The Factors of Speeds and Loads on the Tribological Properties of PVA-H/HA Composites

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ABSTRACT: Poly (vinyl alcohol) (PVA)/Hydroxy apatite (HA) composite prepared from aqueous solution of the polymer and dimethylsulfoxide (DMSO) by freezing and thawing method are developing to repair or replace articular cartilage. In the present study, the tribological behaviors of this composite were investigated in a three-factor, three-level designed experiment using an improved four-ball tester. Factors include sliding velocity, applied load, and HA content of composite. Friction coefficient of the PVA-H/HA was found to depend significantly on load and sliding velocity, while HA content had small effects on the friction coefficient of PVA-HA composite. We also found that wear loss of PVA-H/HA increased sharply with the increasing loads and HA content of specimen. Increased HA content from 0.5% to 1.5% resulted in an increasing of 355% in wear loss, while increasing sliding velocity slightly decreases wear loss of specimen. We also found some correlation between friction coefficient and wear loss of specimen under the given condition. These results may be useful in the tribological design of PVA-H/HA composite for both low wear and low friction using as artificial cartilage substitutes. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3908–3914, 2007

Key words: PVA hydrogel; HA; tribological behavior; composite

INTRODUCTION

Millions of people suffer from joint pain caused by arthritis, making it a prevalent cause of disability in the world. With arthritis, cartilage becomes severely damaged and no longer serves as a cushion or load-bearing surface between the bones in joints. This bone-to-bone contact causes long-term debilitating pain, ultimately resulting patient painful and uncomfortable.[1–4]

Many studies on articular cartilage function have suggested the important role of cartilage layer.[5,6] PVA hydrogel is a three-dimensional network hydrophilic polymer in which a large amount of water is interposed. It has been studied as possible replacement for articulating cartilage due to its highly porous structure, excellent biocompatibility, low elastic modulus, high resilient, and self-lubrication in recently years. Several studies[7–9] have been reported that PVA hydrogel exhibit some mechanical properties that are consistent with human cartilage behavior, with a strain magnitude and rate-dependent compressive tangent modulus. Biocompatibility studies by Oka and coworkers[10,11] on the PVA hydrogel resulted in no significant inflammatory reactions or degeneration in the surrounding articular cartilage and synovial membrane.

Hydroxyapatite, as a kind of natural material, has been widely used as the bioactive component of polymer material for using as bioactive implant.[12,13] It had been proved that the addition of HA accelerated the crystallization of PVA hydrogel and increased the mechanical strength of the PVA-H/HA composite.[14,15] However, there has not been a comprehensive and systematic study on the tribological behavior as a potential artificial cartilage material.

The primary goal of this investigation was to study the friction and wear behavior of PVA-H/HA composite-a class of hydrogel widely studied as possible articular cartilage substitutes. The specific objectives of this research were to carry out a three-factor, three-level designed experiment to determine the effects of applied load, sliding velocity and HA content of PVA-H/HA composite on their friction and wear behaviors.

EXPERIMENTAL

Materials

The calcium carbonate ($CaCO_3$), phosphate (H_3PO_4), dimethyl sulfoxide (DMSO), and PVA used in this study were supplied by the Sinopharm Chemical Reagent Co. Ltd., P.R. China.

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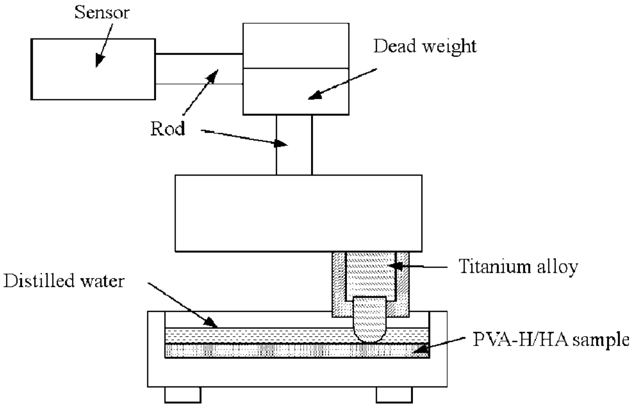

Figure 1 Sketch of tribological testing.

