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Tribological performance of hydrophilic diamond-like carbon coatings on Ti–6Al–4V in biological environment

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ABSTRACT

Tribological performance of diamond-like carbon (DLC) and Si doped DLC (Si-DLC) films on Ti–6Al–4V under bovine serum as well as water and ambient air condition has been studied in terms of surface modification with O_2 plasma treatment for superhydrophilic surface. A tribo-test revealed that bovine serum significantly enhanced the tribological performance on all DLC surfaces in comparison with those under water or in air medium. Especially, O_2 plasma treated Si-DLC coatings with superhydrophilic nature were found to lower the wear and increase coating stability associated with macromolecules especially proteins in the bovine serum and their interactions with surfaces.

1. Introduction

Nowadays, an increasing number of load-bearing joints have been replaced by artificial implants, mainly hip joints and knee joints due to over aging of the population as well as the increasing average weight of people. Additionally, diseases like arthritis could also require the replacement of joints. Different materials for joints have been used with specific advantages and disadvantages [1–5]. Out of all combinations of materials, materials with functional coatings like diamond-like carbon (DLC) have been reported promising for joint prosthesis because of their chemical inertness, extreme hardness, wear resistance and biocompatibility [6,7] even though earlier implanted DLC coated artificial joints turned out to be problematic. The main reason for the failure of specific DLC coatings was partial delamination of coating, resulting in exposure of the base material with high roughness which caused severe wear in the biological system [8,9]. These challenges of DLC coated materials demand further research for long term stability to improve their performance when operated in human body. However, it was reported that delaminated DLC particles did not affect either the cell viability or the proliferation or differentiation, indicating no toxic or inflammatory reaction [9].

DLC coated surface exhibits a combination of low friction and high wear resistance under a wide range of sliding contact conditions [1]. In order to improve the proper functionality for biological application, the surface chemical behavior of DLC can be tuned by the addition of different elements such as Si, Ti, or Ag [1]. In recent progress, Si and SiOx incorporated DLC coatings have been known not only to improve the mechanical stability and corrosion resistance under aqueous environment but also to reduce inflammatory reactions and improve biocompatibility [10–12]. Furthermore, favorable surface properties like hydrophilic and hydrophobic nature of DLC coatings would be the important factors for better performance during tribo-test in biological fluid. Surface wettability of hydrophobic/hydrophilic surface for water has been reported to affect the implanted materials in terms of the biological responses like protein adsorption, platelet adhesion/activation, blood coagulation and cell and bacterial adhesion [13–18]. But the surface wettability effect, especially hydrophilicity, has not been studied on the tribological behavior of a DLC film under a biological environment.

The object of this study is to investigate the influence of surface nature of DLC coatings in the fluids in water and bovine serum on tribological performance and on the stability of the films. To achieve this, we prepared pure DLC, Si-DLC and oxygen plasma treated Si-DLC coatings on Ti–Al–V alloy materials and performed sliding wear experiments using a ball-on-disk type tribometer. Friction curves of these coated materials were measured under three different environmental conditions: air, water and bovine serum. Although this simple setup and chosen experimental parameters for tribo-tests would not reproduce all clinical parameters relevant for the accurate

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simulation of wear in joints (e.g. contact geometry, loading cycle, contact pressure and fluid entrainment or multi-directional sliding), it can give valuable information about the effect of biological environment on friction and wear of DLC coatings and the tribological performance and stability of DLC surfaces with different surface nature. A harder counter face (sapphire ball) has been chosen for a comparative study of different DLC surfaces. Surface wettability of these DLC coatings with water and bovine serum was assessed by using a contact angle measurement setup equipped with an optical microscope. Viscosity of the serum and total proteins in the serum were measured before and after tribo-test for each DLC surface.

