

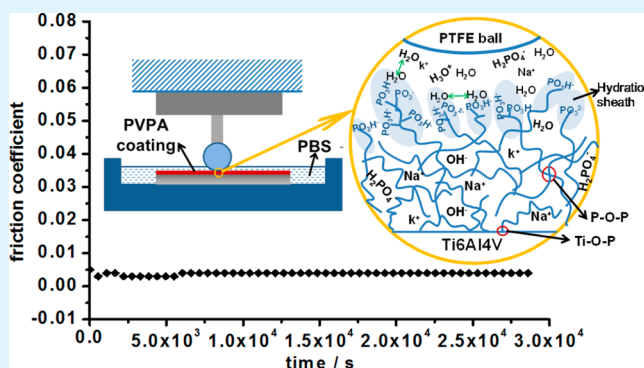
# Poly(vinylphosphonic acid) (PVPA) on Titanium Alloy Acting as Effective Cartilage-like Superlubricity Coatings

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**ABSTRACT:** Poly(vinylphosphonic acid) (PVPA) is a type of hydrophilic polymer that can be used in surface modifications. In our study, PVPA coatings were formed on the surfaces of titanium alloy (Ti6Al4V) using a simple and novel method to achieve efficient lubrication at friction interfaces. The composition and 3D skeletal structure of the PVPA coatings were confirmed by X-ray photoelectron spectroscopy (XPS), focused ion beam/scanning electron microscopy (FIB/SEM), and solid-state nuclear magnetic resonance (NMR). The PVPA-modified Ti6Al4V/polytetrafluoroethylene (PTFE) interface shows a superlow friction coefficient (approximately 0.006) for at least 8 h under a contact pressure of 44.2 MPa (initial pressure), which means it falls into the superlubricity regime. Moreover, wear on the surfaces of both the Ti6Al4V and PTFE after the tribological experiment is superlow. It is proposed that the 3D skeletal structure of the PVPA coating and fluid-like manner at friction interfaces owing to the fast exchange of water molecules are the main factors accounting for the superlow friction and wear. The PVPA-modified Ti6Al4V has the potential uses in artificial cervical discs.

**KEYWORDS:** poly(vinylphosphonic acid), surface modification, Ti6Al4V, superlubricity, superlow wear



## INTRODUCTION

Intervertebral discs are susceptible to degenerative diseases, especially in middle-aged and elderly people. Although cervical total disc replacement has been introduced as a possible treatment, the potential for complications induced by wear debris can cause the failure of the replaced cervical disc replacements.<sup>1,2</sup> Improving the tribological properties of artificial cervical discs will greatly increase their stability and service life. Surface modifications<sup>3,4</sup> by coatings and physical adsorption of proteins on metallic surfaces<sup>5–7</sup> will improve the discs' tribological properties without compromising the bulk mechanical properties.

It is well-known that human synovial joints display excellent tribological properties, with friction coefficients of less than 0.003,<sup>8</sup> despite their water-based lubricants. Their particularly efficient lubrication is related to a synergy between the network-like structure of the articular cartilage coating and hydrophilic macromolecular polymers that may be present on the outer surfaces of the coating.<sup>9–11</sup> Moreover, it has been proposed that highly hydrated macromolecular polymers attached to surfaces play a major role in the extremely efficient lubrication observed in living joints.<sup>12–14</sup> Thus, surface modifications by polymers<sup>15,16</sup> have attracted a lot of attention in efforts to tailor and control interfacial properties such as friction. Research about reducing friction coefficients by modifying surfaces with hydrophilic polymers or polyelectrolytes was widely reported. Klein et al. tailored mica sheets with brushes of poly[2-(meth acryloyloxy) ethyl phosphorylcholine]

(pMPC)<sup>17</sup> and obtained an extremely low friction coefficient (0.001) at mean pressures of up to 7.5 MPa in aqueous media using a surface force balance (SFB), resulted from the influence of highly hydrated phosphorylcholine-like monomers on the pMPC chains.<sup>18</sup> Kyomoto et al. proved that a pMPC-modified Co–Cr–Mo/cross-linked polyethylene interface showed a low friction coefficient of about 0.01 on a pin-on-plate machine.<sup>19,20</sup>

With excellent frictional properties, however, most hydrophilic polymers are fabricated on surfaces using very complex methods.<sup>21</sup> The typically used “grafting from” approach requires the presence of an initiating species on the solid surface. Chains of the polymer can then be grown from the initiating species immobilized on the surface, such as surface-initiated atom transfer radical polymerization.<sup>17,22–24</sup> In another method, which is known as “grafting to”, polymers are first synthesized with reactive end groups. These ready-made polymers can then react with the functional groups of the substrate.<sup>25–28</sup> However, complex experimental procedures in the “grafting from” and “grafting to” methods increase the difficulty of experiments, and can also result in low density or poor uniformity of the polymer coatings. Therefore, a simpler technique is needed to modify surfaces with hydrophilic polymers, and may help to improve the coating quality.

