



## The Effect of Preparation Methods on Tribological Properties of PVA-H/HA Composites

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### ABSTRACT

**N**ano hydroxyapatite (HA) is a potential artificial cartilage material. To study its friction and wear properties, nano hydroxyapatite (HA) particles filled with polyvinyl alcohol hydrogel (PVA-H) composites were slid against a stainless steel disk under water lubrication condition using an improved four-ball tester. The worn surfaces were investigated by using a scanning electron microscope (SEM) to determine the wear mechanisms of pure PVA-H and PVA-H/HA composites prepared by different methods. Experimental results show that the addition of HA slightly decreases the friction coefficient of composites with the increase of HA content under water lubrication condition. The wear resistance of the PVA-H matrix was also improved by the introduction of HA inorganic component. It was also found that the PVA-H/HA composites prepared by in situ synthesis have better tribological properties than the composites prepared by mixed method with the same components and test conditions. The SEM photos show that the wear mechanisms of PVA-H/HA composite prepared by the mixed method with high HA content showed abrasion and adhesion, while that of the composite prepared by in situ synthesis was slightly scratched and fatigued. These results may be useful in the tribological designs for artificial articular cartilage material.

### Key Words:

PVA-H;  
tribology;  
composites;  
in situ synthesis;  
ultrasonic mix.

### INTRODUCTION

The main function of articular cartilage is to serve as the soft bearing of the diarthrodial joint while transmitting large loads, reducing friction coefficient and wear loss [1,2]. Experimental studies have proved that articular cartilage has very low friction coefficient (0.002-0.02) upon loading, which is favourable

for maintaining the high wear resistance of the soft tissue [3]. The lifespan of the average articular cartilage is approximately 70 years; in some rare cases it could be more than 100 years.

Joint replacement has improved for the last 70 years, but many problems yet to be solved, such as

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severe wear and osteolysis. Polyvinyl alcohol hydrogel (PVA-H) is widely used in biomedical fields, such as soft tissue replacement, drug delivery, and hemodialysis membranes for its excellent biocompatibility [3,4]. There has been an attempt recently to develop durable artificial cartilage layer on the artificial joint using PVA-H. However, some disadvantages, such as poor mechanical and tribological properties, should first be overcome. Researchers have made great efforts to reinforce its related properties [5-9]. Many new methods, such as the physical cross-link method and chemical cross-link method, have been invented to increase its mechanical strength and tribological properties. Hyon et al. [3] reported a gelation process using an aqueous solution of dimethylsulphoxide (DMSO) and PVA-H. This process has been claimed to produce PVA-H with improved mechanical properties. However, available information on the tribological properties of such PVA-H is limited.

It is well known that the tribological properties of polymers can sometimes be improved by filling them with inorganic components. Researchers have proved that the wear resistance of filled polymers is related to the load-carrying action of fillers [10]. Hydroxyapatite (HA), an important biocompatible inorganic material with composition similar to bones and teeth, have been widely studied in inorganic/organic composite [11,12]. Therefore, the composition of nano-HA and PVA-H to prepare PVA-H/HA composites not only improves the mechanical properties of the composites but also endows them with excellent bioactivities. In a previous study we found that this composite can form bone-bonding with natural tissues through osteo-conduction mechanism [13]. The mechanical properties of PVA-H/HA composites have also been studied for use as an artificial blood vessel. However, there have been few studies in the past on the tribological properties of PVA-H/HA, the most important properties of biomaterials used for artificial joints.

In this paper, a series of composites, which utilizes a high viscoelastic PVA-H as the matrix and a high strength and biocompatible HA particles as the reinforcement, were prepared with different HA contents by ultrasonic mixed method and in situ synthesis, respectively. The relationship among the contact

pressure, HA content, and synthesis method of composites are studied and analyzed. The wear mechanism of PVA-H/HA composites was explored by using scanning electron microscopy (SEM) to examine their worn surfaces. The effects of HA filled by different methods on the tribological properties are studied and compared. It is expected that this study may be useful to the application of the PVA-H synthesized with HA particles for artificial articular cartilage.