2. Materials and methods

2.1. Synthesis of DLC and Si-DLC thin films

The pure DLC and Si-DLC films were deposited on Ti–6Al–4V alloy by 13.56 MHz radio frequency plasma assisted chemical vapor deposition (RF-PACVD) technique. Details of the deposition equipment have been published previously [19]. The substrates were mechanically polished using a diamond suspension with 0.2 µm diameter particles and ultrasonically cleaned for 30 min in trichloroethylene (TCE), acetone, methanol and ethanol in sequence. Prior to the deposition of DLC films, the substrates were cleaned with Ar plasma at a bias voltage of −400 V and the pressure of 0.49 Pa for 30 min. An initial interlayer of 24 nm thickness of a-Si:H was deposited on all the substrates for better adhesion of DLC and Si-DLC films onto Ti–6Al–4V alloy substrates. The DLC and Si-DLC films were then deposited at a bias voltage of −400 V and a deposition pressure of 1.33 Pa by RF-PACVD with benzene and coupling of benzene and diluted silane ($SiH_4/H_2 = 10{:}90$) as the precursor gases, respectively. The film thickness of both DLC and Si-DLC was 0.5 ± 0.01 µm as measured by an alpha step profilometer. The chosen thickness of the DLC film might not be enough for actual joint load conditions for joint replacement applications and required further optimization. The Si concentration in the Si-DLC films was 4 at.% as measured by XPS (model: PHI 5800 ESCA system).

The hydrophilicity of Si-DLC films was enhanced by surface treatment with exposing the Si-DLC coated specimen to plasma of oxygen gas for 10 min at a bias voltage of −400 V at the pressure of 1.33 Pa [20]. As considerably etched by O_2 plasma during plasma treatment, thicker Si-DLC films were prepared for O_2 plasma treatment to get the final thickness of 0.5 ± 0.01 µm for both DLC and Si-DLC films. A thin silicon strip of thickness of 50 ± 3 µm as a substrate was used to measure the residual compressive stress for Si-DLC and O_2 plasma treated Si-DLC by determining the curvature of the film/substrate using Stoney's equation [21], resulting in 1.06 ± 0.06 GPa, revealing no significant difference between Si-DLC and oxygen treated Si-DLC. The structural and mechanical properties of the Si-DLC film with various Si content had been previously investigated in detail [22,23].

2.2. Observation and Characterization

The contact angle of the liquid droplet on the surface of each DLC surface was measured using an optical device of the VCA-Optima™ machine (AST Products, Inc., Billerica, MA) mounted with a precision camera to capture images of the droplet (see Fig. 1). D.I. water and bovine serum (Gibco-Invitrogen Corporation, catalog number: 16170, lot number: 687676) with an average of 73 mg/ml protein concentration were used during testing with a droplet size of 0.5 µl. Ten individual drops were analyzed on each material surface.

A ball-on-disk type tribometer was used to characterize the tribological properties of the test surfaces. As described with a schematic in Fig. 2, a sapphire ball of diameter 6 mm was used as a counter face material. The ball was loaded onto the disk specimen fixed in a rotating aluminum cup. During the experiment, the disk and the ball were submerged into the medium fluids of water and bovine serum inside the cup of volume 40 ml. Normal loads chosen for experiments were 5 N and 10 N and sliding speed was 5.24 cm/s or equivalently 100 rpm. The total number of rotations was 9000 and the sliding distance was thus 282.7 m. Frictional forces were recorded by the help of a load cell attached to the tribometer. Each tribo-test at specific conditions was repeated 4 times to confirm the results. All tribo-tests were performed under controlled atmosphere at a temperature of 38 ± 2 °C and relative humidity of 50%.

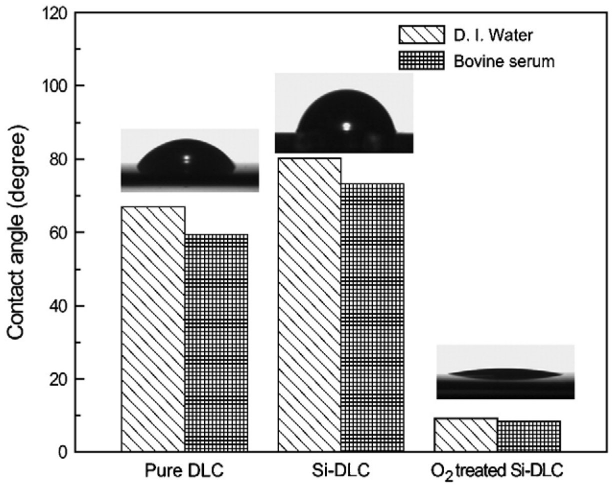

Fig. 1. Contact angle of different DLC coated materials with water and bovine solution.

Worn-out surfaces of DLC coated materials at different experimental and environmental conditions of tribo-test were observed using an optical microscope. Ostwald viscometer was used to measure the kinematic viscosity of bovine serum at 38 °C before and after tribo-tests. The viscometer was suspended in an oil bath to maintain a constant temperature at 38 °C during viscosity measurements. Each serum viscosity measurement was repeated 5 times to estimate the experimental error. The protein concentration in bovine serum before and after tribo-tests were measured using bovine serum albumin as standard protein according to Bradford protein assay method [24], one of the well known methods to quantify the total proteins in the system.

