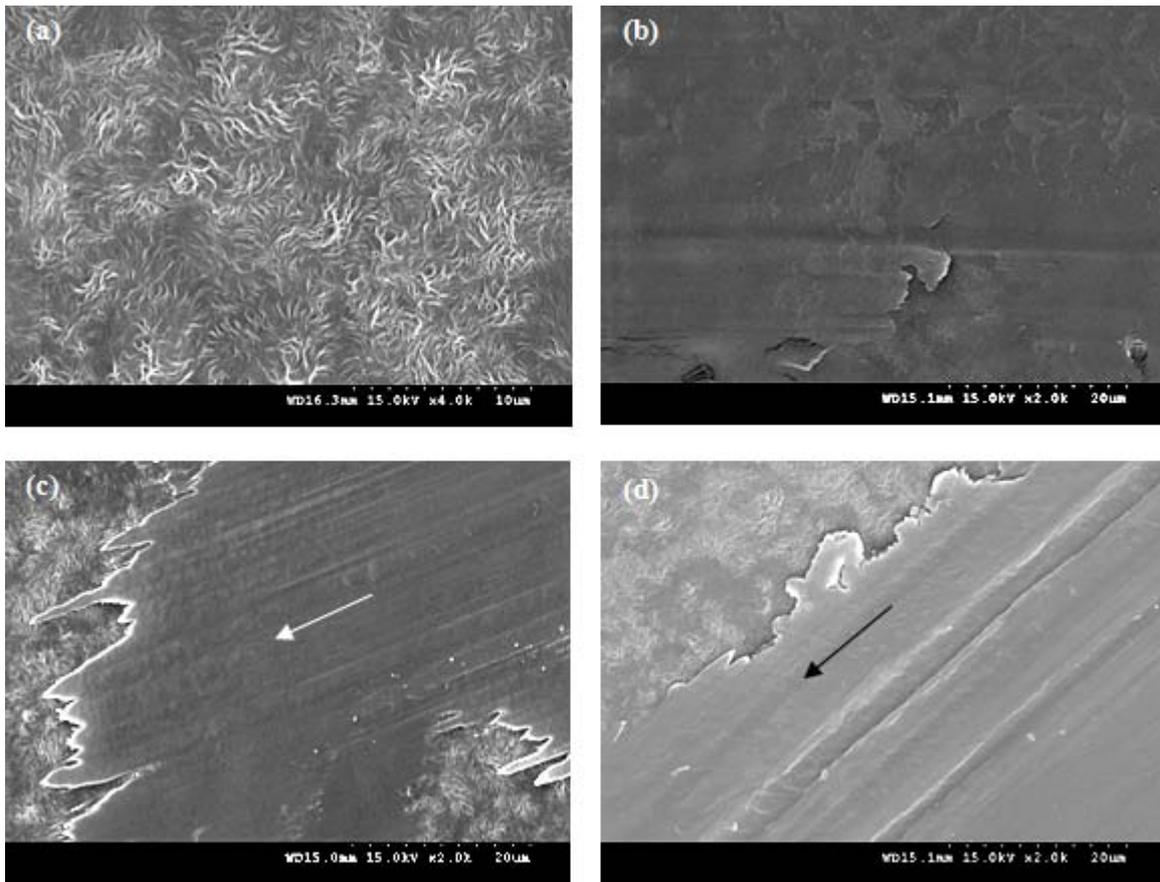
Fig. 8   *The FESEM images of UHMWPE film (a) before sliding and after sliding (b) 10,000 cycles, (c) 30,000 cycles, and (d) 100,000 cycles. Image (a) is taken at 4000 times and the rest are taken at 2000 times magnifications.* ***Solid arrows*** *show the sliding directions.*

5   Summary

This paper has presented a study on the changes in the relative crystallinity and molecular orientation of UHMWPE film in a continuous sliding test against smooth 4 mm diameter Si_3N_4 balls. It is shown that after sliding on the film for several thousands of cycles, the coefficient of friction is different if a new slider is slid in the forward or reverse direction. During the initial sliding several changes in the film occur. The roughness can increase before the surface finally becomes very smooth at around 50,000 cycles or more. There is slight increase in the nanoindentation hardness of the film because of changing molecular orientation and relative crystallinity effects. The coefficient of friction remains on the higher side until the top film surface is completely modified because of the sliding phenomenon.

In the reverse of the initial sliding direction, the relative crystallinity and molecular orientation as well as microchanges in the topography influence the coefficient of friction. As the sliding starts, the asperities of the top layer are plastically deformed that cover the original crystalline region of the film. Initial plastic deformation of the film leads to a decrease in the relative crystallinity in the middle range of sliding cycles (30,000–50,000 cycles) due to the change in the molecular orientation. As the molecules are aligned along the sliding direction, the sharp corners and steps (resembling hair cuticles) appear that can provide obstacles to the slider in the reverse direction. The appearance of these patterns is much more in the middle range of the initial sliding cycles. Because of the lower crystallinity and higher number of sharp edges, the coefficients of friction in the reverse direction after 30,000 cycles and 50,000 cycles of sliding are higher than those of the two extremes; that is, the lower and the higher number of initial sliding cycles. For the lower number of initial sliding cycle case, the relative crystallinity of the film is still high (original film relative crystallinity) and the topography of the film is

not much changed. For very high number of sliding cycle case, the film has been totally covered with highly oriented polymer molecules and the surface is smooth.

This study has shown that the friction coefficient of a polymer film is highly dependent on the molecular orientation and relative crystallinity and hence these parameters should be considered while making highly lubricious polymer films on a substrate. Also, the process of the continuous sliding in one direction can change the above parameters of the film bringing a clear change in the film frictional behavior.

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