Synergistic regulation mechanism of bionic structure and poly (vinylsulfonic acid) sodium (PVSNa) coating for high load bearing lubrication

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Abstract. A low friction coefficient and high bearing capacity can improve the service life of implants in the human body. In this study, the surface performance was improved by coupling the structure with the material. The bionic structure was obtained on the titanium alloy (Ti6Al4V) surface by chemical etching. The mechanical properties of Ti6Al4V with bionic structure were investigated by tribological experiments with different stresses. An interesting phenomenon was found that the friction coefficient of etched surface decreased with the increase of the stress, indicating that bionic structure can effectively improve the stability of Ti6Al4V surface bearing capacity. A poly (vinylsulfonic acid) sodium (PVSNa) coating was further fabricated on etched Ti6Al4V to obtain low friction. During the sliding process, PVSNa molecules were continuously added from the bionic structure to the surface through friction force for lubrication. The synergistic regulation of bionic structure and PVSNa coating made Ti6Al4V surface obtain low friction and high bearing capacity stability. This study can serve as a guide for the design of low friction and high bearing capacity stability.

1. Introduction:
Titanium and its alloys have been used widely in implants due to its high corrosion resistance, strength-to-weight ratio and good biocompatibility [1, 2]. However, owing to the complex environment in vivo, it is necessary to reduce surface friction and increase bearing capacity to obtain a longer service life.

Surface modification can be used to improve the surface properties of the titanium alloy, without destroying its bulk characteristics [3, 4]. Related studies showed that inorganic coatings can improve the wear resistance of the material by improving the surface hardness [5]. Compared to inorganic coatings, polymer coatings exhibit better biocompatibility [6, 7]. Polymer-based surface modification is a very promising method to reduce friction for the application of artificial implants. Xiong et al stated that micro-arc oxidation cooperated with grafting hydrophilic polymer form a kind of composite coating, which exhibited the low friction coefficient and favorable wear resistance [8]. Moreover, inspired by the biphasic structure of articular cartilage, the microstructure on coatings was induced. Laser texturing on surface oneself can enhance the tribological performances of Ti6Al4V alloy. At the same time, the texture structure increased the specific surface area, which is beneficial to the robust adsorption [9-11].
A porous inorganic coating surface was obtained by a two-step anodic treatment. A.I. Costa found that the tribo-corrosion behaviors can be improved [12]. Further, considering the soft phase of articular cartilage, Aosong Li fabricated a thin PTFE layer on top of a porous TiO$_2$ coating on titanium alloy. The PTFE layer ensures low friction and the underlying porous oxide provides the desirable wear resistance [13]. The biphasic structure consisting of soft and hard substances provide both high load bearing and low friction. However, for the application in vivo, there are still a lot of things need to be explored, such as the influence of surface bionic structure, the feature matching of various materials and the cooperation mechanism of each other.

In this study, the Ti6Al4V surface was pretreatment by chemical etch to obtain bionic structure, then the PVSNa coating was grafted to the etched surfaces. The comparison tribological experiments were performed under the same condition except for the stress. The influence of bionic structure on the stability of Ti6Al4V surface bearing capacity was investigated. The novel collaborative mechanism of bionic structure and PVSNa for the low friction and high bearing capacity was explored. The proposed bionic coating modification strategy for titanium alloy will be the theory guide for the implants anti-wear improvement.

2. Materials and Methods

2.1 Materials
PVSNa (97%) was purchased from Sigma Aldrich (St. Louis, Missouri, USA). PBS was provided by J&K Chemicals. Goodfellow, Inc (Cambridge, England) supplied the Ti6Al4V foils (100 mm × 100 mm × 1 mm). Before chemical etching, the cut titanium substrates (10 mm × 10 mm) were polished to mirror surfaces (Ra ≈ 2 nm). PTFE balls (D ≈ 6 mm) were purchased from Taobao, Inc. The average roughness of the balls is about 280 nm. Oxalic acid (98%) was provided by Energy Chemical. All reagents mentioned above were used as without purification.

