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Biosurface and Biotribology 2 (2016) 40–47

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Evaluation of lubrication properties of hydrogel artificial cartilage materials for joint prosthesis

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Received 3 December 2015; received in revised form 18 February 2016; accepted 22 February 2016

Abstract

Poly (vinyl alcohol) (PVA) hydrogel with high water content is the candidate material for artificial cartilage. PVA hydrogels prepared by freeze-thawing (FT) method (PVA-FT gel), cast-drying (CD) method (PVA-CD gel) and hybrid method of FT and CD (PVA-hybrid gel) were developed and their friction and wear behaviors were evaluated. Sliding pairs of a cobalt-chromium-molybdenum alloy or alumina ceramic ball and a PVA hydrogel plate were tested in reciprocating friction test. Ultra-pure water and simulated synovial fluid were used as lubricants for friction test. PVA-FT gel showed high friction and severe wear in ultra-pure water. Friction coefficient of PVA-CD gel in ultra-pure water was quite low such as about 0.005, but scratches were observed on the surface of PVA-CD gel. PVA-hybrid gel lubricated in ultra-pure water showed low friction such as 0.004, and intact surface structure of PVA-hybrid gel remained after friction test. Simulated synovial fluid contributed to the improvement of lubrication property of all PVA hydrogels and PVA-hybrid gel showed the lowest friction coefficient such as 0.003 and minimum wear. These results indicated that PVA-hybrid gel has a great potential as the material for artificial joint.

Keywords: Artificial articular cartilage; PVA hydrogel; Artificial joint; Wear; Friction

1. Introduction

The total joint prosthesis contributes to the recovery of joint function and relief from pain for patients suffering with rheumatoid arthritis and osteoarthritis. In total joint prosthesis, the common bearing surface for artificial joint is a combination of an ultra-high molecular weight polyethylene (UHMWPE) and a cobalt–chromium–molybdenum (Co–Cr–Mo) alloy or ceramics. However, in long-time usage, revision treatment is conducted due to the loosening of joint prostheses derived from wear particles-induced osteolysis [1]. Therefore, wear reduction of joint prosthesis materials is needed to improve the longevity of artificial joints.

The lubrication mode of artificial joints composed of UHMWPE and hard materials is considered to be mixed or boundary lubrication modes. Therefore, artificial articular cartilage with high water content has been proposed for improvement of lubrication mode in artificial joints [2,3] for mimicking the excellent lubrication mechanism of natural synovial joint with extremely-low friction and minimum wear. When artificial articular cartilage is introduced to the frictional surface of artificial joints, fluid film formation by soft elastohydrodynamic lubrication (EHL) and micro-EHL [4] is expected. If hydrogel with high water content is used as artificial articular cartilage, biphasic lubrication mechanism [5] can be obtained by taking advantage of hydration material. Artificial articular cartilage can be used as the implant material for the focal defects of natural articular cartilage, so artificial articular cartilage has great potential for the recovery of joint function.

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Peer review under responsibility of Southwest Jiaotong University.

http://dx.doi.org/10.1016/j.bsbt.2016.02.005

Various elastomer and hydrogels have been proposed as artificial cartilage [6–9], but our group considered that hydrogel with excellent biocompatibility, high mechanical strength and high water content is desirable to mimicking the excellent lubrication mechanism of natural articular cartilage. Therefore, our group has focused on poly (vinyl alcohol)(PVA) hydrogel with high water content as candidate material for artificial cartilage. In previous study, we evaluated the tribological behaviors of PVA hydrogel prepared by repeated freezing-thawing (FT) method [10] (PVA-FT gel) and found that the tribological behaviors of PVA-FT gel were affected by synovial fluid constituents such as proteins, phospholipids and hyaluronic acid [11–14]. In addition, PVA-FT gel showed excellent lubrication property in simulated synovial fluid [15]. However, wear resistance of PVA-FT gel was considered to be not enough under severe direct contact condition. Therefore, improvement of the material property of PVA hydrogel is needed to reduce both friction and wear. Suzuki et al. have newly developed the physically-cross-linked PVA hydrogel by using cast-drying (CD) method [16] (PVA-CD gel) and PVA-hybrid gel by the combination method of FT and CD [17]. Both PVA-CD and PVA-hybrid gels could show lower friction than PVA-FT gel and PVA-hydrid gel kept low friction coefficient such as 0.01 [18] rubbed against glass plate. In addition, friction and wear properties of PVA-hybrid gel have been improved and PVA-hybrid gel showed extremely low friction coefficient such as 0.006 and minimum wear [19].