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It is widely accepted that phosphate groups have a strong affinity to many metal surfaces, including titanium and aluminum.<sup>29–32</sup> PVPA is a kind of macromolecule having a high density of phosphate groups on a polymer backbone. PVPA shows good biocompatibility in the human body, and there has been a good deal of PVPA research reported in the medical community.<sup>33–36</sup> Moreover, phosphate groups linked on PVPA show strong hydration,<sup>37,38</sup> which is a critical factor for improving tribological properties. PVPA's characteristics mentioned above might make it useful in biomaterial tribosystems. Therefore, we modified the surface of Ti6Al4V with PVPA coatings to improve its tribological properties.

In this paper, we introduced a novel and simple method for forming PVPA coatings on the surface of Ti6Al4V. Composition and structure of the PVPA coatings were then analyzed. The tribological properties of the PVPA-modified Ti6Al4V were investigated on a ball-on-disc machine. Our experimental results show superlow friction and wear in the PVPA-modified Ti6Al4V.

## MATERIALS AND METHODS

**Materials.** Poly(vinylphosphonic acid) (PVPA) (97%) was supplied by Sigma-Aldrich. The average molecular weight of the PVPA is 24 817 g/mol. Phosphate-buffered saline (PBS, PH = 7.2) was supplied by Sigma-Aldrich. Ti6Al4V (50 × 50 mm, 1 mm thickness) foils were purchased from Goodfellow, Inc. These foils were then polished using polishing slurry (Research Institute of Tsinghua University, Shenzhen) to achieve flat and smooth surfaces ( $R_a \approx 2$  nm). Polytetrafluoroethylene (PTFE) balls ( $R_a \approx 280$  nm) were obtained from Quanying, Inc. The diameter of PTFE balls is about 6 mm. All reagents mentioned above were used as received.

**Preparation of PVPA Coatings.** PVPA coatings were prepared based on the evaporation-induced self-assembly method. Polished Ti6Al4V (10 × 10 mm, 1 mm thickness) foils were placed horizontally into a PTFE mold, which was designed and constructed by the authors. A 2 mL aqueous solution of PVPA was then dripped onto the Ti6Al4V surfaces before transferring the mold into an oven. The concentration of the PVPA aqueous solution was 1 mg/mL, because that the PVPA coating formed under this concentration is stable and thick enough to mitigate direct asperity contact between the Ti6Al4V surfaces and the PTFE ball surfaces during sliding to reduce wear. The PVPA coatings were formed on the surface of the Ti6Al4V substrates after evaporating the solvent at 50 °C for 30 h in air. Lastly, the Ti6Al4V with PVPA coatings was annealed in an oven at 200 °C for 8 h. This annealing condition can make sure the formation of phosphonic acid anhydride and avoid carbonization of the PVPA molecules. Therefore, the PVPA coatings with 3D skeletal structure were formed on Ti6Al4V.

**X-ray Photoelectron Spectroscopy (XPS) for Evaluating the PVPA Coatings on Ti6Al4V.** The PVPA coatings on the Ti6Al4V samples were characterized by XPS. All XPS measurements were performed on an ESCALAB 250 XI (Thermo Scientific Instrument, USA) equipped with a monochromatized Al K $\alpha$  X-ray source. All binding energy values were calibrated against a C 1s peak at 285 eV. In addition, sputter depth profiles were performed to investigate the internal structure of the PVPA coatings. The analyzing spot was 500  $\mu$ m. The applied acceleration voltage of argon ion beam was 1000 eV. The ion beam current was 10  $\mu$ A. The PVPA coatings on the Ti6Al4V were peeled away layer by layer during the ion sputtering. Data were collected every 300 s.

**Focused Ion Beam/Scanning Electron Microscopy for Determining the Thickness of the PVPA Coatings.** To determine the thickness of the PVPA coatings, a cross section was first produced. An etching process was performed using a dual column focused ion beam/scanning electron microscopy (FIB/SEM, TESCAN Company) with a Ga ion beam. The acceleration voltage and current were set to be 30 kV and 1 nA at a normal incident angle, respectively. Before etching, an Au film (15 nm thickness) was deposited on the PVPA

surface by a Precision Etching Coating System (model Gatan 682) to increase the electrical conductivity of the PVPA coatings. Then a Pt coating was also deposited on the PVPA surface to protect the PVPA coating during etching. After etching, the etching section was polished with 100 pA current to achieve a clearer cross section. The thickness of PVPA coating was measured by SEM at last.

