Evaluation of Lubrication Property of Poly(vinyl alcohol) Hybrid Gel for Artificial Articular Cartilage

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Poly (vinyl alcohol) (PVA) hydrogel is the candidate material for artificial cartilage. PVA hydrogels prepared by hybrid method of freeze-thawing (FT) and cast-drying (CD) method (PVA-hybrid gel) were developed, and lubrication property of PVA-hybrid gel was evaluated. Sliding pairs of an ellipsoidal PVA hydrogel and a flat glass plate were tested in reciprocating friction test. PVA-hybrid gels were prepared by temperature (T) and humidity (H) controlled drying process. Friction of PVA-hybrid gel prepared by drying process at T of 8°C and H of 80%RH gradually increased. PVA-hybrid gel prepared by drying process at T of 8°C and H of 50%RH showed low friction coefficient of 0.013 but it gradually increased with increase of sliding distance and surface damage was progressed. When the additional drying process at T of 20°C and H of 40%RH after the drying process at T of 8°C and H of 50%RH was provided, PVA-hybrid gel showed extremely low friction coefficient such as 0.006 and wear of this hybrid gel was slight. The additional drying process contributes to obtaining the surface layer of PVA-hybrid gel with low friction and low wear.

Keywords: artificial articular cartilage, PVA-hybrid gel, friction, wear, temperature, humidity

1. Introduction

The number of total joint replacement is increasing every year [1]. This type of orthopaedic surgery contributes to relief from pain and recovery of the function of articular joints. The popular bearing surface for artificial joint is a combination of an ultra-high molecular weight polyethylene (UHMWPE) and a cobalt-chromium-molybdenum alloy or ceramics. However, in long time usage, wear particles of UHMWPE are released and they activate macrophages, which lead to necrosis and bone resorption, and finally induce the loosening and the failure of artificial joint [2]. Phospholipid polymer-grafted UHMWPE has been developed to reduce friction and wear of UHMWPE and this showed the excellent results both in joint simulator tests and clinical usage [3,4]. Vitamin E-blended UHMWPE could suppress the oxidation of UHMWPE and delamination wear of UHMWPE [5,6]. However, the problems related to the wear of UHMWPE and complication caused by the wear particles of UHMWPE have not been solved completely. The lubrication mode of artificial joints composed of those materials appears to be mixed or boundary lubrication mode, so it is necessary to improve the lubrication mode of artificial joint. Introduction of compliant materials like elastomers and hydrogels has been proposed [7,8]. Fluid film formation by soft elastohydrodynamic lubrication (EHL) and micro-EHL [9] are expected by application of artificial articular cartilage layer to the bearing surface of artificial joint. Poly (vinyl alcohol) (PVA) hydrogel is one of the candidate material for artificial articular cartilage and it was reported that fluid film formation was enhanced in knee joint simulator test by using PVA hydrogel [10].

In previous study, we evaluated the tribological behaviors of PVA hydrogels prepared by repeated freezing-thawing (FT) method [11] (PVA-FT gel) and we found that the friction and wear behavior of PVA-FT gel depended on the composition of lubricants that contain synovial fluid constituents such as proteins, phospholipids and hyaluronic acid [12-14]. In addition, PVA-FT gel showed excellent tribological property in
simulated synovial fluid [15]. However, wear of PVA-FT gel would progress 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. newly developed the physically-crosslinked 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-hybrid gel kept low friction coefficient such as 0.01 [18]. However, wear of PVA-hybrid gel could not be completely supressed. Therefore, it is necessary to improve the wear resistance of PVA-hybrid gel.

The aim of this study is to develop the PVA-hybrid gel with extremely-low friction and minimum wear by improvement of preparation protocols.