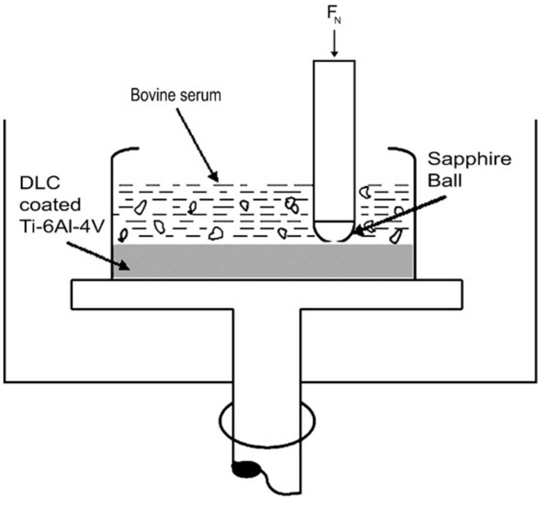

Fig. 2. A schematic diagram of a ball-on-disk type tribology test equipment.

3. Results and discussions

3.1. Wettability

Fig. 1 shows the wetting angle of the DLC films. Samples of pure DLC, Si-DLC and Si-DLC with oxygen plasma treatment produced contact angles of 67° ± 1.2°, 80.3° ± 1.4° and 9.2° ± 2.1° with D.I. water, respectively, which are similar to the previous work on Si-DLC with plasma treatment [20]. These same surfaces produced contact angles with bovine serum as 59.4° ± 1.1°, 73.2° ± 1.5° and 8.3° ± 2.3°, signifying around 10% reduction in comparison to those using D.I. water, indicating an increase of wettability compared to those with D.I. water droplets. The high wettability or low contact angle property between bovine serum and D.I. water might be due to the differences in rheological properties of bovine serum with that of D.I. water.

As no significant difference in the residual stress between Si-DLC and oxygen treated Si-DLC coatings with the same thickness was found, the major influence imposed on frictional resistance and damage resistance of coated surfaces can be caused by surface properties of DLC coatings (hydrophobic and hydrophilic) and physicochemical properties like viscosity and protein interactions with surfaces.

3.2. Tribology tests under different environmental conditions

Fig. 3 shows the dependence of the friction coefficients on the sliding distance of three different DLC coatings in three controlled environments. The quantitative deference of the coefficient of friction among the oxygen plasma treated Si-DLC, untreated Si-DLC and pure DLC coatings before delamination of the coatings was not significant at given experimental conditions in Fig. 3(a), (b) and (c). But, bovine serum media during sliding wear experiments significantly reduced the frictional force irrespective of the surface nature in comparison with D.I. water and air. It should be noted that the friction coefficient of Si-DLC under water condition was lower than that on pure DLC, consistent with the previous works [25,26]. The frictional curves further reveal the instability of DLC coatings in air and D.I. water media in comparison with bovine serum, indicated by a sudden jump in the coefficient of friction. Based on the stability of the coatings, oxygen plasma treated Si-DLC surfaces performed well in air, D.I. water and bovine serum media, whereas other surfaces failed or were unstable either in D.I. water or in air media.

The optical microscope images in Fig. 4 revealed noticeable difference in the worn-out surface morphology of the oxygen plasma treated Si-DLC coatings versus those of untreated Si-DLC coatings sliding against a sapphire ball in bovine serum, and D.I. water media. The wear scars of oxygen plasma treated Si-DLC surfaces were not visible for the normal load of 10 N in bovine serum in Fig. 4(b). But for untreated Si-DLC surfaces, wear scars and damaged surfaces were significant under the same experimental conditions in Fig. 4(a). In case of D.I. water and air media, oxygen plasma treated Si-DLC materials also showed the same superiority in terms of damage of surfaces, i.e., lower severity of damage on the surfaces of oxygen plasma treated Si-DLC coatings than those of Si-DLC coatings in Fig. 4 (c) and (d). High coefficient of friction and shorter time duration for delamination of coatings, noticed by a sudden increase in the friction coefficient, were measured for severely damaged surface in Fig. 4(c). The morphology variations of sapphire balls corresponding to the counter face of the DLC coatings after the tribo-tests are shown in Fig. 4(e)–(h). In some cases where surface damage did not occur severely, sapphire ball surfaces were covered by a thin layer in bovine solution in Fig. 4(e) and (f). This layer might be formed with the bovine serum. Unfortunately, the chemical composition of the layer hasn't been measured in this work. Ball surfaces under water condition were worn at a large contact region (Fig. 4(g)) against Si-DLC surfaces with large damage (Fig. 4(c)), while smaller contact region (Fig. 4(h)) was found against oxygen treated Si-DLC with less damage (Fig. 4(d)). These friction curves and micrographs together revealed that the tribological performance for Si-DLC with oxygen plasma treated materials was better than those of pure DLC and Si-DLC materials irrespective of load conditions and working media.