## EXPERIMENTAL

### Materials

Calcium hydroxide, phosphoric acid, dimethylsulphoxide (DMSO) and PVA powders used were supplied by the Sinopharm Chemical Reagent Co. Ltd, PR China. The PVA powder used had viscosity-average degree of polymerization (DP) of  $1750 \pm 50$ , with a saponification of 99.5 mol%. The concentration of DMSO,  $\text{Ca}(\text{OH})_2$  and  $\text{H}_3\text{PO}_4$  were 99%, 95%, and 95%, respectively. All chemical substances were of analytical reagent grades. Nanoscale hydroxyapatite (HA) fine powders in a diameter of approximately 70-80 nm, produced by our laboratory, were used in this investigation.

In order to study the influence of the synthetic method, two different prepared methods were used in our investigation.

### Methods

#### *1- Ultrasonic Mix Method*

First, 0.2 g HA was added into 20 g distilled water and ultrasonically treated for 5 min to form a mixed solution. DMSO was added to form a DMSO/ $\text{H}_2\text{O}$  mix solution by 80/20 wt%. Then, 20 g PVA powder was added into it in constant temperature equipment and stirred at  $90^\circ\text{C}$  for several hours. After the PVA powder was fully dissolved, the mixture was poured into a mould and then cooled at  $-20^\circ\text{C}$  for 24 h. After being released from this mould, the PVA hydrogels formed were immersed in fluid water for 10 days at room temperature to fully exchange organic solvent in the gels, and then air-dried overnight at room temperature. The resultant 1% PVA-H/HA was placed in water for further tests. The diameter of sample was 10 mm.

Other PVA-H/HA composites were prepared according to the above method with different HA contents.

### 2- In Situ Synthesis

Two chemical materials were used to produce HA in the mix solution directly. First, the  $\text{Ca}(\text{OH})_2$  water solution was mixed with proportional DMSO and water, then  $\text{H}_3\text{PO}_4$  was introduced into this mixed solution at the Ca/P proportion of 1:1.67. After proportional PVA powder was introduced into the mixed solution, the mixture was heated in constant temperature equipment and stirred at  $90^\circ\text{C}$  for several hours. The subsequent treatment process was carried out the same as the above-mentioned method.

The chemical equation of producing HA in this mixing solution was [12]:



A stainless steel disk, with a finished surface of roughness of  $0.72\text{--}0.86\ \mu\text{m}$  (measured by a surface profilometer), was used as friction counterpart.

### Mechanical Testing

The most common defining mechanical properties used to characterize plastics are the tensile and shear properties. To analyze the effects of mechanical properties on the wear resistance and friction coefficient of PVA-H and its composites, the tensile strength and shear resistance of PVA-H/HA composites were measured. The tensile tests and shear resistance tests were conducted on an Instron-4465 (Instron Corp., USA) tester. The test was carried out following ASTM d 638.

### Tribological Testing

The friction and wear tests were performed at room temperature in ambient atmosphere under water lubrication conditions on a four-ball tester (MRS-10A, Jinan Shijin Tester Company, PR China). Each test was performed for 30 min. To accelerate the wear process, the sliding speed used was 100 r/min (about 0.21 m/s; the speed found in the hip joint is about 0-50 mm/s) The nominal normal pressures exerted by the tester were 0.5 MPa, 1 MPa, and 1.5 MPa, which lie in the range of what is typically found in hip joints

(0-2.5 MPa). Distilled water was used as lubricant in this investigation. The sample was fixed on the sample holder of wear tester. Soft cloth was used to clean the surface of the composite and the bearing stainless steel disk before and after each test. The friction coefficients were calculated by dividing the normal loads by the friction force showing on the display after the friction force gained stability.

PVA-H is a typical hydrated material. Because the water in the samples evaporates slowly into the air, it is hard to measure the actual weight by photoelectricity balance (accuracy is 0.1 mg). In our investigation, we cleared the water on the surface of the samples using filter paper and then put the sample in dry Petri dishes immediately after the wear tests. Comparing the total weight before test and after test, the weight loss of each sample was obtained.