However, this result was obtained by friction test with sliding pair of hydrogels and glass plate. Considering the actual use of PVA hydrogels as artificial articular cartilage, the evaluation of lubrication property of PVA hydrogels sliding against the artificial joint material is needed. Therefore, the aim of this study is to investigate the lubrication property of PVA hydrogels sliding against representative materials for artificial joints such as Co–Cr–Mo alloy and alumina ceramic.

2. Materials and methods

2.1. Preparation of PVA hydrogels

2.1.1. PVA-FT gel

15 wt% aqueous solution of PVA (polymerization degree: 1700, saponification degree: 98.0–99.0 mol%, Kuraray Co. Ltd.) was used as raw material for the preparation of PVA-FT gel. PVA solution was poured into acrylic mold ($160 \times 140 \times 2$ mm^3) to the limit capacity of the mold and PVA solution-containing mold was sealed by acrylic plate and treated by repeated FT method in temperature and humidity controlled chamber (SH-242, ESPEC CORP., Japan). Temperature and treating time for freezing and thawing process were -20 °C, 8 h and 4 °C, 16 h, respectively. The number of repeated FT cycles was 4 times. As shown in Fig. 1(a), PVA-FT gel is opaque due to the inhomogeneous network structure and distribution of microcrystallites [16,17]. The thickness of PVA-FT gel in its swollen state is 1.91 ± 0.06 mm ($n=5$).

2.1.2. PVA-CD gel

15 wt% aqueous solution of PVA (polymerization degree: 1700, saponification degree: 98.0–99.0 mol%, Kuraray Co. Ltd.) was used as raw material for the preparation of PVA-FT gel. 30 g of PVA solution was poured into polystyrene dish (diameter: 90 mm) and was dried in the temperature and humidity controlled chamber (SH-242, Espec Corp.).The temperature and relative humidity during drying process was 8 °C and 50 %RH, respectively. When the ratio of the weight of residual water in dried samples to the weight of polymer reached to 0.12–0.13, drying process was finished. The dried samples were swollen in pure water for longer than 3 days and PVA-CD gel was obtained. As shown in Fig. 1(b), PVA-CD is transparent due to the uniform network structure and

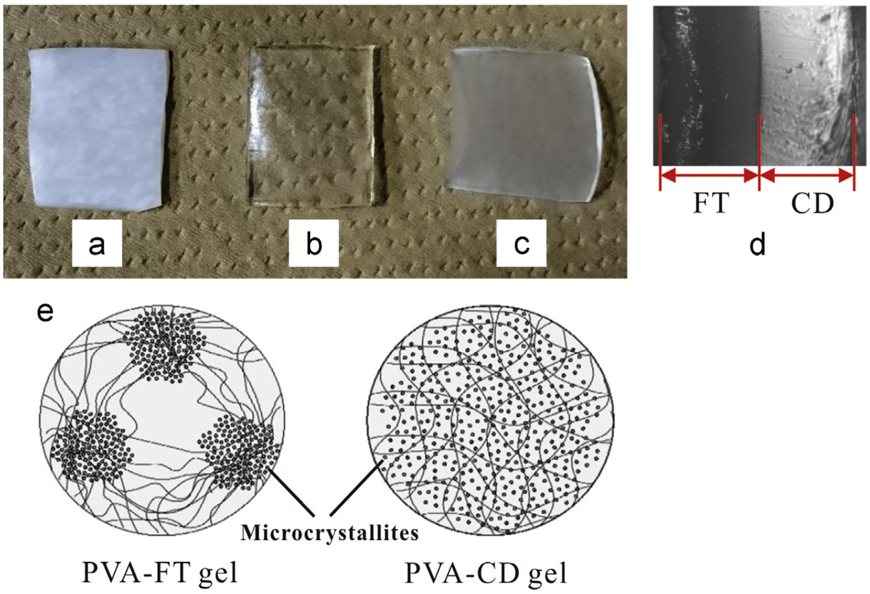
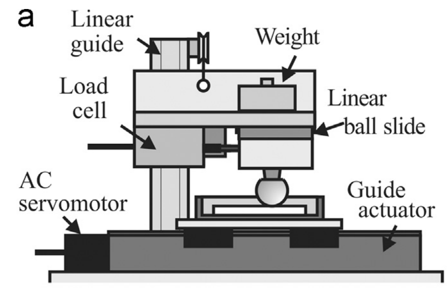


Fig. 1. PVA hydrogels: (a) PVA-FT gel, (b) PVA-CD gel, (c) PVA-hybrid gel, (d) cross-section of PVA-hybrid gel, (e) schematic images of the structure of PVA-FT and CD gels [19].