2. Materials and methods

2.1. Preparation of PVA-hybrid gel

15 wt% aqueous solution of PVA (polymerization degree: 1,700, saponification degree: 98.0 ~ 99.0 mol%, Kuraray Co., Ltd.) was used as raw material for the preparation of PVA-hybrid gels. 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 of freezing and thawing process were −20°C, 8 hours and 4°C, 16 hours, respectively. The number of repeated FT cycles was 4 times. Then, 15 g of PVA solution was poured onto the PVA-FT gel and the sample was dried in the temperature and humidity controlled chamber (SH-242, Espec Corp.). The variations of temperature and relative humidity during drying process were ± 0.2°C and ± 1%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-hybrid gel with laminar structure composed of PVA-FT and CD gels were obtained (Fig. 1). The drying conditions in the preparation of PVA-hybrid gels used in this study are listed in Table 1. It was reported that temperature and relative humidity during drying process are key factors for the formation of cross-linking and micro-crystalline structure of PVA-CD gel [19-22]. If we set the high temperature at the first step during drying process, the shape of PVA-CD and PVA-hybrid gels become undulated and we cannot use these specimens for friction test. We choose the lower temperature such as 8°C at first step in drying process for obtaining the uniform specimen. The three types of PVA-hybrid gel were prepared in temperature ($T$) of 8°C and relative humidity ($H$) of 80, 60 and 50%RH (Sample A, B and C). To clarify the effect of accelerating the drying speed, we changed the temperature and relative humidity at the second step in drying process. Two types of PVA-hybrid gels were prepared by two-stage drying process. 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 50%RH (sample D) and 20°C 40%RH (sample E). The criteria for judgement of finishing the drying process of these two PVA-hybrid gels were same as the PVA-hybrid gels prepared by single-stage drying process.

2.2. Reciprocating friction test

The reciprocating friction tester used in this study is shown in Fig. 2. Sliding pairs of an ellipsoidal (major axis: 40 mm diameter, minor axis: 25 mm diameter) PVA-hybrid gels as 2 mm thickness and a flat glass plate were tested in reciprocating friction test. The applied load was 2.94 N. In this study, pre-load before starting friction test was not applied, so friction tests started immediately after applying the normal load. The sliding speed of 20 mm/s was selected and the reciprocating stroke was 35 mm. The total sliding distance was 140 m. Normal saline (Otsuka Pharmaceutical Factory, Inc.) was used as a lubricant for friction test. All tests were conducted in room temperature (25°C). To confirm the repeatability, each test was repeated 3 times and PVA-hybrid gels used in each test are prepared in

Table 1 Temperature ($T$) and relative humidity ($H$) in drying process

<table>
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<tr>
<th>Sample</th>
<th>1st process</th>
<th>2nd process</th>
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<tr>
<td>Sample A</td>
<td>8</td>
<td>80</td>
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<tr>
<td>B</td>
<td>60</td>
<td>-</td>
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<tr>
<td>C</td>
<td>50</td>
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</tr>
<tr>
<td>D</td>
<td>50</td>
<td>20</td>
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<tr>
<td>E</td>
<td>50</td>
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Calculation method of friction coefficient in each reciprocating cycle is shown in Fig. 3. During the tests, we acquired 40 data points of friction force measured by the tension-compression load-cell in each reciprocating cycle. To eliminate the data of each stroke-end, we choose 12 data points each from forward and backward pass and calculate the average friction force. The average friction force is divided by applied vertical load and we obtained the representative friction coefficient in each reciprocating cycle. Each test was repeated 3 times and mean friction coefficient was obtained.

3. Results and discussion

The transient of friction coefficient and initial (at first cycle) and steady state (at last cycle) friction coefficient of PVA-hybrid gels were shown in Figs.4 and 5. Friction coefficient of PVA-hybrid gel prepared by drying process at $T$ of 8°C and $H$ of 50%RH (Sample A) gradually increased such as above 0.25. PVA-hybrid gel prepared by drying process at $T$ of 8°C and $H$ of 60%RH (Sample B) showed lower friction coefficient than sample A but friction coefficient gradually increased and reached 0.04. PVA-hybrid gel prepared by drying process at $T$ of 8°C and $H$ of 50%RH (Sample C) showed the lowest friction coefficient in PVA-hybrid gels prepared by single-drying process. However, friction coefficient of sample C also gradually increased with sliding distance. When the additional drying process at $T$ of 20°C and $H$ of 50%RH after the drying process at $T$ of 8°C and $H$ of 50%RH was provided (sample D), friction coefficient rapidly increased immediately after starting test and reached 0.04. The sample E that was prepared by two-stage drying process ($T$ of 20°C and $H$ of 40%RH after the drying process at $T$ of 8°C and $H$ of 50%RH) showed extremely low friction coefficient such as 0.006 and kept it during the test. Only sample E could keep low friction coefficient such as below 0.01 from initial to steady state in friction test.