2.2 Preparation and characterization of bionic structure on surface
The bionic structure of Ti6Al4V surface was obtained by chemical etching. Oxalic acid and deionized water were prepared in a ratio of 1:10 for oxalic solution. The prepared oxalic acid solution was heated to 50°C and bare Ti6Al4V was immersed in the solution for 5 hours. Then taking it out and washing with a lot of deionized water. After drying, it was put into the petri dish for later use. The surface morphologies of the bare and etched Ti6Al4V surfaces were observed by field-emission scanning electron microscopy (Gemini SEM 300). X-ray diffraction (XRD, Bruker D8 Advance) with Cu Kα radiation over the 2θ range of 15-60° was used to determine the phase of the bare and etched Ti6Al4V surfaces.

2.3 Methods of the formation of PVSNa coating and characterization
PVSNa coatings were prepared based on the method of evaporating self-assembly horizontally. The pretreated foils were placed horizontally into a PTFE mold with square grooves (10.2mm×10.2mm×10mm). Right amount of PVSNa aqueous solution was injected into the mold. The pretreated Ti6Al4V substrates with physically adsorbed PVSNa coatings were obtained after evaporating the solvent at 50°C for 30h in air. Lastly, after heating samples at 240°C for 6h, the PVSNa coatings were robust tethered onto the pretreated Ti6Al4V surfaces.

The morphology of the PVSNa coating was observed by field-emission scanning electron microscopy (Gemini SEM 300). EDS dark-field (HAADF) imaged in an aberration-corrected scanning transmission electron microscope operated at 300 kV.

2.4 The evaluation of tribological properties evaluated by Universal micro-tribometer
A universal micro-tribometer (UMT-3, BRUKER) was applied to test the tribological behaviors of the bare and etched Ti6Al4V, and the PVSNa-modified etched Ti6Al4V, using the lubricant of PBS. Another tribo-pair, PTFE ball, was used to rub against Ti6Al4V. The reciprocating movement mode was chosen.
Temperature during the sliding experiment was controlled at 37°C considering human body temperature. The average sliding speed used was 12 mm/s.

2.5 Microscopic Observation of Surface Morphology after Sliding
The surface morphologies of the wear scars and scratches after sliding were observed using a stereo light microscope (BX53M, OLYMPUS, Tokyo, Japan). Before each test, the tribo-pairs were washed using PBS. The magnification of sample surfaces was 100 times. The tests were repeated at least thrice for each group.

3. Result and Discussion

3.1 The influence of bionic structure on the stability of Ti6Al4V surface bearing capacity
Related study showed that the bionic structure on the surface of the material can make the material acquire the ability of self-repair, which can effectively reduce the friction and wear of materials [13]. In this study, the contribution of bionic structure to the stability of Ti6Al4V surface bearing capacity was further explored. The bionic structure on Ti6Al4V surface was obtained using oxalic acid etching. Surface morphologies of bare and etched Ti6Al4V were examined using SEM, as shown in Figure 1. Compared with bare Ti6Al4V (Figure 1(a)), the etched Ti6Al4V surface obtained obvious bionic structure, as shown in Figure 1(b).

Friction experiments were carried out using the UMT to study the tribological properties of bare and etched Ti6Al4V surfaces. The friction experiments were performed in the reciprocating mode with different loads at 37 °C. Bare/etched Ti6Al4V and PTFE balls were sampled as tribo-pairs. The reciprocating frequency was 2 Hz, which corresponds to a sliding speed of 12 mm/s. PBS was used as the lubricant. The tribological properties of bare and etched Ti6Al4V surfaces were shown in Figure 2 and 3, respectively. For bare Ti6Al4V, when the applied load was 2.5N, which corresponds to a stress of 22 MPa, the friction coefficient was only 0.016. When the applied load was 5N, the friction coefficient reached 0.063. Compared with 2.5N, the friction coefficient at the load of 5N increased obviously. When the loads were 10N, 20N and 40N, the corresponding friction coefficients were 0.068, 0.078 and 0.085, respectively. With the increase of stress, the corresponding friction coefficient showed a trend of increase. The results of the width of scratches on bare surfaces were shown in Figure 2(b-f). It can be seen from the friction coefficients and wear of the bare Ti6Al4V under different loads that when the applied load was 5N, which corresponds to a stress of 44 MPa, the friction coefficient and wear were obviously greater than that at the stress of 22MPa. It was believed that the bearing capacity of the bare Ti6Al4V was less than 44 MPa. The stability of Ti6Al4V surface bearing capacity was poor.