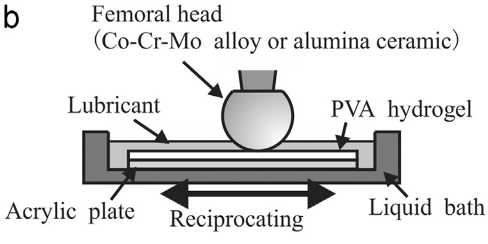
distribution of microcrystallites [16,17]. The thickness of PVA-CD gel in its swollen state is 1.57 ± 0.09 mm ($n = 5$).

2.1.3. PVA-hybrid gel

15 wt% aqueous solution of PVA (polymerization degree: 1700, saponification degree: 98.0–99.0 mol%, Kuraray Co. Ltd.) was used as raw material for the preparation of PVA-hybrid gel. 15 g of PVA solution was poured into polystyrene dish (diameter: 90 mm) and this sample was treated by repeated FT method for the preparation of PVA-FT gel layer. Temperature and treating time for freezing and thawing process were −20 °C, 8 h and 4 °C, 16 h, respectively. The number of repeated FT cycles was 4 times. Then, 15 g of PVA solution was poured onto the PVA-FT gel layer in polystyrene dish and the sample was dried in the temperature and humidity controlled chamber (SH-242, Espec Corp.). We used the multi-stage drying method developed in previous study. Temperature and relative humidity of first stage in drying process were 8 °C and 50 %RH for 7 days and those in second process were 20 °C and 40 %RH. When the ratio of the weight of residual water in dried samples to the weight of polymer in dried samples reached to 0.12–0.13, drying process was finished. The dried samples were swollen in pure water for longer than 3 days and PVA-hybrid gel with laminar structure by PVA-FT and CD gels were obtained (Fig. 1(c) and (d)). Our previous study indicated that PVA-hybrid gel prepared by this method could show extremely low friction and minimum wear [16]. In this study, PVA-CD gel side in PVA-hybrid gel was used as frictional surface in reciprocating friction test to be described. The thickness of PVA-hybrid gel in its swollen state is 1.79 ± 0.07 mm ($n = 5$).



Schematic view



Detailed view

Fig. 2. Reciprocating friction tester.

2.2. Measurement of water content of PVA hydrogels

The water content of PVA hydrogels were measured by the method as follows. Pieces of swollen PVA hydrogels were cut from PVA hydrogel sheet as quadrangular-shape (approx. 10 mm × 10 mm). The weights of these pieces were measured, and then they were dried in force-convection type oven (DK240S, Yamato Scientific Co., Ltd., Japan) at 60 °C for 3 days. The weight of dried samples were measured and water content of PVA hydrogels was calculated as a weight ratio of water in swollen samples to the swollen samples themselves.

2.3. Surface observation by atomic force microscope

To observe the surface of PVA hydrogels in micro-meter scale and measure the surface roughness, we use the atomic force microscope (AFM) (Dimension ICON, Bruker Corporation, USA). All observations were conducted by using peak-force tapping mode in ultra-pure water, and nominal tip diameter and spring constant of AFM probe are 2 nm and 0.7 N/m, respectively.

2.4. Reciprocating friction test

2.4.1. Test condition

The reciprocating friction tester used in this study is shown in Fig. 2. Sliding pairs of a cobalt-chromium-molybdenum (Co–Cr–Mo) alloy or alumina ceramic ball (φ26 mm) and a PVA hydrogel plate were tested in reciprocating friction test. The arithmetic average roughness of Co–Cr–Mo alloy and alumina ceramic ball was less than 0.01 μm. PVA hydrogels were glued on the acrylic plate by using cyanoacrylate adhesive. The applied load was 5.88 N and mean contact pressure on PVA-FT gel, PVA-CD gel and PVA-hybrid gel were 0.22, 0.41 and 0.32 MPa, respectively. The sliding velocity was 20 mm/s and the total sliding distance was 100 m. We put no pre-loading time at starting reciprocating friction test. All tests were conducted in room temperature.

2.4.2. Lubricants

In this study ultra-pure water and simulated synovial fluid were used as lubricants. The composition of simulated synovial fluid is shown in Table 1. Normal saline solution (Otsuka Pharmaceutical Factory, Inc., Japan) was used as the solvent for simulated synovial fluid. Molecular weight of hyaluronic acid is 9.2×10^5. As a phospholipid component, L-α dipalmitoyl phosphatidylcholine (DPPC; Wako Pure Chemical Industries, Ltd., Japan) was chosen. DPPC was dispersed in saline as liposomes. Albumin (Wako Pure Chemical Industries, Ltd., Japan) and γ-globulin (Wako Pure

Table 1
Composition of simulated synovial fluid.