To remove water from this hydrated material entirely, the samples were dried by maintaining them at  $40^\circ\text{C}$  in a heated chamber for about 4 h after wear testing. Then the worn surface of dried sample was examined by a S2150 Hitachi SEM, Japan. The surfaces of samples were gold sputtered before examination.

## RESULTS AND DISCUSSION

### Mechanical Properties

Table 1 shows the results of the tensile tests of the pure PVA-H and PVA-H/HA composites by different methods with varied HA contents. Kazuyasu Ushio [5] have also studied the tensile strength of pure PVA-H and obtained similar results. However, the corresponding properties of PVA-H/HA composite have not been studied by the same workers.

It can be seen that the tensile strength of the PVA-H/HA composites prepared by mixed method decreased with the increase of HA content, while that of the in situ composites increased with the increase of HA content when the HA content was lower than 3%. The highest tensile strength of all samples was obtained with 3% HA content by in situ synthesis.

The shear resistances of PVA-H and PVA-H/HA are also shown in Table 1. The shear resistances of PVA-H/HA prepared by in situ synthesis were also better than those of pure PVA-H and PVA-H/HA

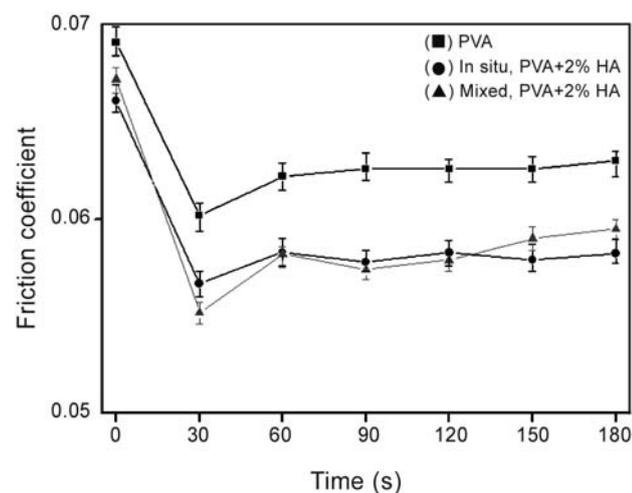
**Table 1.** Tensile strength and shear resistance of pure PVA-H and PVA-H/HA composite prepared by different methods.

Sample	Prepared method	HA content (%)	Tensile strength (MPa)	Shear resistance (MPa)
Pure PVA	/	0	31.5	7.39
PVA-H/HA	mix	1	31.8	7.52
PVA-H/HA	mix	2	30.8	7.14
PVA-H/HA	mix	3	25.7	6.86
PVA-H/HA	in situ	1	32.2	7.66
PVA-H/HA	in situ	2	33.7	7.92
PVA-H/HA	in situ	3	35.1	8.18
PVA-H/HA	in situ	4	32.3	7.83

composites prepared by mixed method. These results indicate that the introduction of HA particles can improve the mechanical properties of the PVA-H matrix.

### Friction Coefficient

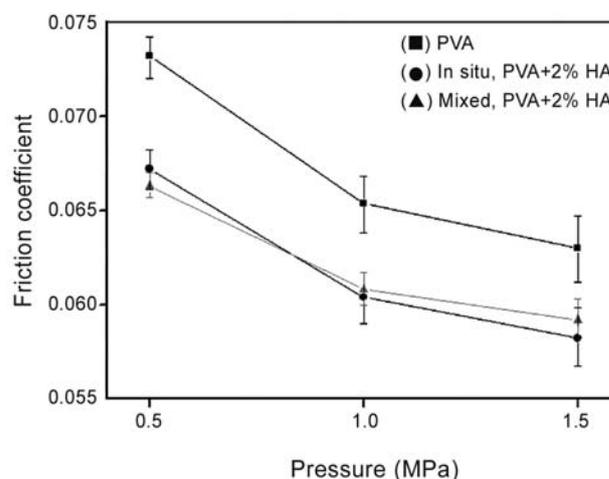
Figure 1 shows the evolution of friction coefficient versus time of pure PVA-H and HA reinforced PVA-H composites prepared by different methods. When sliding against stainless steel surface, the friction coefficient of pure PVA and PVA-H/HA composites are slightly higher in the beginning of the wear testing than in the later stage of the same test. When the friction coefficient is monitored against time, further information can be obtained. We have found that the