The PVA powder used have viscosity-average degree of polymerization (D.P.) of 1750 ± 50, with an average molecular weight of 124,000 and saponification of 99.5 mol %. The concentrations of DMSO and H_3PO_4 were 99 and 95%, respectively. The chemical substances used are analytical reagent grade.

Preparations of composites

One hundred grams of $CaCO_3$ powder was heated at 1050°C for 3 h, and the resultant CaO powder was hydrated with distilled water to produce $Ca(OH)_2$. One thousand milliliter of 0.6M H_3PO_4 were dropped into 2000 mL of 0.5M $Ca(OH)_2$ suspension, and then stirred vigorously for 5 min at room temperature. The obtained suspension was aged overnight; the final pH was adjusted to 7.5. The suspension was atomized under a pressure of 1.5 MPa with a flow rate of 500 mL/h, Then the HA particles were calcined at 1200°C for 30 min. The diameter of HA particles we obtained are about 70 nm.

Separately, several grams of these HA particle were added in 100 mL of DMSO/water (80:20) mixed solvent, ultrasonic treated was used to fully distribute the HA particles on the solution. After these processes, 15 wt % of PVA powder was dissolved in this mixed solvent under autoclave condition at 110°C for 3 h, and until well blended to prepare the viscous slurry. The PVA/HA slurry was cast in the glass vessel and kept in refrigerator at −20°C for 24 h to make PVA-H/HA composite which are the physically crosslinked hydrogel with the HA particles. All specimens were placed in distilled water for fully swelling before wear testing.

Tribological testing

The friction and wear investigation of PVA-H/HA composite were performed at room temperature in ambient atmosphere under distilled water lubrication conditions on a reformed four-ball testers (MRS-10A, Jinan Shijin Tester Company, P.R. China). A simplified sketch of the device is shown in Figure 1.

PVA-H/HA specimen was fixed on the specimen holder. Titanium alloy sphere, with average roughness of 0.12–0.16 um (measured by Hommel T8000-C roughness tester, Made in German) and diameter of 6 mm, is rotating on the surface of PVA-H/HA specimen under given velocity and applied load. Hydrogel specimen and titanium alloy sphere maintained contact at applied load for 30 s before all the friction testing and the test time is 30 min. Soft cloth was used to clean the surface of composites and titanium alloy sphere before testing.

A three-factor, three-level design experiment was conducted to determine the effects of applied load, sliding velocity and HA content on the friction and wear behaviors of PVA-H/HA composite. The variables and levels used are summarized in Table I. Two specimens were tested within each combination for a total of 30 tests.

In this article, pressure at the interface of the friction counterparts were theoretically calculated using Hertzian contact assumptions and given material properties. Loads were tested at 5, 10, and 15N, which correlated to pressures of ~ 0.43–0.97 MPa (calculated by Rennie's modeling[16]), which lie in the range typically found in human knee joints (0–2.5 MPa). The sliding velocity was varied from 0.105 to 0.42 m/s to model different human activities such as walking and running sliding velocity in the human knee.[17] Under distilled water lubrication, the specimen of PVA-H/HA works completely immersed in distilled water.

Measurement

Measurements were made of friction and wear loss for each of these tests. The friction coefficient can be calculated from $\mu = F/N$, where μ, F, and N represent friction coefficient, friction force and applied load, respectively. Friction force was the average value of the whole process. The repeatability of measurements from two specimens of each composition was good. Therefore, only averaged data were plotted without error bars to present results clearly.