The friction coefficients of etched Ti6Al4V surfaces at different applied loads were shown in Figure 3(a). When the applied load was 2.5N, the friction coefficients of etched Ti6Al4V surface was 0.1513. As the loads increasing to 5N, 10N, 20N and 40N, the corresponding friction coefficients of etched
Ti6Al4V surfaces were 0.1213, 0.1099, 0.1028 and 0.0988, respectively. An interesting phenomenon was found that the friction coefficients of etched Ti6Al4V surfaces decreased with the increase of stress. In addition, with the increase of stress, the width of the scratches on etched surfaces decreased. When the applied load was above 10N, the scratch width was almost unchanged. The results were shown in Figure 3(b-f). It can be believed that the bearing capacity of etched Ti6Al4V surfaces was more than 40N, which corresponds to a bearing stress of more than 352 MPa.

Figure 2. Tribological properties of bare Ti6Al4V surfaces at different loads: (a) friction coefficient versus time, (b-f) wear morphologies at (b) 2.5N, (c) 5N, (d) 10N, (e) 20N and (f) 40N.
Figure 3. Tribological properties of the Ti6Al4V surface etched with oxalic acid at different loads: (a) friction coefficient versus time, (b-f) wear morphologies at (b) 2.5N, (c) 5N, (d) 10N, (e) 20N and (f) 40N.

The friction coefficients and wear trend of bare and etched Ti6Al4V showed that the surface bionic structure can increase the surface bearing capacity of Ti6Al4V by at least 16 times. The existence of bionic structure on surface can effectively increase the stability of Ti6Al4V surface bearing capacity. However, the surface bionic structure increased the surface roughness, resulting in the high friction coefficient of Ti6Al4V surfaces. Considering the excellent antifriction properties of the polymers, the PVSNa coating was further prepared on the etched surface to overcome the increase of friction coefficient caused by the bionic structure.

3.2 Synergistic effect of bionic structure and the PVSNa coating
PVSNa coatings were prepared on bare and etched Ti6Al4V surfaces, respectively. The typical microstructures of the modified bare and etched Ti6Al4V surfaces were shown in Figures 4(a1) and 4(a2). It can be found that the surface morphologies of the bare Ti6Al4V before and after modification were similar. The etched Ti6Al4V surface was smoother after modification and the bionic structure
disappeared. The elemental distributions of modified bare and etched Ti6Al4V surfaces were investigated by EDS, as shown in Figures 4(b1)–(f1) and Figures 4(b2)–(h2). The atomic percentage of modified surface elements were shown in Table 1. For the modified etched Ti6Al4V surface, the appearance of Na and S elements indicates that the PVSNa coating was formed on the surface. In addition, the near disappearance of Ti, Al and V elements confirmed the success of PVSNa coating preparation as well. However, the typical elements S and Na of PVSNa did not appear on the surface of the modified bare Ti6Al4V, indicating that PVSNa had not been successfully modified on the bare Ti6Al4V surface or that the coverage of PVSNa on the bare Ti6Al4V surface was very low.