Hyaluronic acid [wt%]	DPPC [wt%]	Albumin [wt%]	γ-globulin [wt%]
0.5	0.01	1.4	0.7

Chemical Industries, Ltd., Japan) which are the main protein constituents in synovial fluid were chosen as protein additives.

3. Results

Water content of PVA hydrogels are shown in Fig. 3. The water content of PVA-FT, CD and hybrid gels are 84.4 %, 75.4 % and 71.9 %, respectively. This result indicated that water content of PVA hydrogels changed depending on the preparation condition in spite of using PVA solution with same concentration.

AFM images and the arithmetic average roughness (Ra) are shown in Fig. 4. PVA-FT gel has porous and fibrous surface structure and the highest Ra. PVA-CD gel has smoother surface than PVA-FT gel but there is no distinguishing surface structure. PVA-hybrid gel has the lowest Ra value such as 0.007 and has quite smooth surface.

Friction coefficient at first cycle and steady state in friction test when Co–Cr–Mo alloy was used as counterface material for PVA hydrogels are shown in Fig. 5(a) and (b). Friction coefficient at first cycle was high such as above 0.20 but friction was reduced due to the running-in effect both in ultra-pure water and simulated synovial fluid. However, PVA-FT gel showed the highest friction coefficient both in ultra-pure water and simulated synovial fluid. PVA-CD gel showed quite low friction coefficient such as below 0.005 and kept it during the friction test. There was almost no lubricant-type dependence on the friction behavior of PVA-CD gel rubbed against Co–Cr–Mo alloy. PVA-hybrid gel showed very low friction same as PVA-CD gel in all lubricants.

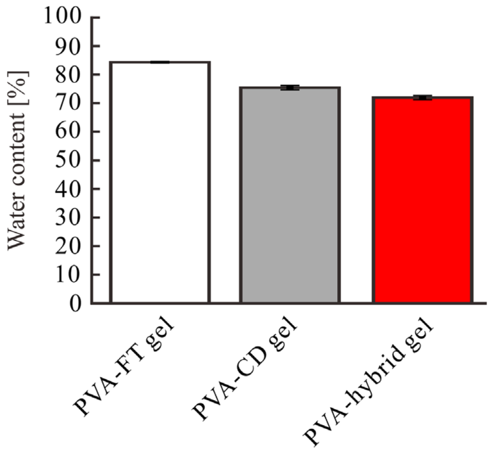
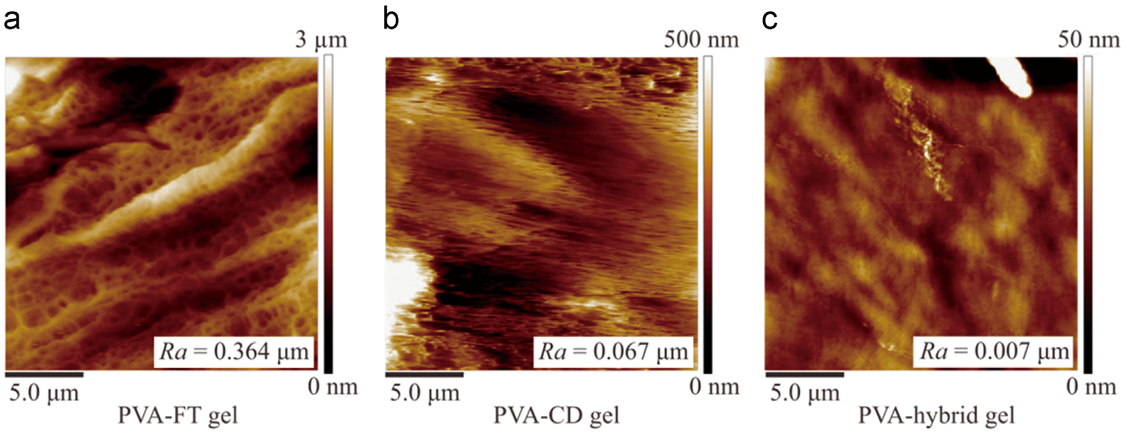


Fig. 3. Water content in PVA hydrogels (Values = mean ± standard deviation ($n=5$)).