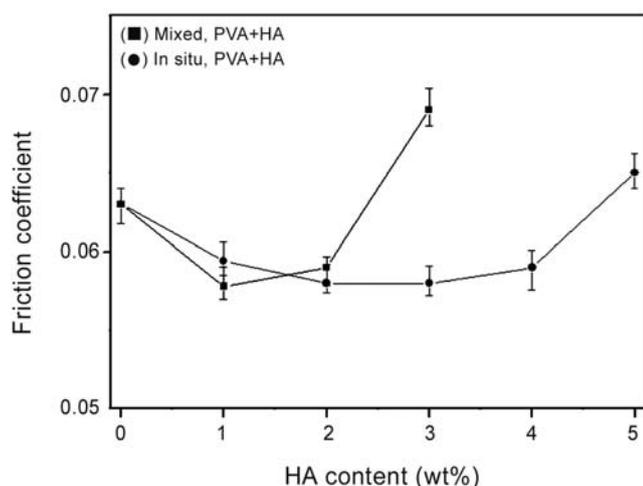
**Figure 1.** Variations of friction coefficients with times for pure PVA-H and PVA-H/HA composites sliding against stainless steel disk.

later friction coefficients of PVA/HA composites by both methods decreased by 7-9% compared to that of pure PVA-H. It is interesting to note that after the running-in period, the friction coefficients of pure PVA-H and PVA-H/HA composite prepared by in situ synthesis remained approximately constant, while that of the other samples prepared by mixed method tended to increase in time.

The variations of friction coefficients under different pressures for pure PVA-H and HA-filled PVA-H composites sliding against stainless steel disk under water lubrication condition are shown in Figure 2. The results show that the friction coefficient of each sample decreases with the increase of contact pressure. Though both methods reduced the friction coefficient with the variation of contact pressure, the in situ synthesis was more effective in decreasing the



**Figure 2.** Friction coefficient curves of pure PVA-H and PVA-H/HA composites under different pressures.



**Figure 3.** Friction coefficient curves of PVA-H/HA composites with different HA contents.

friction coefficient of the PVA-H/HA composites than the mixed method under higher contact pressure. Therefore, the variations of friction coefficient ( $\mu$ ) with loads ( $p$ ) are related by the following equation:

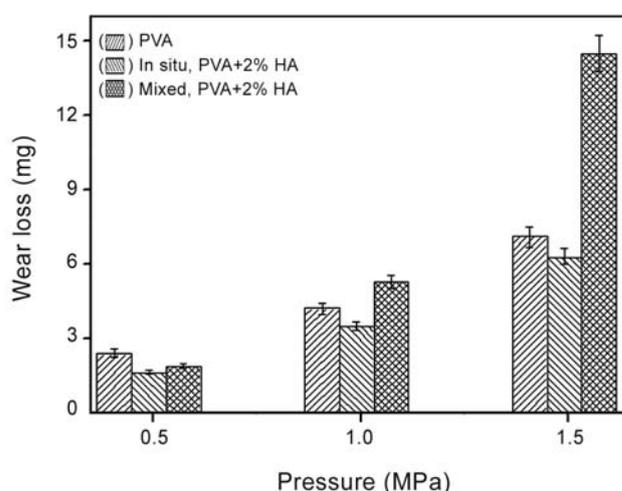
$$\mu = Kp^{n-1}$$

Here,  $K$  and  $n$  are constants related to the composites, and  $2/3 < n < 1$  for the materials tested in this investigation.