Table 1. The atomic percentage of modified surface elements

| Atomic percentage | Ti   | Al   | V     | O     | C    | S    | Na   |
|-------------------|------|------|-------|-------|------|------|------|
| modified bare Ti6Al4V | 80.45 | 9.34 | 3.47  | 6.74  | 0    | 0    | 0    |
| modified etched Ti6Al4V | 0.08  | 0    | 0     | 45.38 | 26.21| 14   | 14.33|

PVSNa can be prepared on etched Ti6Al4V surface better than that on bare surface, which may be due to the change in the composition of surface oxides during chemical etching. In previous study, it has been proved that oxide layer can be used as the intermediate connecting layer, which enables the organic layer to be better connected with the substrate [1]. XRD analysis was carried out to further determine the state of the composition of bare and etched Ti6Al4V surface oxides. The representative XRD patterns of the surface oxides were shown in Figure 5. The ingredients of oxides on the bare and etched surfaces were the same. This indicated that the etching process does not change the surface oxide composition of Ti6Al4V.
Friction experiments under different loads were carried out to study the antifriction properties of PVSNa coating and the influence of bionic structure on the bearing capacity stability of PVSNa coating. The friction results were shown in Figure 6. Under applied loads of 2.5N, 5N, 10N, 20N and 40N, the friction coefficients of PVSNa coatings were 0.0658, 0.0460, 0.0245, 0.0212 and 0.0200, respectively. Compared with etched surfaces, the friction coefficient of PVSNa-modified etched Ti6Al4V was greatly reduced under the same load. Besides, with the increase of stress, the friction coefficient of the PVSNa coating decreased.
friction coefficient, which was consistent with Li [13].

Figure 7. The synergistic action of bionic structure and the composite coating on friction.

4. Conclusion
The bionic structure and PVSNa coating were designed and fabricated on the Ti6Al4V surface. The synergistic regulation mechanism of the bionic structure on surface and the PVSNa coating in terms of antifriction and high stability of bearing capacity were studied and analyzed. The results showed that the bionic structure on Ti6Al4V surface can effectively improve the stability of the Ti6Al4V surface bearing capacity. The synergistic effect of the bionic structure on surface and the PVSNa coating was able to maintain a low friction coefficient at a high stress exceeding 352MPa. This study provides insights for the design and preparation of coatings with low friction and high load bearing capacity.

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Reference
[1] Zhang C X, Liu Y H, Wen S Z, Luo J B 2014 Colloid Surface A. 447 51-58
[2] Zhou Z Y, Liu X B, Zhuang S G, Yang X H, Wang M, Sun C F 2019 Appl. Surf. Sci. 481(Jul.1) 209-218
[3] Liu Z F, Liu M M, Liu Y, Zhang C X, Wang X Z, Ma L R, Cai H Y, Cheng Q 2020 Appl. Surf. Sci. 521 146364
[4] Fioek A, Zimowski S, Kopia A, Sitarz M, Moskalewicz T 2020 Metall Mater Trans A. 51 4786-4798
[5] Wang S, Liao Z H, Liu Y H, Liu W Q 2015 Mater Chem Phys 159 139-151
[6] Xiong D S, Deng Y L, Wang N, Yang Y Y 2014 Appl. Surf. Sci. 298 56-61
[7] Liu M M, Liu Z F, Chen J M, Jiang L, Zhang C X, Li X Y 2021 Appl Sci-Basel 11 416
[8] Wang K, Xiong D S 2018 Mat Sci Eng C-Mater 90 219-226
[9] Sadeghi M, Khazrazi M, Salimijazi H R, Tabesh E 2019 Surf. Coat. Technol. 362 282-292
[10] Zhao X, Liu H, Li S, Wang X, Sheng Y, Zhang P, Li W 2020 J. Alloys Compd. 842 155750
[11] Wang K, Xiong D S, Deng Y L, Niu Y X 2017 Mater. Des. 114 18-24
[12] Costa A I, Sousa L, Alves A C, Toptan F 2020 Corros Sci 166 108467
[13] Li A, Su F H, Chu P K, Sun J F 2020 Appl. Surf. Sci. 515 146065