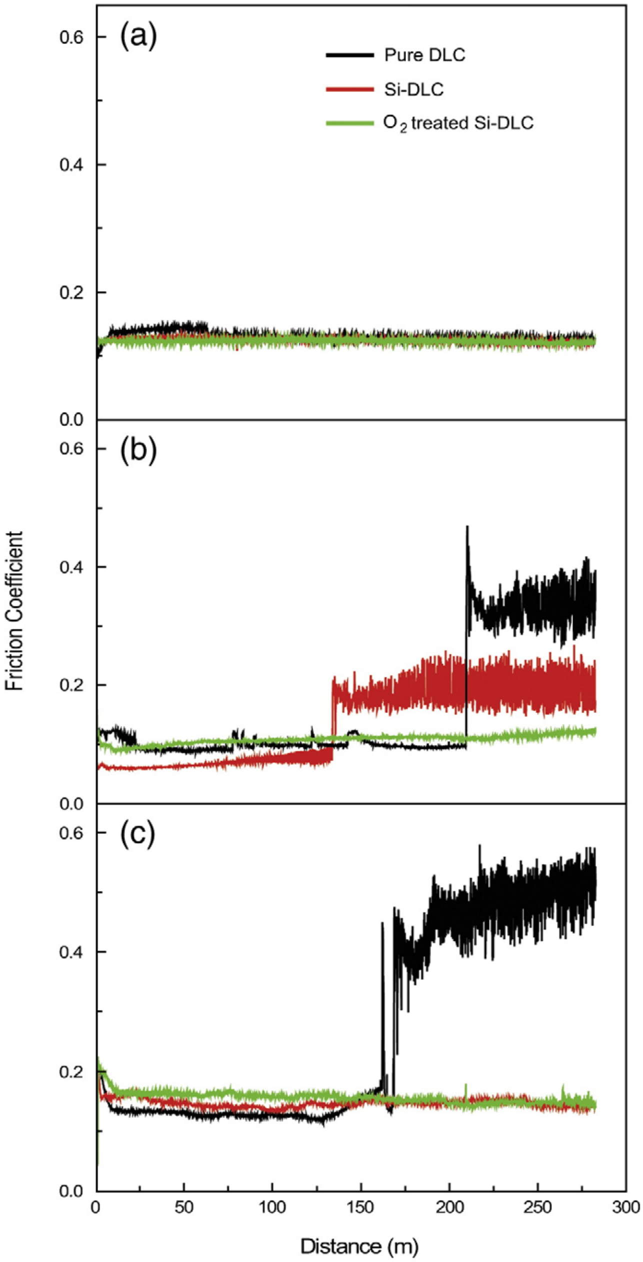

Fig. 3. Frictional curve of different DLC coated materials in (a) bovine serum at 10 N load, (b) D.I. water at 10 N load and (c) air at 5 N load.

3.3. Viscosity and protein concentration of bovine serum

The appearance of bovine serum (lubricant) was changed slightly from initial light wine color to dark wine color after sliding wear test. Fig. 5 shows the kinematic viscosity of the bovine serum collected after sliding wear test of different DLC coated materials at specific load conditions. In all cases, the viscosity of the bovine serum after the sliding tests increased in comparison to the viscosity of the initial serum irrespective of the nature of the surface of the DLC coatings, but the difference in the change of viscosity of different DLC coatings was