PVA-H is a typical hydrated material. Part of the water in the specimens will evaporate slowly to the

TABLE I
The Three Factors, Three-Level Designed Experiment

	Low level	Middle level	High level
Load (N)	5	10	15
Velocity (m/s)	0.105	0.21	0.42
HA content (wt %)	0.5	1	1.5

atmosphere, so it is hard to measure the actual weight of specimens by photoelectric balance (accuracy is 0.1 mg). We clear the water and debris on the surface of specimens with filter paper after their preset testing time had been reached, and then put the specimens in dry Petri dishes very quickly. Comparing the total weight before and after wear testing, the weight loss of each specimen was obtained.

RESULTS

Friction coefficient

The influences of different factors on the friction coefficient of PVA-H/HA composite are shown in Figure 2. Every data in Figure 2 means the average value of friction coefficient of specimen at the various levels of each test. The results show that the apparent effects of load, sliding velocity, and HA content of composite are quite different. The average friction coefficient of PVA-H/HA composite under all factors varies from minimum value of 0.037 to maximum value of 0.094, almost increasing three times. There are significantly different influences on the average friction of PVA-H/HA composite of these three factors test. HA content has little effect on friction results. The maximum of friction coefficients of specimens are 0.055 at high HA content, just a little higher than that of specimen at low HA content. On the other hand, friction coefficient of the PVA-H/HA composite is significantly dependent on the load and sliding velocity. Friction coefficient decreased as increasing sliding velocity in our test. Applied load has the most effect on the average friction in these three factors that the average friction coefficient at high load is about two times of that at low load.

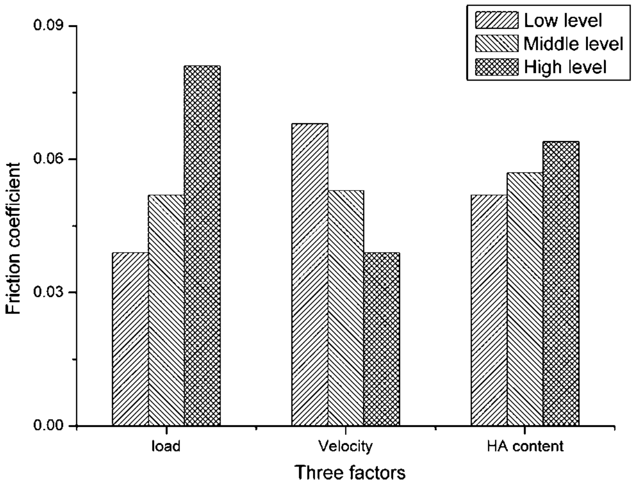

Figure 2 Main effect of the factors on friction coefficient of PVA-H/HA composite.

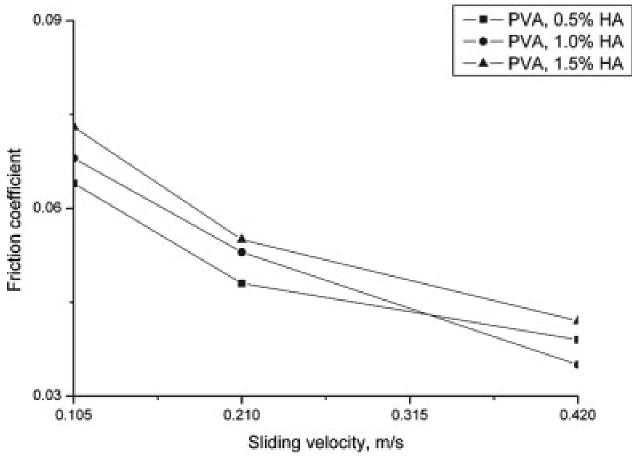

Figure 3 Effect of sliding velocity on friction coefficient.

Figure 3 shows the friction coefficient of PVA-H/HA specimens with various HA content sliding with titanium alloy at the velocity of 0.105, 0.21, and 0.42 m/s, respectively. Friction coefficient of the gel, under all friction condition, decreases continuously with the increase of sliding velocity. When the sliding velocity increases from 0.105 m/s to 0.42 m/s, friction coefficient decreases from 0.064 to 0.039 at low HA content, or from 0.073 to 0.042 at high HA content.