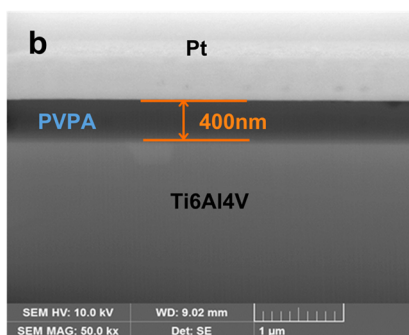
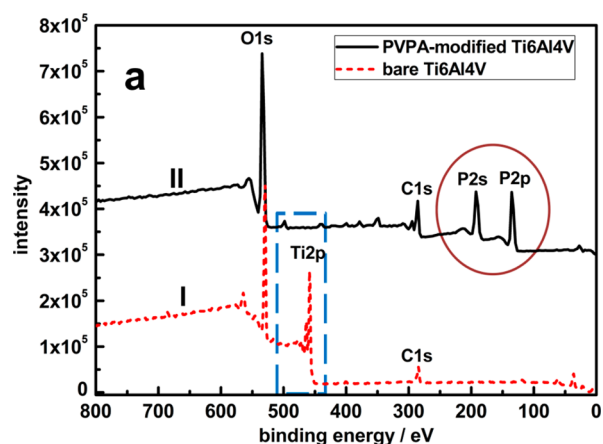
**Solid-State Nuclear Magnetic Resonance for Analyzing the Internal Structure of the PVPA Coatings.** <sup>31</sup>P magic-angle spinning (MAS) nuclear magnetic resonance (NMR) experiments were performed on a Bruker Avance III 400 MHz WB solid-state NMR spectrometer equipped with a wide variable temperature (WVT) 4 mm fast MAS double resonance probe head. <sup>31</sup>P MAS NMR spectra were obtained at an operating frequency of 161.976 MHz. The 90° pulse length and recycle delay were 3  $\mu$ s and 2 s, respectively. To investigate the cross-link among PVPA molecules in the coatings after annealing, appropriate PVPA powder was put into a crucible first. Then, the crucible with PVPA powder was heated at 200 °C for 8 h in an oven. This experimental condition can make sure that the reactions occurring in the molecules of PVPA powder and the molecules in PVPA coatings on Ti6Al4V are the same. Then, the annealed and control PVPA powder were packed into 4 mm double-bearing rotors and spun at 10 kHz.

**Universal Microtribometer for the Evaluation of Tribological Properties.** The tribological properties of PVPA-modified Ti6Al4V were characterized using a ball-on-disc machine called universal microtribometer (UMT-3, CETR). Briefly, the sliding speed was controlled by a motor underneath the disc. The load and frictional forces generated during sliding contact were measured simultaneously by a two-dimension sensor. All experiments were carried out using Ti6Al4V with or without the PVPA coatings and PTFE balls as tribo-pairs under a reciprocating movement. Temperature was controlled at 37 °C for all measurements. The average sliding speed used in our experiments was 12 mm/s, because that the motion frequency was chosen as 2 Hz (ISO 18192-1 and ASTM F2423) while the reciprocating stroke was 3 mm (nearly the same to the sliding distance of artificial cervical disc). The normal load was 2.5 N, which yielded a maximum Hertzian pressure of 44.2 MPa (initial pressure). This contact pressure is large enough to make sure that artificial cervical discs are used safely in human body. To minimize error, the down-holder was regulated carefully to ensure the same friction coefficient during the back and forth movements. All experimental results were obtained by averaging the values of at least four repetitions.

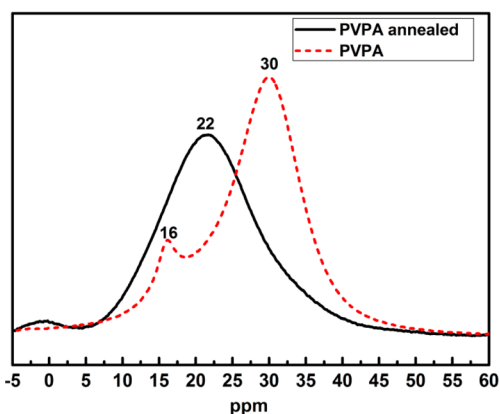
## RESULTS AND DISCUSSION

**Formation of PVPA Coatings on Ti6Al4V.** A surface coating can improve the tribological properties of titanium alloys without compromising its bulk mechanical properties. In this study, PVPA coatings were formed on the surfaces of Ti6Al4V in a novel way, and were confirmed by XPS and FIB/SEM. In addition, solid-state NMR measurement was performed to investigate the internal structure of the PVPA coatings. Figure 1a shows the XPS survey scans for bare Ti6Al4V substrates and PVPA-modified Ti6Al4V. High intensity peaks at P 2s and 2p (inside the solid circle) appear clearly on the PVPA-modified Ti6Al4V (Figure 1a II). This indicates that the PVPA coatings were successfully formed on the PVPA-modified Ti6Al4V surfaces. Besides, the Ti element (inside the dashed boxes) exists in the bare Ti6Al4V substrate but disappears in the PVPA-modified Ti6Al4V surfaces. Therefore, it can be inferred that the thickness of the PVPA coatings on the PVPA-modified Ti6Al4V is greater than the XPS detection depth.

