Friction Properties of Laminated Composite Materials of Alpha-Tricalcium Phosphate–Filled Poly (Vinyl Alcohol) Hydrogels

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The aim of this study was to examine the mechanical characteristics of a polyvinyl alcohol hydrogel (PV A-H) as a candidate material for artificial joint cartilage. In the study, PV A-H was filled with α-tricalcium phosphate (α-TCP) in order to improve its mechanical properties. In addition, laminated composite materials with 3 layers were prepared by laminating α-TCP–filled PV A-H and unfilled PV A-H. The samples were prepared with different numbers of repeated freeze–thaw cycles and several concentrations of α-TCP. Compression tests and friction tests were carried out to investigate the mechanical and friction properties of the PV A-H. The results of the tests showed that the compressive modulus and the friction coefficient of the α-TCP–filled PV A-H were higher than those of the unfilled PV A-H. Thus, α-TCP was found to be effective in reinforcing the PV A-H. In the friction tests, the friction coefficient of the laminated material was approximately equal to the values of the unfilled PV A-H. Furthermore, the compressive moduli of the laminated materials that underwent 5 and 7 freeze–thaw cycles improved to a level equal to that of the α-TCP–filled PV A-Hs. Therefore, the lamination of PV A-H made it possible to achieve both a low friction coefficient and high compressive strength.

Keywords: polyvinyl alcohol hydrogel, friction coefficient, Stribeck curve, laminated composite material, alpha-tricalcium phosphate, hydroxyapatite

1. Introduction

In recent years, there has been an increase in the number of patients with knee joint diseases or disorders such as knee osteoarthritis, rheumatoid arthritis and others. Total joint replacement is an effective treatment method for patients with severe disorders. Generally, the combinations of materials in current use for artificial joints are ultra-high-molecular-weight polyethylene and a metal or ceramic [1]. Because the friction surface of the materials is a boundary lubrication state, the friction force is large and wear occurs, leading to loosening of the artificial joint and the potentially detrimental influence of wear debris on biological cells. Therefore, the use of polyvinyl alcohol hydrogels (PVA-Hs) as the friction surfaces of artificial joints has been proposed to reduce friction and wear [2-7]. PVA is known to be a biocompatible material. PVA-Hs have a low friction coefficient and their mechanical properties are similar to those of natural cartilage. A PVA-H is a soft material that has elasticity, and it is therefore expected that the lubrication state of the friction surfaces of the joint would shift closer to a hydrodynamic lubrication state by using a PVA-H [4]. However, the mechanical strength of PVA-H is lower than that of natural cartilage. To reinforce the PVA-H, it is effective to fill it with fine particles such as hydroxyapatite (HAp), which is often used [6, 7]. HAp is a bioactive ceramic with a crystal structure similar to that of natural bone and is used as a bone repair material in medical fields [8]. In addition, the mechanical and friction properties of the PVA-H is affected by the concentration, polymerization, saponification of PVA [9], and the number of freeze–thaw cycles in the preparation of the PVA-H [7, 10-12].

In the present study, PVA-H was filled with α-tricalcium phosphate (α-TCP) to improve its mechanical properties. α-TCP is also a bioactive ceramic [13], and it transforms into HAp crystals when heated in hot water and hydrolyzed [14]. Moreover,
Laminated composite materials were prepared by laminating \( \alpha \)-TCP–filled PVA-H and unfilled PVA-H to achieve both low friction and high strength. The samples were prepared with different numbers of freeze–thaw cycles and several concentrations of \( \alpha \)-TCP. Compression tests and a friction tests were carried out to examine the mechanical and friction properties of the samples.

2. Materials

2.1. Preparation of PVA-H

PVA powder with a polymerization degree of 2,000 and a saponification degree of 98 mol% or more was used to prepare PVA-H samples. \( \alpha \)-TCP (\( \text{Ca}_3(\text{PO}_4)_2 \)) was pulverized to a particle size of 5-10 \( \mu \)m in a mortar. The PVA concentration of the samples was 15 mass% and several concentrations of \( \alpha \)-TCP powder were added. The sample preparation conditions are shown in Table 1. Hereafter, samples with \( \alpha \)-TCP concentrations of 0, 1.5, and 3 mass% are called unfilled PVA-H, \( \alpha \)-TCP–1.5 mass%–filled PVA-H, and \( \alpha \)-TCP–3 mass%–filled PVA-H, respectively.