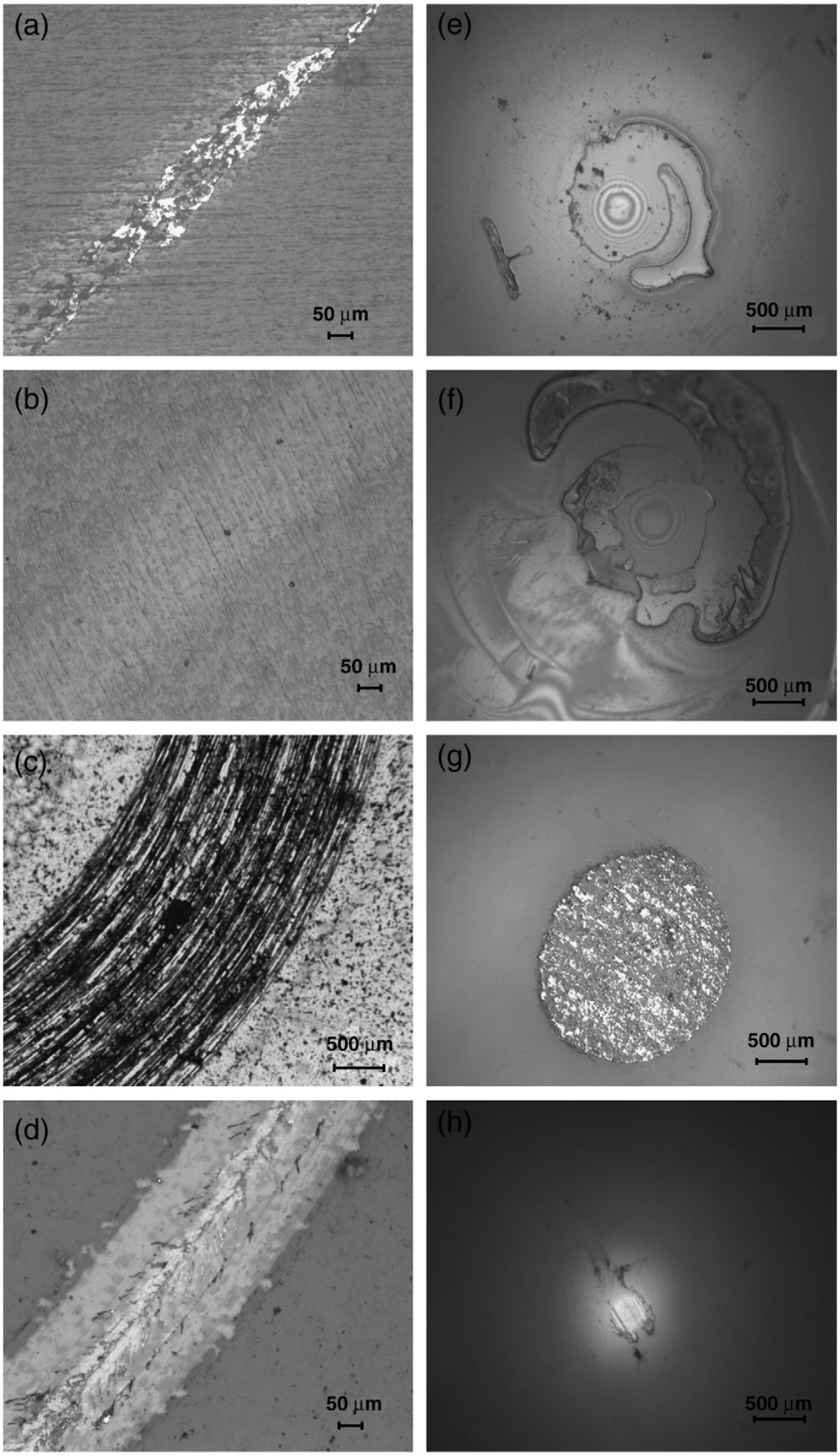

Fig. 4. Surface morphology of the different DLC coatings after tribology tests (a) Si-DLC in bovine serum, (b) O_2 treated Si-DLC in bovine serum, (c) Si-DLC in D.I. water, (d) O_2 treated Si-DLC in D.I. water and the surface morphology of the sapphire ball corresponding to their counter face DLC coatings, (e) Si-DLC in bovine serum, (f) O_2 treated Si-DLC in bovine serum, (g) Si-DLC in D.I. water, and (h) O_2 treated Si-DLC in D.I. water at 10 N load.