The synthesis method and the HA content are the other two obvious factors for the tribological properties of the PVA composite. Their relationship can be seen in Figure 3. Wear tests were carried out by normal pressure of 1.0 MPa and sliding speed of 100 r/min using water as lubricant. Under the given condition, the friction coefficient of PVA-H/HA composites prepared through the mixed method first decreased with the increase of HA content, and then increased with the increase of HA content when the HA content was higher than 1 wt%. On the other hand, the friction coefficient of composites prepared by in situ synthesis also increased with the increase of HA content when the HA content was higher than 4 wt%. Meanwhile, it was found that the friction-reducing property of in situ PVA-H/HA was better than that of the mixed PVA-H/HA composites with the same HA content under the same condition.

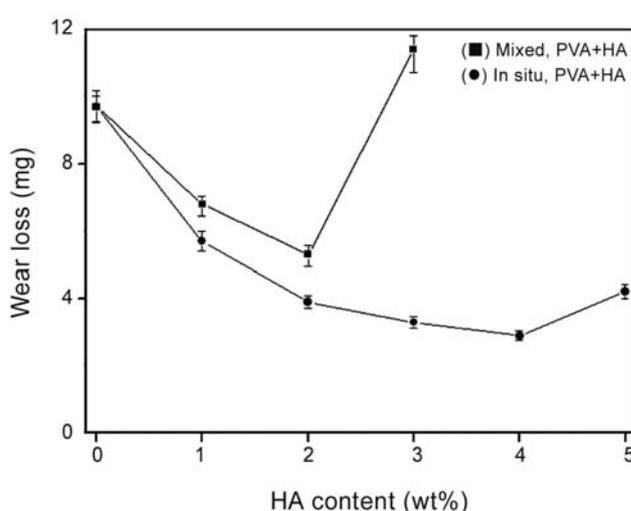
### Wear Properties

The wear losses of the pure PVA-H sample and



**Figure 4.** Variations of wear loss with contact pressure for pure PVA-H and PVA-H/HA prepared by different methods.

PVA-H/HA composites under different contact pressure conditions are shown in Figure 4. In our investigation, the wear loss of each sample under lower contact pressure (0.5 MPa) was obviously less than that of the samples under higher pressure. Though the wear loss of mixed composite was lower than that of pure PVA-H under lower pressure, it increased faster and was higher than that of pure PVA under higher pressure. For example, the wear loss of composites prepared by the mixed method was lower than that of pure PVA-H samples by 21% under 0.5 MPa pressures, while it was higher than pure PVA-H by 103% under 1.5 MPa pressure. Under the same condition,



**Figure 5.** Variation of wear loss with HA content for PVA-H/HA composites prepared by different methods.

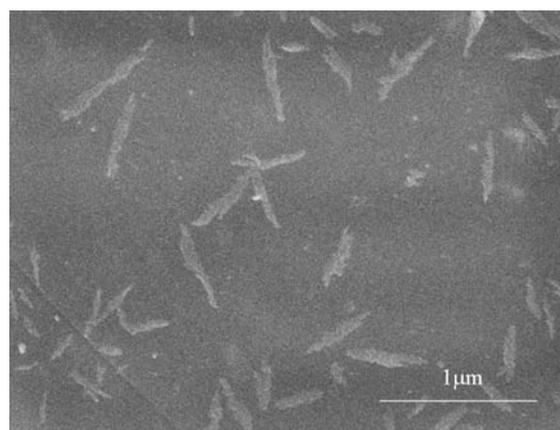
the wear losses of samples prepared by in situ synthesis were less than those of pure PVA-H by 31.7% and 12%.

The relationship between wear loss and the synthesis method/HA content can be seen from the experiment data shown in Figure 5. The wear tests condition was the same as that in Figure 3. It was obvious that the synthesis method and HA content greatly affected the wear loss. The wear loss of PVA-H/HA composites prepared by mixed method decreased initially with the increase of HA content, but then increased rapidly with the increase of HA content when the HA content was higher than 2 wt%. The PVA-H/HA composites prepared by in situ synthesis method have much better wear resistance than the composites prepared by the mixed method with the same components under the same conditions. The wear resistance of the composites was highest when the HA content was about 4% prepared by in situ synthesis in our investigation.