General trends in friction coefficient of PVA-H/HA composite at different loads are illustrated by the curves in Figure 4. It can be concluded from Figure 4 that the friction coefficient increases sharply with the increase of applied load.

Wear loss

The wear loss of the entire study varied from a low value of 4.5 mg to a high of 52 mg, a factor of over 11. Analysis of variance of the wear data showed

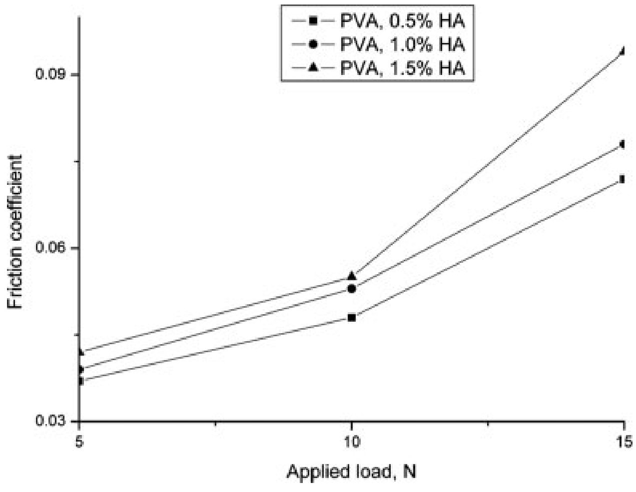

Figure 4 Effect of applied load on friction coefficient.

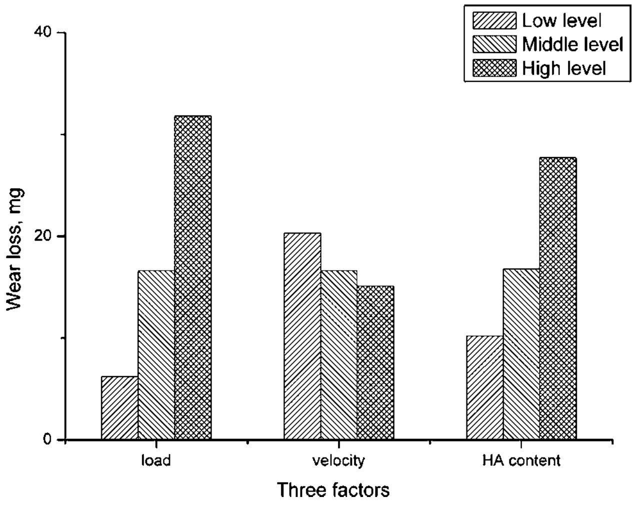

Figure 5 Main effects of the factors on wear loss of PVA-H/HA composite.

that load, sliding velocity, and HA content had significant effects on wear loss. These results are illustrated by the bar graph in Figure 5 where each bar represents the average of three data with in one of the three levels. It can be seen that on average, increasing the applied load from 5 to 15*N* results in a large increase in wear, roughly 312%. PVA hydrogel with high HA content showed a 355% increase in wear on average than that of specimen with low HA content as well. On the other hand, increase sliding velocity play a role in decreasing wear loss of specimen. HA content has the most effect on the wear loss in these three factors in our study.

Figure 6 shows the curves of wear loss versus the applied load of the composites. The sliding velocity was 0.21 m/s. As the load increases the wear loss increases as well. When the load was more than 10*N*, the wear loss began to increase rapidly. It suggests that this is a critical load value for transition from mild wear to severe wear of the materials. If the load exceeds the value, the pressure on the wear surface is so big that the surface of PVA-H/HA composite is serious destroyed and severe wear occurs. Note that wear loss of specimen with high HA content increased greatly, reflecting the effectiveness of the addition of HA particle on increasing wear loss of specimen.

Figure 7 shows the curves of wear loss versus sliding velocity. The applied load was 10*N* and tribological test was run for 60, 30, and 15 min for the same sliding distances. From this figure, it was found that as the sliding velocity increases the wear loss decreases slightly. For example, wear loss decreased from 12.4 to 9.7 mg while the sliding velocity increased from 0.105 to 0.42 m/s with 0.5% HA content. Sliding velocity does not have as strong effect on wear loss as the applied load and HA content do.