The thickness of the PVPA coatings was investigated with the help of FIB etching. Figure 1b is an SEM image that displays the cross section of the PVPA-modified Ti6Al4V. The dark gray layer in Figure 1b is the PVPA coating, which has a



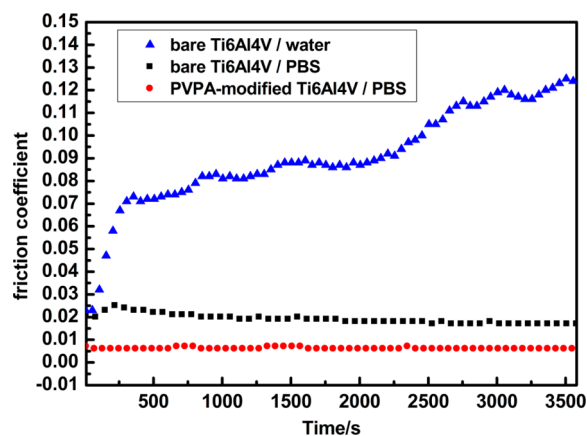
**Figure 1.** (a) XPS survey scans of (I) bare Ti6Al4V, (II) PVPA-modified Ti6Al4V; (b) thickness of the PVPA coatings measured by FIB/SEM.



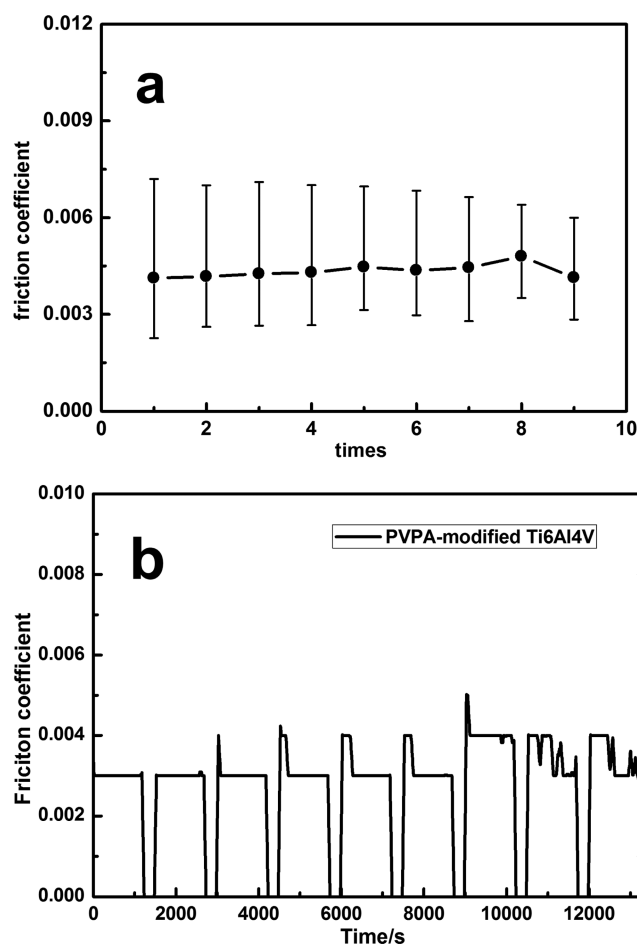
**Figure 2.** Room temperature  $^{31}\text{P}$  NMR spectra of PVPA before (dash line) and after 8 h annealing at 200 °C (solid line).

thickness of approximately 400 nm. However, because the sample stage was inclined  $55^\circ$  during measurement, the actual thickness of the PVPA coating was approximately 490 nm.

In our study, the length of a PVPA molecule is only about 50 nm, so the coatings (490 nm thick) are composed of more than one layer of molecules. The cross-link, which was formed during annealing treatment, among PVPA molecules in the coatings was explored by MAS NMR measurement. The  $^{31}\text{P}$  MAS NMR spectra of original PVPA powder before and after annealing at 200 °C for 8 h are shown in Figure 2. The spectrum of normal PVPA (without heating) shows the main peaks at 30 ppm, which is attributed to the resonance of the phosphate groups in the PVPA.<sup>33,39</sup> Moreover, a peak also appears at 16 ppm due to the residual monomer complex,<sup>33,39</sup>



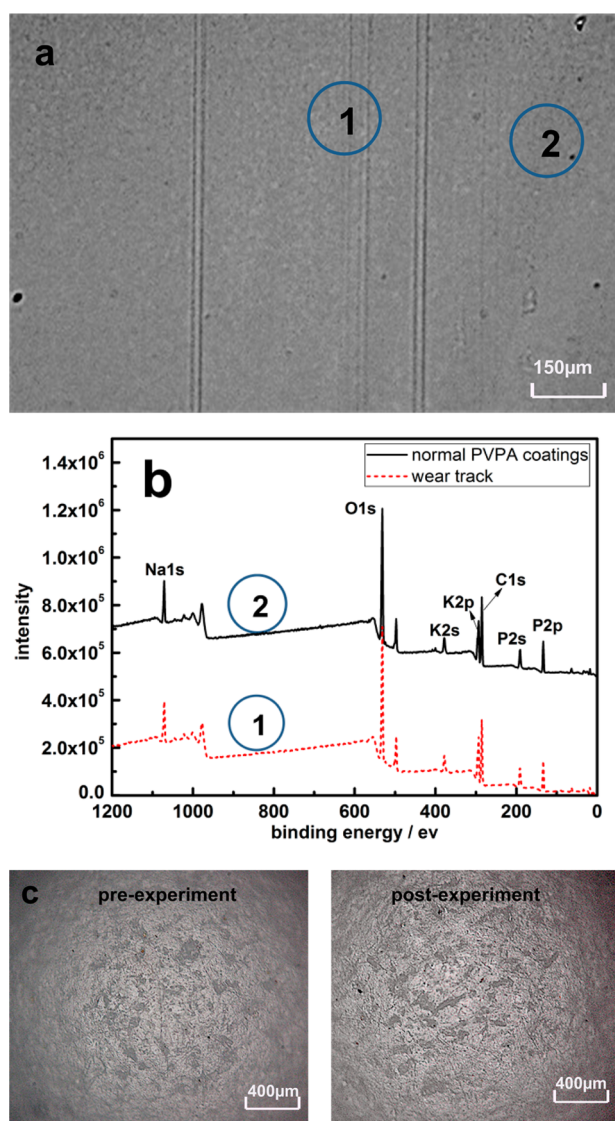
**Figure 3.** Variations of the friction coefficient versus time for the bare Ti6Al4V and PVPA-modified Ti6Al4V samples.



