WEAR REDUCTION BY FUNCTIONAL PROTEIN BOUNDARY FILM ON POLY(VINYL ALCOHOL) HYDROGEL

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ABSTRACT
Poly(vinyl alcohol) (PVA) hydrogel is a candidate material for artificial cartilage of joint prostheses. From previous researches[1-4] it is shown that the wear of PVA hydrogel depends on the concentration of proteins in lubricants. Therefore it is considered that the adsorbed film formation by protein of albumin or γ-globulin influences upon the wear grade of PVA hydrogel. The remaining film of proteins on the glass plate was observed in fluorescence microscope. The adsorption condition of albumin and γ-globulin was different. The adsorbed film with effective reduction of the wear showed cooperative stratification of albumin and γ-globulin, but the condition of increased the wear showed separation of albumin and γ-globulin. Consequently, to reduce the wear of PVA hydrogel, cooperative stratification layers are effective.

1. INTRODUCTION
PVA hydrogel is soft material containing high content of water and has low elastic modulus similar to articular cartilage. Therefore it is anticipated to form enough fluid film. Low friction is actualized by soft EHL under mild operating condition, however, under thin film condition such as mixed or boundary lubrication the wear will make rapid progress. Then authors investigated the wear of PVA hydrogel against itself under the severe conditions[1-4]. As a result, it was shown that the wear depends on the proteins contained in lubricants, i.e., albumin and γ-globulin that are contained in natural synovial fluid. The hyaluronate solution containing proteins as the ratio of albumin and γ-globulin (AG ratio) at 1/2 or 2/1 was effective in the wear reduction at total protein content of 2.1wt%. The excessive protein concentration of 2.8wt% increases the wear. Therefore it is possible to reduce the wear by changing content of protein in lubricants. To consider the effect of the wear resistance of the functional boundary film, atomic force microscopy (AFM) measurements were applied after friction tests of sliding pair of PVA hydrogel and glass plates[4]. Glass plates were applied because of the difficulty in the observation of PVA hydrogel under AFM measurement. It seemed that the adsorptive force of γ-globulin was stronger than that of albumin. However, AFM images showed only height information. Therefore, fluorescent staining techniques were used to discriminate the type of proteins.

2. EXPERIMENTAL METHOD
Proteins of γ-globulin and albumin were stained with FITC (Fluorescein-isothiocyanate) and RITC (Rhodamine B-Isothiocyanate) respectively before being mixed in the lubricants. The lubricants tested in this study are shown in Table 1. The concentration of proteins was picked out from the map of the wear grade [3]. The lubricants were tested in a reciprocating wear tester. After the wear test, glass plates were observed in a fluorescence microscope. The remaining film on the glass plate was divided as 3 layers, i.e., the surface, the middle and the deep layers.

3. RESULT AND DISCUSSIONS
The fluorescent images of Lubricants A and B are shown in Figs. 1 and 2. The lubricant containing only albumin showed thin adsorbed layer on glass plate and γ-globulin adsorbed thickly. It is considered in these conditions that the adsorption strength of albumin is weaker than that of γ-globulin.

The results of the condition with the effective wear reduction at AG ratio 1/2 are shown in Fig.3, where glass plate was covered with γ-globulin generally and cohesive albumin adsorbed on γ-globulin layer. Therefore it is
Table 1 Tested lubricant

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Albumin (wt%)</th>
<th>γ-globulin (wt%)</th>
<th>AG ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.7</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>1.4</td>
<td>0.7</td>
<td>2/1</td>
</tr>
<tr>
<td>D</td>
<td>1.05</td>
<td>1.05</td>
<td>1/1</td>
</tr>
<tr>
<td>E</td>
<td>1.4</td>
<td>1.4</td>
<td>1/1</td>
</tr>
</tbody>
</table>

Figure 1. Fluorescent images of lubricant A (from left to right: surface, middle and deep layer)

Figure 2. Fluorescent images of lubricant B (from left to right: surface, middle and deep layer)

Figure 3. Fluorescent images of lubricant C (upper: albumin, lower: γ-globulin, from left to right: surface, middle and deep layer)

Figure 4. Fluorescent images of lubricant D (upper: albumin, lower: γ-globulin, from left to right: surface, middle and deep layer)

Figure 5. Fluorescent images of lubricant E (upper: albumin, lower: γ-globulin, from left to right: surface, middle and deep layer)

 indicated that γ-globulin is effective to protect PVA hydrogel from the wear and albumin plays a part of low shear.

Lubricant D (Fig. 4) containing same quantity of proteins showed more wear than lubricant C. γ-globulin layer was a little detected in the deep layer. Hence the wear will increase compared with lubricant C.

In lubricant E (Fig. 5) containing 2.8wt% of proteins, very thick layer was formed, and albumin and γ-globulin adsorbed separately. The wear was increased due to excessively thick adsorption layer and the lack of low shear layer under this condition.

4. CONCLUSIONS

It is supposed that albumin and γ-globulin adsorbed in different structure. It is indicated that the difference of adsorption is capable of controlling the roles for friction and wear. It is in need of the cooperative stratification layers to reduce the wear of PVA hydrogel.