DISCUSSION

Increasing the applied load resulted in large increase in wear and friction coefficient, while increased wear velocity reduced wear as well as friction coefficient. Obviously, the tribological processes involved in this investigation are complex. The effects of applied load, sliding velocity and HA content on the tribological behaviors of PVA-H/HA composite were examined.

Figure 8 summarizes the average wear and friction coefficient data for each 15 test groups in our study. It can be seen that there are large variation in wear as well as friction coefficient. In some case, friction is high while wear is low, or friction is low while wear is high. A better way to look at these data would be to plot these average wear values against the friction coefficient, as shown in Figure 9. The first obvious

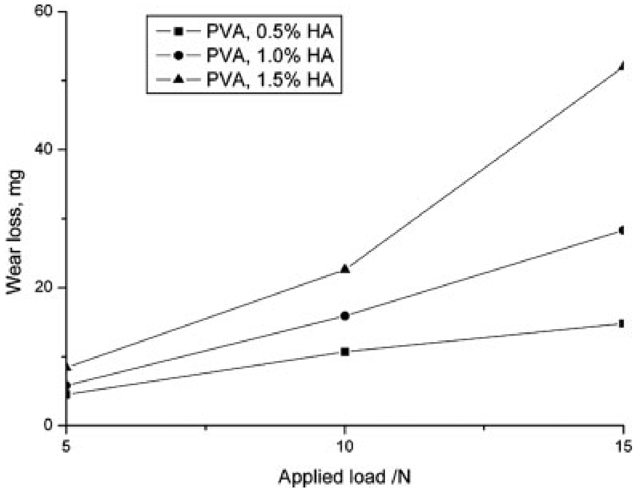

Figure 6 Effect of applied load on wear loss.

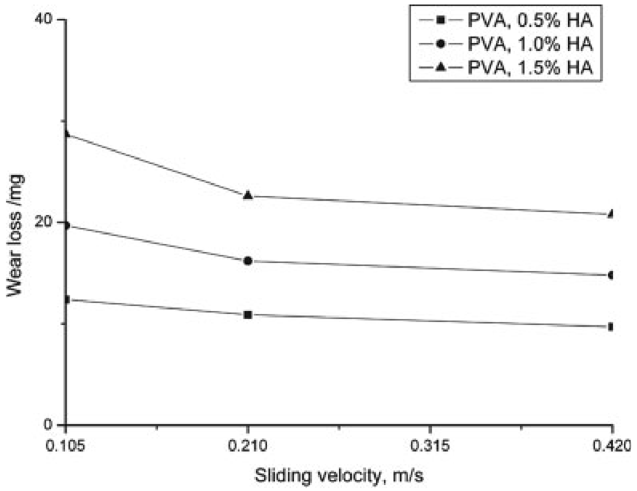

Figure 7 Effect of sliding velocity on wear loss.

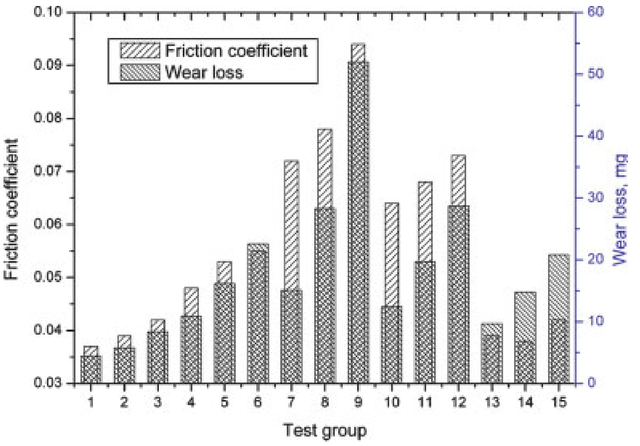

Figure 8 Average friction coefficient and wear loss for each of the 15 test groups.