**Figure 4.** (a) Variations of the average friction coefficient for PVPA-modified Ti6Al4V of nine on and off experiments; (b) friction coefficient versus time plots of the whole experiment.

because the PVPA used in our experiment is not 100% pure (approximately 97%). After annealing at 200 °C, only one distinct resonance peak at 22 ppm can be found, which is commonly assigned to the phosphonic acid anhydride.<sup>40,41</sup> Thus, it is certain that annealing during formation of the coating leads to condensation between two phosphonic acid groups and the formation of phosphonic acid anhydrides. Interchain condensation<sup>42</sup> ensures that different PVPA

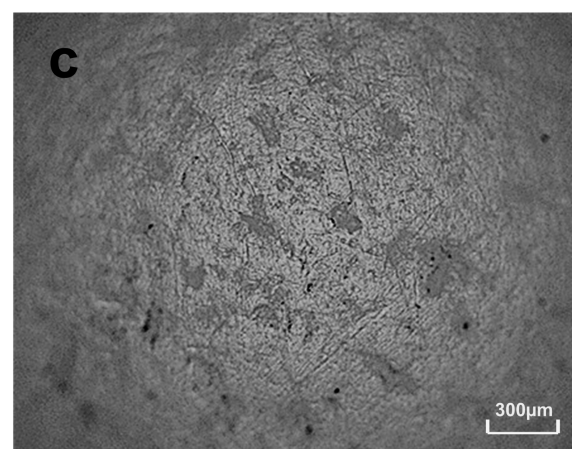
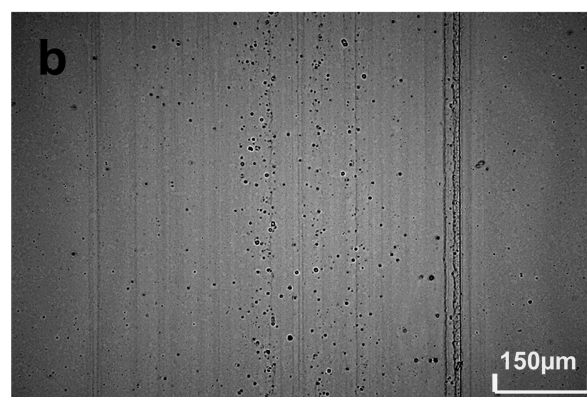
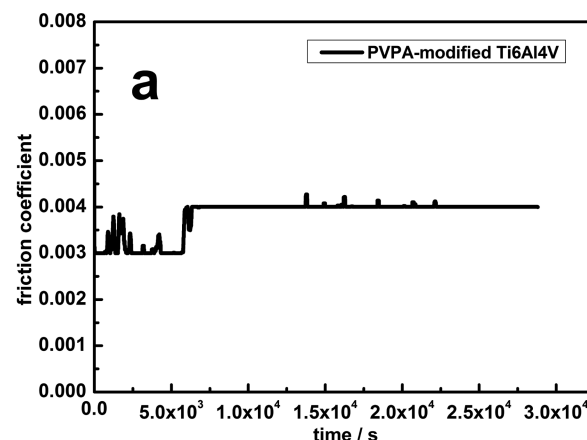




**Figure 5.** (a) Wear track on the PVPA-modified Ti6Al4V; (b) XPS survey scans of the normal PVPA coatings and the wear track, respectively; (c) topographies of the PTFE balls before and after the tribological experiment.

molecules are cross-linked by the phosphonic acid anhydrides. In fact, some unreacted phosphate groups exist in the annealed PVPA coatings. Therefore, the  $^{31}\text{P}$  MAS NMR spectrum of the annealed PVPA powder is asymmetric. However, the small number of unreacted phosphate groups cannot influence the cross-link among PVPA molecules through phosphonic acid anhydrides because that every PVPA molecule contains a lot of phosphate groups. In addition, it has been well confirmed that phosphonic acids can be linked to titanium alloy through Ti–O–P<sup>43,44</sup> due to the chelating properties of the phosphate groups to the titanium. These two characteristics described above indicate that all the PVPA coatings are attached to Ti6Al4V substrates by covalent bonds, which confirms the stability of the PVPA coatings.