Friction coefficient at first cycle and steady state in friction test when alumina ceramic was used as counterface material for PVA hydrogels are shown in Fig. 6(a) and (b). When alumina ceramic was used as counterface material for PVA hydrogels, friction coefficient of PVA-FT gel at first cycle in ultra-pure water was lower than that of rubbed against Co–Cr–Mo alloy. However, friction coefficient of PVA-FT gel at steady state in ultra-pure water was almost the same level with that of rubbed against Co–Cr–Mo alloy. In simulated synovial fluid, there was no difference between friction coefficients of PVA-FT gel rubbed against Co–Cr–Mo alloy and alumina ceramic. PVA-CD and PVA-hybrid gels rubbed against alumina ceramic showed extremely low friction such as below 0.005 both in ultra-pure water and simulated synovial fluid, and there is no dependence of friction coefficient of these two hydrogels on counterface material.

The microscopic images of intact and worn surface of PVA hydrogels are shown in Figs. 7–9. When Co–Cr–Mo alloy was used as counterface material in ultra-pure water, PVA-FT gel showed severe wear (Fig. 8(a)) and some scratches and roughing of surface were observed on PVA-CD gel surface (Fig. 8(b)). However, PVA-hybrid gel could maintain intact surface structure (Fig. 8(c)). In simulated synovial fluid, wear of PVA-FT and hybrid gels were not detected by surface observation (Fig. 8(d) and (f)) but some scratches were observed on the surface of PVA-CD gel (Fig. 8(e)). When alumina ceramic was used as counterface material in ultra-pure water, PVA-FT gel completely lost its intact surface structure (Fig. 9(a)) and some scratches and roughing of surface were observed on PVA-CD gel surface (Fig. 9(b)). However, PVA-hybrid gel showed excellent wear resistance in ultra-pure water (Fig. 9(c)). In simulated synovial fluid, wear of PVA-FT and hybrid gels were not detected (Fig. 9(d), (f)) but some morphological changes were observed on the surface of PVA-CD gel (Fig. 9(e)).



PVA-FT gel PVA-CD gel PVA-hybrid gel

Fig. 4. AFM images and surface roughness (Ra) of PVA hydrogels.

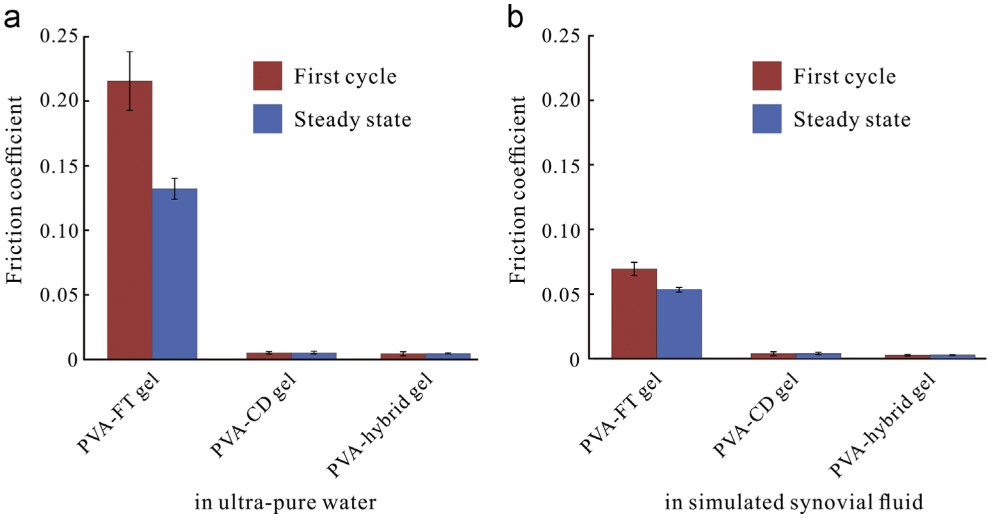


Fig. 5. Friction coefficient of PVA hydrogels rubbed against Co–Cr–Mo alloy (Values = mean ± standard deviation ($n = 3$)).