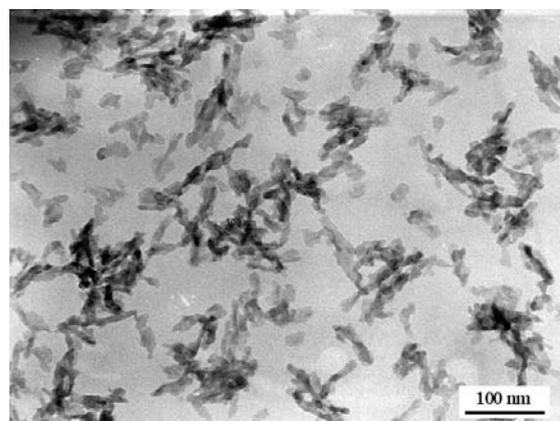
#### Friction and Wear Mechanisms

The small image in Figure 6 is the SEM photo of the HA particle used in the mixed method. The big image shows the shape and size of nano HA, which was prepared by in situ synthesis in PVA-H (2 wt%). The shape of HA particles in big image is similar to those of HA particles shown in small image. The dimension of the HA particle is about  $500 \text{ nm} \times 70 \text{ nm}$ . These results show that the particles were nano HA and uniformly dispersed in the PVA-H matrix.

It is usually assumed that the PVA-H is a material that consists of three-dimensional network structure formed by the hydrogen bond interaction of the hydroxide radical in the PVA molecule. The network contains many micropores similar to the natural articular cartilage in which a large amount of water is interposed. Water can permeate into or be squeezed out from the gel network to provide lubrication under loading force. That is one reason why the PVA-H has lower friction coefficient than other artificial materials. The friction coefficient approximately decreased linearly with increasing pressure. Under high pressure, more water was squeezed out of the matrix and provided better lubricant condition between the counterparts. This resulted in decreased friction coefficient of the counterpart.



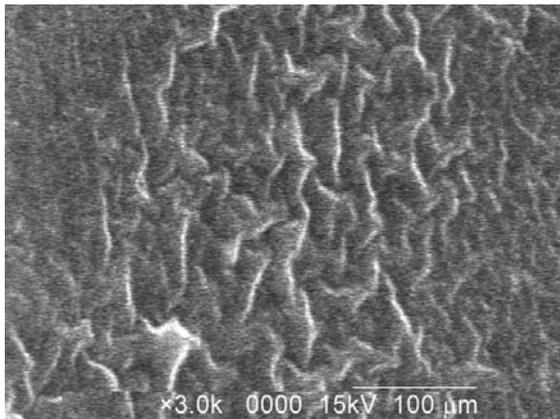
(a)



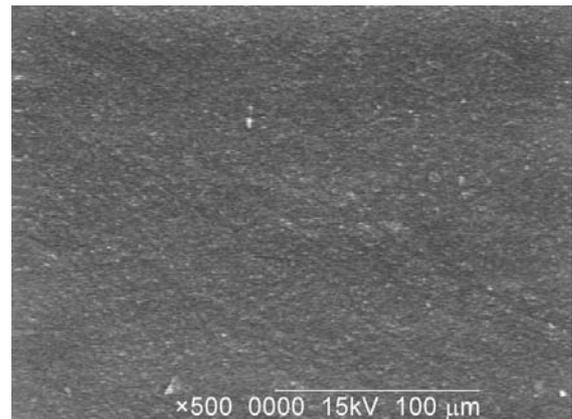
(b)

**Figure 6.** SEM photos of worn surface of pure PVA and PVA-H/HA composites: (a) pure PVA-H, 0.5 MPa; (b) mixed PVA-H/HA composite, 1 wt%, 0.5 MPa.