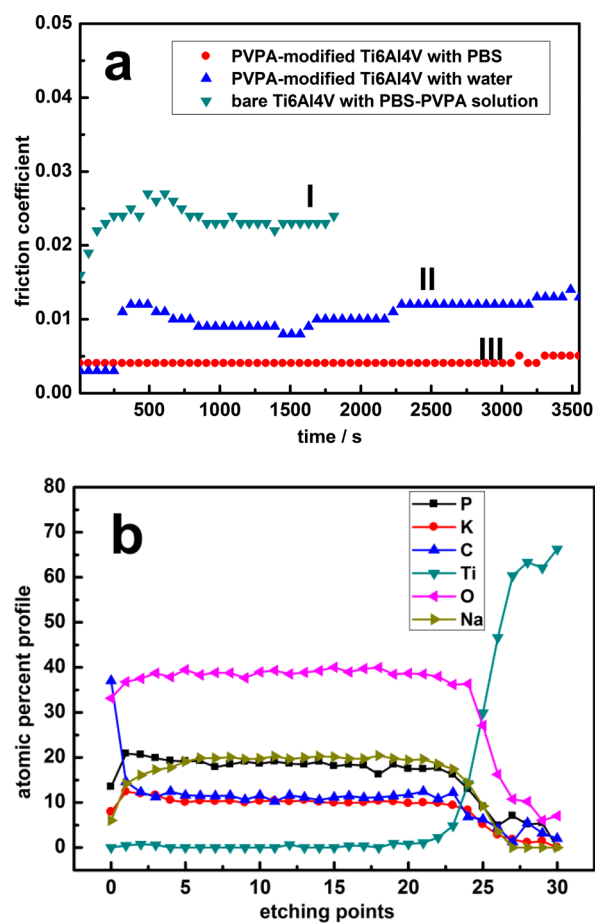
**Superlow Friction Coefficient (Superlubricity) of the PVPA-Modified Ti6Al4V.** The tribological behaviors of both the PVPA-modified and the bare Ti6Al4V were evaluated using the ball-on-disc equipment. The variation curves of friction coefficient versus time for the PVPA-modified and the bare



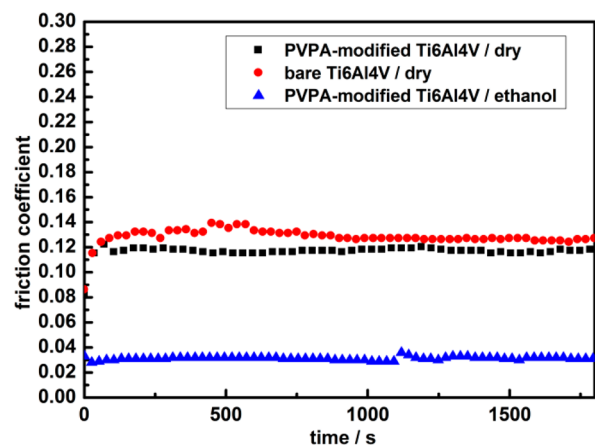
**Figure 6.** (a) Variations of the friction coefficient for the PVPA-modified Ti6Al4V over the 8 h period; (b) wear track on the PVPA-modified Ti6Al4V; (c) wear scar on the PTFE ball.

Ti6Al4V are shown in Figure 3. Compared with the bare Ti6Al4V substrates, PVPA-modified Ti6Al4V shows a significant reduction in its friction coefficient throughout the experiment. This very low friction coefficient for the PVPA-modified Ti6Al4V (about 0.006) represents a 70% decline. This phenomenon, typically called superlubricity, is a special characteristic of natural human joints and is what researchers try to achieve in artificial joints.

The superlow friction coefficient for the PVPA-modified Ti6Al4V suggests an important role of PVPA coatings in reducing the friction coefficient. In our system, every PVPA molecule contains a high concentration of phosphate groups, which display strong hydration properties.<sup>37</sup> It is assumed that



**Figure 7.** (a) Variations of the friction coefficient for the PVPA-modified Ti6Al4V and bare Ti6Al4V; (b) variations in relative contents for different elements during XPS depth profiling.



**Figure 8.** Variations of the friction coefficient for the PVPA-modified Ti6Al4V under dry conditions and using ethanol as lubricant; and bare Ti6Al4V under dry conditions.