TABLE II
Low Friction and Low Wear Combination

Group	Load	Velocity	HA content
1	Low	Middle	Low
2	Low	Middle	Middle
3	Low	Middle	High
13	Middle	High	Low
14	Middle	High	Middle

conclusion is that there is some correlation between the friction coefficient and wear loss. Low friction and low wear, middle friction and middle wear, high friction and high wear were observed in this figure. It should be pointed out that the data shown in Figures 8 and 9 are average values and the variation in both friction coefficient and wear loss within a pair of tests do exist. In fact, if we plots wear versus friction coefficient, the resultant figure is similar to Figure 9 and the general conclusions remain the same-showing low friction/low wear, middle friction/middle wear, high friction/high wear combinations.

However, it may be of interest to make some observations. The group producing low friction and low wear loss consists of test combinations 1, 2, 3, 13, 14, as shown in Table II. It is obviously found that three of the five favorable combinations are at the low load and middle sliding velocity, and the other two are at the middle load and high velocity. PVA hydrogel has strain lag properties under stress because of its visco-elastic characteristics, which had proved by Ansth et al. and Jason et al.[18,19] PVA-H/HA composite also shows this property in other research.[14] When the sliding velocity increased, the surface elastic deformation rate of PVA-H/HA composite lags the relative sliding velocity of titanium alloy sphere. The surface distortion of PVA-H/HA composite cannot keep up with the sliding velocity in the test. Ripple-like deformations were found on the worn surface of PVA-H/HA composite, as shown in Figure 10. The titanium alloy sphere passed the deformation region of the PVA-H/HA specimen before the deformation region forms. This causes the contact area of the friction counterpart to be smaller at higher sliding velocity, with resultant lower friction force. This results in the friction coefficient decreased with increasing sliding velocity. This phenomenon is similar to be observed other scholars on the PVA hydrogel which exhibited an increase in friction coefficient with the increase of loads.[17,20,21] At the same time, most solid materials follow Amonton's friction law, with frictional loads depending only on normal loads. The PVA-H/HA does not follow this model, showing dependence not only applied load but also sliding velocity in our tests.

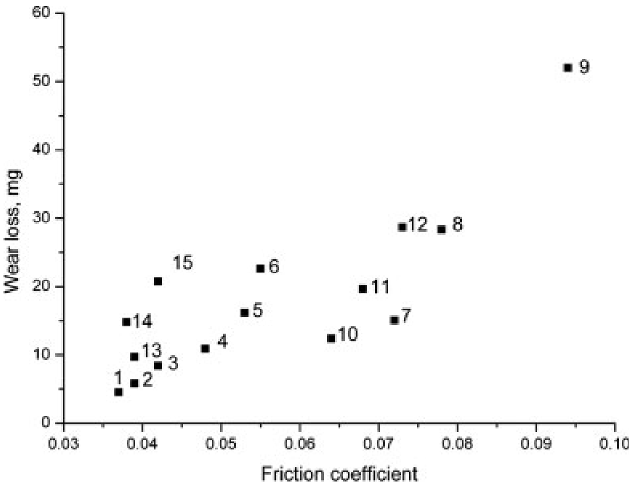

Figure 9 Average wear loss versus friction coefficient for all combinations.

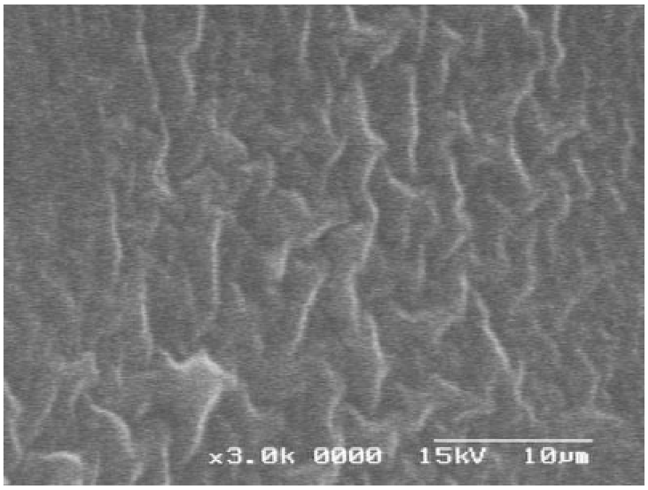

Figure 10 SEM photograph of worn surface of PVA-H/HA composite (0.5%HA, 0.42 m/s), ripple-like structure.