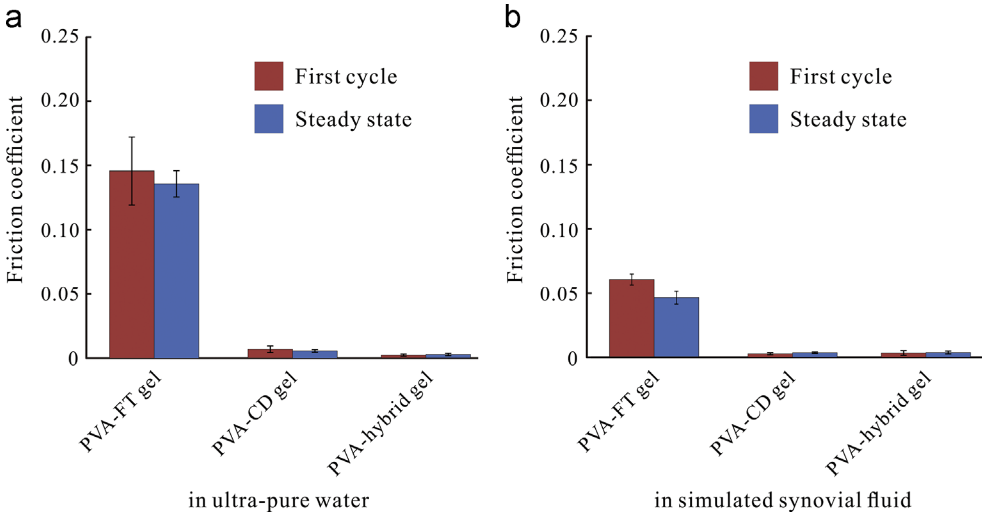
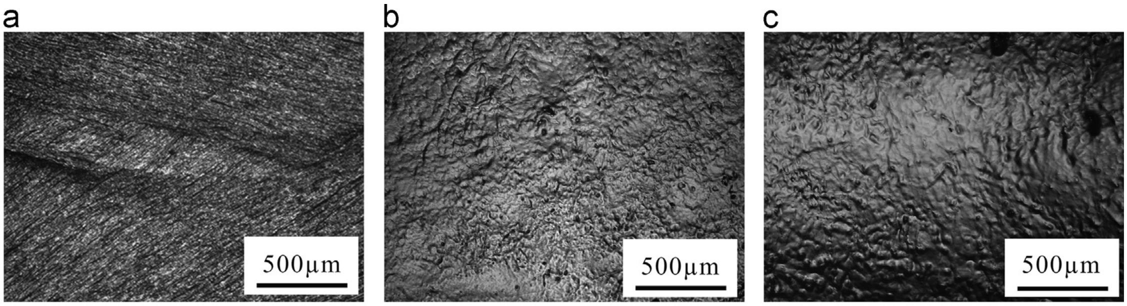


Fig. 6. Friction coefficient of PVA hydrogels rubbed against alumina ceramic (Values = mean ± standard deviation ($n = 3$)).



PVA-FT gel
(Intact surface)

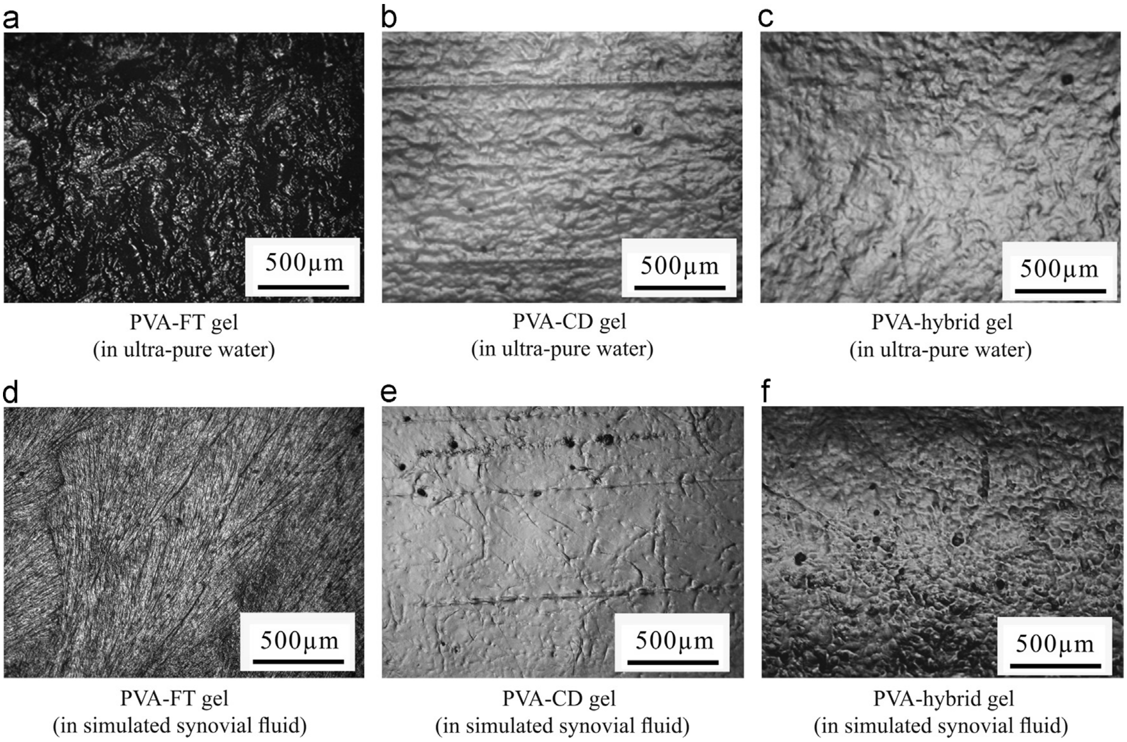
PVA-CD gel
(Intact surface)