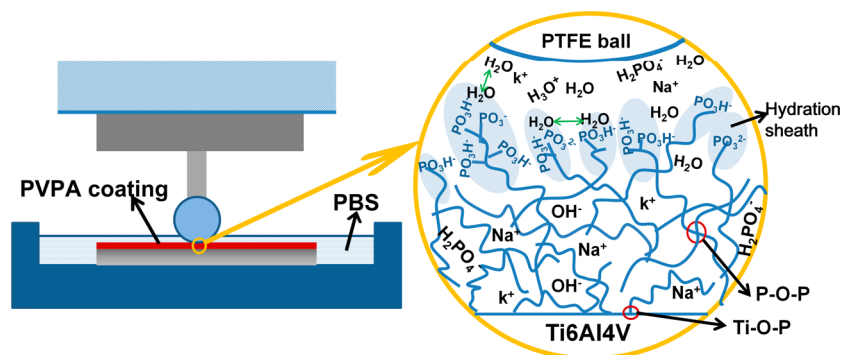
hydration sheaths may be formed around PVPA molecule chains that stretch outward from the surface of the PVPA coatings. Nevertheless, water molecules trapped in these hydration sheaths are not immobile. They are exchanged quickly with other hydration or free water molecules.<sup>18,45</sup> The water molecules in the hydration layers maintain a fluid-like manner at the interface, which increases the lubricity in the contact region. It needs to be pointed out that some protons in

PVPA will be ionized<sup>46,47</sup> and bond with water molecules to form  $\text{H}_3\text{O}^+$ . Therefore, in fact, the hydration layers contain  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$ . Their fast movement at the interface improves the lubricity in the contact region. In addition, PBS is used as a lubricant in the experiment. The hydrated salt ions in PBS can support the boundary lubrication.<sup>48</sup> When bare Ti6Al4V substrates are lubricated by PBS, the friction coefficient is about 0.02, which is lower than the friction coefficient of bare Ti6Al4V using water as a lubricant, as shown in Figure 3. Besides, PTFE, which only consists of carbon and fluorine, is very hydrophobic. The adhesive force between the PTFE and the PVPA coatings is extremely small, which may also partly contribute to the superlubricity.

The superlubricity of the PVPA coatings is surely exciting. Because natural human joints do not move all the time in the body, quick starts and stops occur regularly. Therefore, in our experiment, the same area of the PVPA coatings was rubbed on and off. The average friction coefficients for all repetitions are superlow and almost unchanged, as shown in Figure 4a. In the first experiment, the average friction coefficient was approximately 0.004. Then the upper holder was lifted up to separate the two counter surfaces. Five minutes later, the same experiment was performed for another 20 min without making any other changes (the same PTFE ball and the same area of PVPA coatings). A superlow average friction coefficient of approximately 0.004 was also obtained in the second experiment. This process was repeated nine times. The average friction coefficient remained almost the same. In addition, Figure 4b shows the plots of friction coefficient versus time of the whole experiment. The friction coefficient is stable in every repetition. Therefore, it can be said that the PVPA coatings are very stable. The superlow friction coefficient and high stability of the coatings are vital for artificial implants, which require good stability for long-term use in the human body.

**Superlow Wear for the PVPA-Modified Ti6Al4V and PTFE Ball.** Debris is one of the major concerns of cervical disc replacement due to the implants being adjacent to neural structures. Therefore, the antiwear properties of modified surfaces are important considerations. In our research, PVPA coatings on Ti6Al4V surfaces can reduce wear not only for the Ti6Al4V but also for the PTFE. A few barely visible wear tracks on the two surfaces can be found after the tribological experiment for 2 h, as shown in Figure 5. Figure 5a depicts the surface of the PVPA-modified Ti6Al4V after the tribological experiment. Only a few shallow scratches can be detected along the sliding direction. Typical XPS survey scans were then collected from point 1 and point 2, respectively, after washing off residual PBS solution, as shown in Figure 5b. There is no Ti element in the spectrum of the track-area, indicating that the thickness of the remaining PVPA coating is greater than the XPS detection depth. Therefore, the PVPA coatings in the track-area were not worn through. In addition, the surface topographies of the PTFE balls before and after the tribological experiment are shown in Figure 5c. Only superlow wear on the PTFE ball can be detected.

Several reasons lead to the superlow wear for the two tribo-pairs together. One of the reasons should be the stability of the soft PVPA coatings, which cannot be sheared off easily during friction. Therefore, they can help to mitigate direct asperity contact between the Ti6Al4V surfaces and the PTFE ball surfaces during sliding. At the same time, the hydrated saline ions and the hydrated PVPA molecules chain stretching outward from the frictional interface will partly sustain normal



**Figure 9.** Presumed tribological interface between the hydrated PVPA-modified Ti6Al4V and the PTFE ball in PBS solution.

loads,<sup>18,48</sup> and are therefore capable of keeping the surfaces separated to reduce adhesive wear. Moreover, observing Figure 3 carefully, an interesting phenomenon occurs. The modified Ti6Al4V achieves superlubricity without any running-in stage, which serves to avoid severe wear on the two counter surfaces. Therefore, little wear debris is produced in our system. Without wear debris, abrasive wear will be weakened. It can be speculated that ignorable abrasive wear during sliding should also be an important reason for the extremely slight wear after the test.