PVA-H is a low mechanical resistance material which easily occur deformation. The contact area and wear loss of the counterpart is proportional to applied load. The less deformation of the composite, the smaller friction force and wear loss of the friction counterpart is, due to the decreased contact area between the friction counterparts. On the other hand, the low load actually produces an extreme regime of ''boundary lubrication'' which might occur under lubrication condition. In addition, synovial liquid, which presents in articulating joint, would be expected to be superior to distilled water used in this study as for as wear in concerned. Articular cartilage has complicated lubrication modes, previously described as hydrodynamic, squeeze-film, hydrostatic, boosted or ''weeping'', and/or boundary lubrication.[22] PVA-H/HA may be found to exhibit these lubrication modes as well at low load, but this work was out of the scope of the current study.

Only combination 9 produces high friction and high wear loss. It consists of a high load, low velocity, and high HA content situation. In the wear testing, the outline peak of the harder titanium alloy disk lowed on the surface of the softer PVA-H/HA composites and formed a lot of furrows. With the increase of load, the wedge depth of the outline peak on the PVA-H/HA composite surface increased and more material was removed. This process hinders the relative movement between titanium sphere and specimen, and obviously friction coefficient increases. At the same time, the friction surface temperature rose; the specimen surface was intenerated and viscous flow occurred increasing the wear loss of the material thus forming large quantities of wear debris. Therefore, the wear loss of PVA-H/HA increased with load, resulted in middle wear (combination 11, 12, at low/middle load), and high wear (combination 9, at high load) at middle sliding velocity shown in Figure 8. The high HA content of composite is another factor contribute to the extreme high wear loss. Increasing HA content increases the chance of nano-HA particle adding into PVA matrix reunite with each other. These reunited particles act as grains between titanium alloy and PVA-H/HA composite, resulting in high wear loss of PVA-H/HA composite. This also can be proved by comparing combination 15, which produces middle wear loss under high HA content, with combination 13/14 that produces low wear loss under low/middle HA content at the same sliding velocity. Addition of HA plays an important role in increasing wear loss of specimen in this study.

Others factors, such as lubricant, material of counterpart, roughness of the counterface also influence the friction and wear behaviors, but these works were out of the scope of the current study. A limitation in this test included use of water lubrication and a counterface of titanium alloy instead of articular synovial fluid and cartilage/bone, respectively. Future work will include testing at articular synovial fluid to determine what other factors may play a role in determining the tribological behaviors of this biphasic, visco-elastic biomaterials.

It also should be noticed that we could not make extrapolations from this ''*in vitro*'' titanium alloy-on-hydrogel situation (water lubrication) to a vastly more complex ''*in vivo*'' cartilage-on-hydrogel system. Additional studies of each type would be necessary to fully evaluate the performance of these hydrogels as synthetic articular cartilage.

CONCLUSIONS

This article presents an experimental study on the tribological properties of PVA-H/HA composite against titanium alloy

1. Friction coefficient of the PVA-H/HA was found to depend significantly on applied load and sliding velocity. HA content has small effect on the friction coefficient of PVA-HA composite.
2. Wear loss of PVA-H/HA composite is positively proportional to loads and HA content of specimen. Increasing sliding velocity slightly decreases wear loss of specimen. Although different factors play different role on the tribological behavior of specimen, wear loss and friction coefficient show similar trend.
3. The overall study demonstrates the complexity of tribological processes involving PVA-H/HA composite even in an ''*in vitro*'' more easily controlled experimental situation.

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