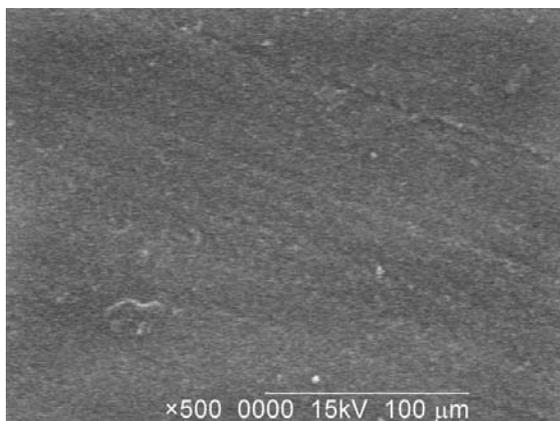
The wear properties of the composites are related to the proportion of the nano HA and the prepared method. When the nano HA content is below a certain level, all the HA particles are fully embedded in the PVA-H material and the distribution of the particles is approximately uniform. Under these conditions, the HA particles can effectively play a role in increasing wear resistance against the stainless steel disk. The wear resistance increases as the HA content is increased up to the critical level. When the HA content is above the critical value, the dispersion property of the nano HA particles decreases so that nano HA occurs and big HA particles are formed, which act as grains during the wear process. Under these conditions, the wear and friction coefficients were increased with the increase of HA content. In this work, it was found that the critical nano HA content optimized the wear resistance to 2 wt% (by mixed



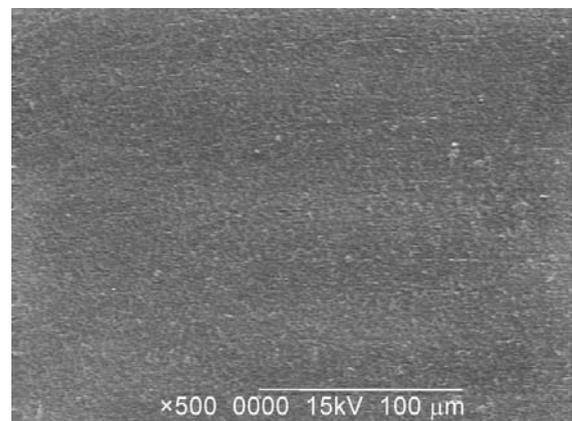
(a)



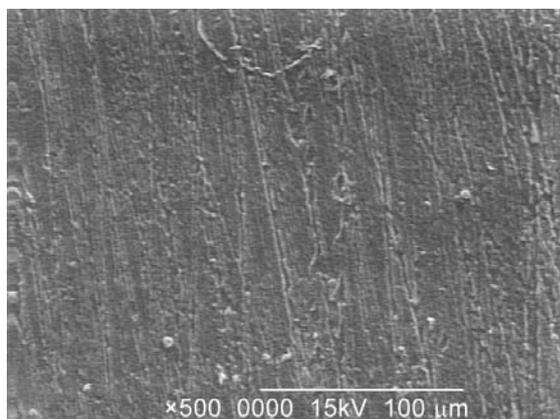
(d)



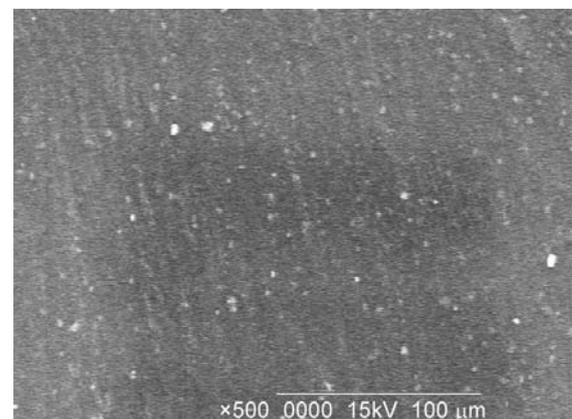
(b)



(e)



(c)



(f)

**Figure 7.** SEM photos of worn surfaces of pure PVA and PVA-H/HA composites: (a) pure PVA-H, 0.5 MPa; (b) mixed PVA-H/HA composite with 1 wt%, 0.5 MPa; (c) mixed PVA-H/HA composite, 1 wt%, 1.5 MPa; (d) in situ PVA-H/HA, with 1 wt% HA, 0.5 MPa; (e) in situ PVA-H/HA composite with 3 wt% HA, 0.5 MPa; (f) in situ PVA-H/HA composite with 4 wt%, 0.5 MPa.

method) and to 4 wt% (by the in situ synthesis), respectively.