The superlow wear during sliding ensures the efficient lubrication between the two surfaces in turn. Therefore, a superlow friction coefficient for the PVPA-modified Ti6Al4V can be maintained over a long period of time. Figure 6a shows the variation curves of the friction coefficient versus time for the PVPA-modified Ti6Al4V over the 8 h measurement period. The friction coefficient is superlow (approximately 0.005) and stable. Moreover, only slight wear appears on the two counter surfaces, as shown in Figure 6b,c. In other words, in our tribological system, superlow friction and wear can be realized at the same time, and be sustained for a long time.

**Mechanisms for the Superlow Friction and Wear of the PVPA-Modified Ti6Al4V in PBS.** Our results clearly show that PVPA-modified Ti6Al4V displays near-perfect tribological properties. Several factors are found to be crucial in improving the tribological properties. The first important factor is the PVPA coatings with 3D skeletal structure formed by the PVPA molecules cross-linking with each other. The free PVPA molecules dissolved into PBS cannot reduce friction like the PVPA coatings, as shown in Figure 7a I. The friction coefficient is approximately 0.02. The reasons may be that the spontaneously adsorbed PVPA molecules on bare Ti6Al4V through phosphate groups is very little and unstable. They can be sheared off easily. Therefore, direct asperity contact occurs when they slide with each other, leading to a large friction force and severe wear. However, the PVPA coatings with 3D skeletal structure, which improves the lubricity and load-bearing properties during sliding, can sufficiently avoid the direct asperity contact between the two surfaces to reduce friction.

The second important factor for the superlow friction and wear is the hydrated salt ions in PBS. Hydrated salt ions can improve the bearing capability and stability of the PVPA coatings. Therefore, when the tribological experiment for the PVPA-modified Ti6Al4V is performed in deionized water, the PVPA coatings will be damaged quickly (about 250 s) with the sharply increased friction coefficient, as shown in Figure 7a II. In fact, using PBS as the lubricant, the hydrated salt ions will seep into the gaps of the 3D skeletal structure of the PVPA

coatings during experiments. This phenomenon was proved by XPS depth profiling. PVPA-modified Ti6Al4V was immersed into PBS solution for 12 h at 37 °C. XPS depth profiling was then performed after air-drying. Figure 7b shows the variation trends for the relative amounts of different elements with increased etching depth. The variation trends for sodium and potassium that exist only in PBS are the same as those of phosphorus, carbon, and oxygen in PVPA coatings, confirming that salt ions in the PBS seep into the PVPA coatings when the tribological experiments are carried out in PBS. According to these experimental results, we speculate that when a normal load is performed on the PVPA coatings, some of the hydrated salt ions may be squeezed out to the surface of PVPA coatings, improving the boundary lubrication in the contact area. However, some hydrated salt ions are likely to be still confined in the gaps, bearing the normal load along with the PVPA coatings. These functions of hydrated salt ions improve the tribological properties in our system.

The third important factor for the superlow friction and wear is water molecules. Figure 8 shows the curves of the friction coefficient versus time for the PVPA-modified Ti6Al4V under dry friction. The friction coefficient is very high, nearly the same as the result of the bare Ti6Al4V. In fact, the PVPA coatings are peeled off quickly due to the huge friction force between the two surfaces under dry friction. Without the presence of water molecules, the fluid-like manner at the interface (produced by fast exchange of water molecules) cannot play a role in improving the lubricity in the contact region. In addition, the adhesive force between PTFE and PVPA coatings will increase without water molecules. Therefore, when using ethanol as the lubricant, the friction coefficient for the PVPA-modified Ti6Al4V is approximately 0.02 (as shown in Figure 8). The reasons may be that although the ethanol molecules can also adsorb on the PVPA coatings like water molecules, its molecular dynamics property is different from water molecules. Fluid-like manner cannot appear at the interface. Moreover, the adhesive force between PTFE and ethanol is larger than that between PTFE and water, leading to a larger friction force. In a word, water molecules play a very important role in the superlow friction and wear.

On the basis of our analysis, the likely status between two asperities in tribological interface when the tribological experiment is performed in PBS ( $\text{KH}_2\text{PO}_4$  (0.05M) and NaOH) is shown in Figure 9. The PVPA coatings with 3D skeletal structure cover the surface of Ti6Al4V. The hydrated salt ions will seep into the coatings during experiments. Water molecules trapped in the hydration sheaths around PVPA molecule chains are exchanged quickly with other hydration or



free water molecules. These characteristics mentioned above work together to achieve the ultralow friction and wear.

## CONCLUSION

PVPA coatings with a 3D skeletal structure, as confirmed by <sup>31</sup>P MAS NMR, and XPS, were successfully formed on surfaces of Ti6Al4V using a simple and novel method. The PVPA-modified Ti6Al4V displays a phenomenon of superlubricity with a superlow friction coefficient of approximately 0.006. In addition, experimental results show an almost unmeasurable wear on the two counterfaces after a period of long-term friction. The PVPA coatings with 3D skeletal structure, hydrated salt ions, and water molecules have been proved to be the main factors influencing the superlow friction and wear in our tribological system. The superlow friction and wear, along with the stability of the coatings, makes the PVPA-modified Ti6Al4V a potential material for use in artificial cervical discs.

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### Notes

The authors declare no competing financial interest.

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