The microscopy images of worn surface of PVA-hybrid gels (in air) are shown in Fig. 6. The samples A, B, D completely lost their intact surface structure after friction test. Surface damage of the sample C was milder than those of the samples A, B and D, but intact surface structure of the sample C did not remain. As shown in Figs. 6(i,j), surface damage of the sample E was slight and intact surface structure remained after friction test.

The atomic force microscope (AFM) images of the intact surface of the sample C, D and E (in water) are
shown in Fig. 7 and water content of these PVA-hybrid gels are listed in Table 2. PVA-hybrid gels that showed high friction (sample C and D) have fibrous structure and PVA-hybrid gel that showed extremely low friction (sample E) has quite smooth structure. The arithmetic average roughness (Ra) in micron-scale region of the sample E is two-ordered lower than those of the sample C and D. The water contents of these three PVA-hybrid gels are almost the same level. These results indicated that the additional drying process mainly influence on the structure of the superficial layer of PVA-hybrid gel.

The structure of superficial layer of PVA-CD gel and PVA-hybrid gels was a key to the extremely low friction property, and the results in this study indicated that two-stage drying process with higher temperature and lower relative humidity as the second drying stage is effective to reduce friction and reinforce the surface of PVA-hybrid gel. It is indicated that non-cross-linked polymers elute from hydrogel during the swelling process [23,24]. We proposed a model for the surface of PVA-hybrid gel that showed poor or excellent friction and wear properties as shown in Fig. 8. The parts of non-cross-linked PVA molecular chains protrude from superficial layer of swollen PVA-hybrid gels, and those molecular chains retain water and form hydration layer. This layer contributes to the reduction of friction (especially initial state friction coefficient) by the similar effect of surface-gel hydration lubrication [25]. However, the superficial layer mainly formed by non-cross-linked or low extent cross-linked PVA molecules does not have enough wear resistance. Therefore, by applying repeated frictional load, this layer would be gradually worn out and friction increased with sliding distance as shown in PVA-hybrid gels except for sample E. If the appropriate additional drying process with higher temperature and lower humidity is applied, cross-linking points between PVA molecules protruded from the superficial layer of PVA-hybrid gel increased and superficial structure is reinforced. This contributes to the improvement of the wear resistance of superficial lubricious layer of PVA-hybrid gel, and thus extremely low friction will be maintained for long term. Drying speed of sample D was lower than that of sample E because of higher relative humidity. It is indicated that low-speed drying leads to the growth of micro-crystalline structure and reinforcement of cross-linking in PVA-CD gel [20]. It is considered that extent of cross-linking in sample D is higher than that of sample E. If excess cross-linking is applied, protruding of PVA molecules was reduced and superficial hydration layer is not sufficiently formed. It is considered that this will lead the degradation of friction and wear properties of PVA-hybrid gel. The microscopic roughness of sample D is two-ordered higher than that of

Table 2 Water content of PVA-hybrid gels (n = 5, Values: average ± standard deviation)

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<th>Sample C</th>
<th>Sample D</th>
<th>Sample E</th>
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<tr>
<td>Water content [%]</td>
<td>72.2 ± 1.9</td>
<td>70.1 ± 0.5</td>
<td>71.9 ± 0.7</td>
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sample E. It is considered that the local contact pressure was increased and wear of superficial layer of sample D progressed.

The details of the mechanism of the excellent lubrication property of PVA-hybrid gel prepared by two-stage drying process have not been elucidated. The superficial structure, surface and bulk properties of PVA-hybrid gels (adhesivity, viscoelasticity, hydraulic permeability) should be researched in the next study, and preparation condition would be optimized to obtain PVA-hybrid gel with extremely low friction and minimum wear.

4. Conclusion

In this study, friction and wear properties of the newly-developed PVA-hybrid gels were evaluated in reciprocating friction test. It is indicated that the tribological property of PVA-hybrid gel is influenced by the temperature and relative humidity during preparation process, and the two-stage drying process for changing the drying speed at the latter half during preparation of PVA-hybrid gel contributes to obtaining the surface layer with extremely low friction and minimum wear.

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References