insignificant. The maximum viscosity was 1.58 cSt at 10 N load with O_2 plasma treated Si-DLC and the minimum was 1.56 cSt at the same load with Si-DLC while it was 1.31 cSt for pure DLC coating. The possible reasons for the increase of viscosity of bovine serum in our experiments might be evaporation of water content in the bovine serum during wear test at 38 ± 2 °C. And also other well known reasons for increasing viscosity are thermal denaturation induced by frictional heat and mechanical shearing of protein molecules at sliding surfaces [27]. Unfortunately in our experiments, the viscosity variations under bovine serum within different surfaces were observed in no

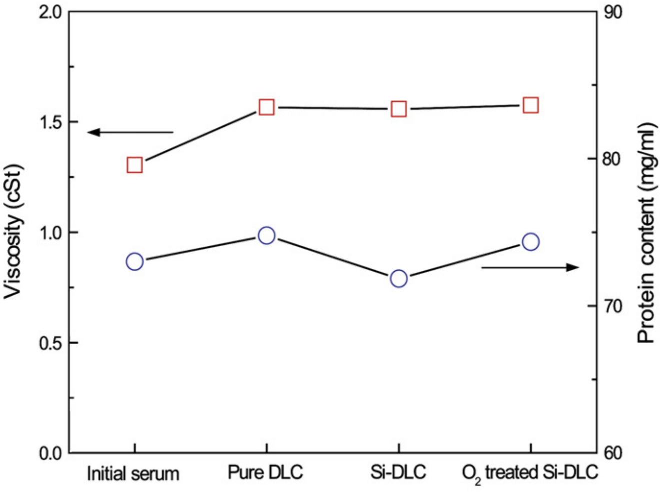

Fig. 5. Change of viscosity and proteins of bovine serum before and after tribology tests with different surfaces.

significant difference after tribo-tests in Fig. 5, resulting in no direct clue for denaturation of proteins based on the nature of surfaces.

In our experimental results, oxygen plasma treated Si-DLC has shown better performance in terms of friction coefficient (Fig. 3) as well as damage resistance, i.e. stability of surface (Fig. 4) against both pure DLC and Si-DLC. These observations clearly show that hydrophilic DLC surfaces are favorable for tribological applications at given experimental conditions. One of the possible reasons for low frictional forces of hydrophilic surfaces based on protein adsorption was studied by Heuberger et al. [28]. They have studied adsorption capability of native and denatured proteins on the polymer surfaces by using an aqueous solution of human serum albumin (HSA) as a model lubricant. And they have shown that unfolded/denatured proteins (HSA) in the solution are preferentially adsorbed onto hydrophobic surfaces. The adsorbed layer of denatured HSA effectively passivates the surface and prevents adsorption of further proteins from the solution, whereas native-HSA is preferentially adsorb on hydrophilic polymer surfaces with high molecular density. They further mentioned that during frictional studies denatured HSA is adsorbed to form a compact, passivating layer on hydrophobic polymers and increase sliding friction whereas hydrophilic surfaces preferentially adsorb proteins of native conformation, which form thicker and denser films that have the potential to reduce boundary-lubricated friction. Generally hydrophobic surfaces are considered to be more protein-adsorbent than hydrophilic surfaces because of the strong hydrophobic interactions occurring at these surfaces, in direct contrast to the repulsive solvation forces arising from strongly bound water at the hydrophilic surface [29–31]. And also the affinity of proteins towards solid surface (hydrophobic or hydrophilic surfaces) depends on the type of protein. Albumin has a stronger affinity toward the OH terminated surface having hydrophilic nature while fibrinogen shows a slightly higher affinity towards the hydrophobic surface [32].

Considering the above mentioned controversial results made by earlier researchers as well as our experimental observation of the hydrophilic surfaces showing better tribological performance and stability, the optimization of surface wettability is required for better control of tribological performance for joint prosthesis application.

4. Conclusion

In conclusion, this study revealed that hydrophilic DLC surfaces reduced the wear and improved the stability of DLC coatings in a biological fluid. It was found that bovine serum significantly affected the tribological performance of DLC coated materials in comparison to water and air media irrespective of the nature of DLC surfaces. O_2 plasma treated Si-DLC surfaces, showing superhydrophilic nature, have shown better tribological performance than those of pure DLC and Si-DLC surfaces. Further systematic investigation on the role of a specific protein on the specific functions like formation of boundary lubrication and its adsorption and desorption on target surfaces would suggest guidelines for the development of optimized surfaces of DLC coated Ti–6Al–4V materials with better control of the friction and wear in total joint prostheses.

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