The SEM image shows that there were many plas-

tic features caused by adhesion on the worn surfaces of the pure PVA-H under the pressure of 0.5 MPa, as shown in Figure 7a. These damages have been

attributed to a plastic strain accumulation process caused by the continuous sliding of the hard counterpart during the wear testing. This structure directly enhances the friction coefficient of the pure PVA-H sample.

The observation of the worn surfaces of PVA-H/HA composites (Figure 7b) shows that when the contact pressure is about 0.5 MPa, the wear mechanisms are slightly scratch and adhesion, identified by the slightly parallel groove and debris on the worn surface. The scratch and ripple-like structure on the worn surface of the PVA-H/HA composite became obvious under higher loads (1.5 MPa, Figure 7c). The wear mechanism is abrasion and adhesion. Based on these evidences, we believe that the introduction of HA enhances the wear resistance of PVA-H matrix.

The SEM photos of the worn surface of PVA-H/HA composites prepared by in situ synthesis and variant HA content are shown in Figures 6d and 6e. For the PVA-H/HA composites prepared by in situ synthesis with 1 wt% HA (Figure 7d), the worn surfaces are smooth. The same is true with the samples prepared by the mixed method with the same HA content under the same pressure (Figure 7b). This indicates that the HA particles play a role in decreasing the wear loss under low contact pressure with low addition. HA particles possess high strength and high clash modulus, and the load action on the composites was mainly borne by HA particles; thus, the wear-reducing action of the composites was mainly determined by HA particles. Considering the enhancement of mechanical properties by introducing HA to the PVA-H matrix, we believe that the enhancement of wear resistance should be attributed to the increase of shear resistance of the PVA-H matrix.

Figures 7e and 7f show the worn surface of PVA-H/HA composites prepared by in situ synthesis with 3 wt% HA and 4 wt% HA, respectively. Comparing Figure 7e with Figure 7d, we can clearly note that the grooves are slightly less obvious on the high HA content composite than that of the low HA content, indicating that the wear resistance has been enhanced with the increase of HA content by the in situ synthesis. At the same time, we did not find agglomeration HA particles on the worn surface. Figure 7f shows some particles were embedded on the worn surface after the wear test. We believe that these particles

were agglomeration HA because HA content was too high. This is the reason why the wear resistance of PVA-H/HA composite decreased when the HA content was higher than 4%.

From Figure 7 we can see that the scratches or ridges on the wear surface of mixed PVA-H/HA composites are much more obvious and deeper than those of in situ synthesized ones. The surface morphology mainly shows fleet scratches with small white fatigued fracture fringes on the wear surface of in situ synthesized PVA-H/HA, while they are mainly torn grooves on the wear surface of the mixed one. Thus, fatigue wear and abrasion wear are the main wear mechanisms of the PVA-H/HA composites when sliding against stainless steel disk. Scratch and fatigue are dominant in the in situ synthesized PVA-H/HA, while abrasion cannot be ignored as the main cause for the mixed PVA-H/HA composites under the same conditions.

## CONCLUSION

- The PVA-H/HA composites prepared by the in situ synthesis method have much better mechanical and tribological properties than the ones prepared by the mixed method with the same components under the same conditions. The wear resistance of PVA-H/HA composites was highest when the HA content was about 4 wt% prepared by in situ synthesis.
- Contact pressure exerts great influence on the wear loss and friction coefficient of PVA-H/HA composites. The wear loss of samples increases with the increase of contact pressure.
- The dominant wear mechanism for in situ synthesized PVA-H/HA was scratch and fatigue. Abrasion is the main cause of the mixed PVA-H/HA composites under the same conditions.

## ACKNOWLEDGEMENTS

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