PVA-hybrid gel
(Intact surface)

Fig. 7. Intact surface of PVA hydrogels.

4. Discussion

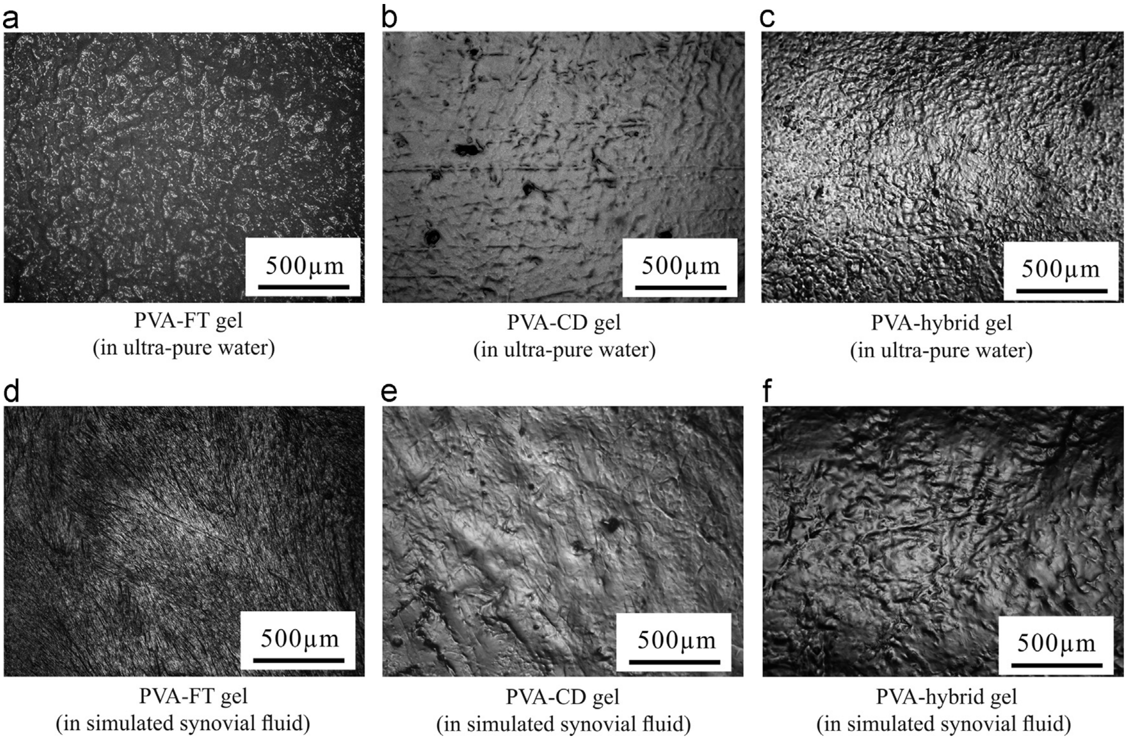
The water content of PVA hydrogels depends on the preparation condition. In previous study, it is indicated that PVA-CD gel has homogeneous distribution of microscrystallites and has a tendency to show the higher crystallinity than PVA-FT gel [20,21]. It is considered that higher crystallinity means the increase of cross-linking points by hydrogen bonding and leads to the decrease of water content. PVA-hybrid gel has lower water content than PVA-CD gel, and it is considered that this is due to



PVA-FT gel (in ultra-pure water) PVA-CD gel (in ultra-pure water) PVA-hybrid gel (in ultra-pure water)

PVA-FT gel (in simulated synovial fluid) PVA-CD gel (in simulated synovial fluid) PVA-hybrid gel (in simulated synovial fluid)

Fig. 8. Worn surface of PVA hydrogels (counterface: Co–Cr–Mo alloy).



PVA-FT gel (in ultra-pure water) PVA-CD gel (in ultra-pure water) PVA-hybrid gel (in ultra-pure water)

PVA-FT gel (in simulated synovial fluid) PVA-CD gel (in simulated synovial fluid) PVA-hybrid gel (in simulated synovial fluid)

Fig. 9. Worn surface of PVA hydrogels (counterface: alumina ceramic).

the increase of cross-linking points in PVA-FT gel layer in PVA-hybrid gel during the drying process.

PVA-FT gel showed higher friction than other two hydrogels regardless of the lubricant and couterface material. When PVA-FT gel was used, mean contact pressure is the lowest so contact area and indentation depth of ball specimen is the largest. It is considered that these actualize the adhesive and digging friction and friction of PVA-FT gel become higher. The low friction of PVA-CD and hybrid gel is due to the lubricious surface structure and effect of biphasic lubrication. Biphasic lubrication is the lubrication mechanism of biphasic material composed of solid and fluid phases, and in this mechanism, interstitial fluid pressure supports the applied force and friction was reduced. We found that PVA-CD and PVA-hybrid gel have the specific lubricious surface structure and this layer on PVA-hybrid gel can be reinforced by multi-stage drying method [22,23]. It was indicated by experimental and analytical approach that low hydraulic permeability of PVA-CD gel contributes to the maintaining of low friction by biphasic lubrication mechanism and synergistic effect by low hydraulic permeability of PVA-CD gel layer and specific lubricious surface layer of PVA-hybrid gel actualizes the extremely low friction of PVA-hybrid gel [24]. Water in PVA hydrogels is squeezed out by applied load but PVA hydrogels have a chance to recover hydration condition because the contact condition in this friction test is migration contact. PVA-FT gel has the highest water content but the hydraulic permeability is also the highest. So if internal water in PVA-FT gel is excessively squeezed out, friction coefficient would increase. However, friction coefficient of PVA-FT gel decreased from start to steady state so running-in effect become obvious in this study. PVA-CD and hybrid gels have the low hydraulic permeability layer so internal water cannot be easily squeezed out and low friction by the effect of biphasic lubrication would maintain. In addition, superficial layer of PVA-hybrid gel is reinforced by multi-stage drying method newly developed in our study [21] so PVA-hybrid gel could show both extremely low friction and excellent wear resistance. Comparing the surface roughness of PVA-CD and hybrid gels, Ra of PVA-hybrid gel is one-ordered lower than that of PVA-CD gel. The mean contact pressure of PVA-hybrid gel is lower so contact pressure at the local contact area at the asperities become lower than that of PVA-CD gel. This leads to the moderation of severity of contact and contributes to maintaining the lubricious superficial layer of PVA-hybrid gel.

The results in this study indicated that PVA-hybrid gel has the great potential as hydrogel artificial cartilage sliding against existing artificial joint materials. However, the mean contact pressure in this study is lower than 0.5 MPa and this is mild condition compared with the expected condition in clinical use. Therefore, evaluation of friction and wear properties of PVA-hybrid gel under severer condition must be conducted in the next study. We discussed on the effect of biphasic lubrication property of PVA hydrogels and behavior of water in PVA hydrogel is a key factor on it. In previous study, it is indicated that PVA-FT gel contains both free water and bound water [25]. If the ratio of free water and bound water in PVA hydrogel changes, the behavior of water in PVA hydrogels changes and this may influence on the biphasic lubrication property of PVA hydrogel. The ratio of free water and bound water in polymeric materials influences on the adsorption behavior of proteins [26] and this would lead to the change of boundary lubrication property by protein adsorbed film. Therefore, the analysis of the existence of free water and bound water in PVA-CD and hybrid gels is needed for further understanding of the changes of lubrication property of PVA hydrogels by preparation method.

5. Conclusion

In this study, we evaluated the friction and wear properties of PVA-FT, CD and hybrid gels as artificial cartilage material. It was indicated that PVA-hybrid gel showed extremely low friction and minimum wear rubbed against artificial joint materials such as Co–Cr–Mo alloy and alumina ceramic in biological environment. Therefore, PVA-hybrid gel has a potential as candidate material as artificial cartilage for joint prosthesis.

Acknowledgment

This research was supported by Grant-in-Aid for Specially Promoted Research of JSPS (23000011).

The authors would like to make a most cordial acknowledgment to Mrs. A. Yoshida who is former technical staff in Kyushu University for her effort in this research activity.

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