The PVA powder and \( \alpha \)-TCP were mixed with pure water and the mixture was continuously stirred and heated at 95°C for 90 minutes to obtain PVA aqueous solution. The solution was then sandwiched between two glass plates to form it into a sheet for the friction test, and was poured into a column mold for the compression test. The thickness of the sheet was maintained by spacers between the glass plates. The solution was gelated by alternately repeating a freezing process at \(-23°C\) and a thawing process at 3.5°C several times. In the present study, the freezing time was 24 hours and the thawing time was 8 or 12 hours to make samples for the friction test or the compression test, respectively.

2.2. Preparation of laminated material

The laminated material had three layers: unfilled PVA-H, \( \alpha \)-TCP–1.5 mass%–filled PVA-H, and \( \alpha \)-TCP–3 mass%–filled PVA-H. The first layer, unfilled PVA-H, was used as a friction surface in the friction test. To prepare the laminated material, the PVA solution of the first layer was poured into the mold and was frozen and thawed once. Then the second layer, \( \alpha \)-TCP–1.5 mass%–filled PVA-H, was poured onto it and the material was frozen and thawed again. The third layer, \( \alpha \)-TCP–3 mass%–filled PVA-H, was processed in the same way, and finally the material was frozen and thawed several times to produce the laminated PVA-H sample. The sample for the friction test was formed into a sheet with a thickness of 3 mm by spacers with a thickness of 1 mm for each layer. The sample for the compression test was formed into a column with a thickness of 12.5 mm (i.e., the thickness of each layer was approximately 4.2 mm) and a diameter of 29 mm on the basis of JIS (Japanese Industrial Standards) K6254. The number of freeze–thaw cycles for each layer of the samples is shown in Table 2. Cross-section images of the laminated material are shown in Figs. 1 and 2.

2.3. Transformation of \( \alpha \)-TCP

Figure 3(a) shows the pulverized \( \alpha \)-TCP and Fig. 3(b) shows the \( \alpha \)-TCP particles after heating in hot pure water at 95°C for 90 minutes. As shown in these figures, the \( \alpha \)-TCP transformed into needle-like HAp. Figure 4(a) shows the fracture surface of the \( \alpha \)-TCP–filled PVA-H sample frozen and broken by liquid.
nitrogen. The dispersing particles grew into needle-like shapes and entangled with the PVA-H. Therefore, the $\alpha$-TCP heated in the PVA aqueous solution was found to transform into HAp. Figure 4(b) shows the fracture surface of the $\alpha$-TCP–filled PVA-H after a tensile test. The particles were covered by the PVA-H without exposing the fracture surface.

3. Experimental method

3.1. Compression test

Compressive modulus was measured to research the mechanical properties of the PVA-H samples on the basis of JIS K6254. The shape of the samples was a column with a diameter of 29 mm and a thickness of 12.5 mm. Three samples were prepared for each preparation condition. The test was conducted with a tension and compression testing machine (LSC-1 / 300-2, Tokyo Testing Machine, Inc.) at room temperature (23°C). The compression speed was 10 mm/min. The compression was repeated 4 times for each sample and the compressive modulus at 60% strain was obtained from the 4th stress-strain curve.

3.2. Friction test

The friction coefficient was measured using a ball-on-disk tribometer as shown in Fig. 5 under the experimental conditions shown in Table 3. A PVA-H sheet with a thickness of 3 mm was used as the friction surface. Various counterparts were used as shown in Fig. 6: high-carbon chromium bearing steel balls (SUJ2 (in JIS), AISI 52100) with diameters of 20 mm and 30 mm, the same PVA-H sheet as the friction surface with a thickness of 3 mm fixed to a pin with a radius of curvature of 50 mm. The sample was rotated repeatedly on a friction track with a diameter of 37.5 mm at a constant sliding speed and a constant normal load. The test was conducted at room temperature (23°C). The friction force was measured by using the parallel leaf spring and the strain gauge. The friction surface was lubricated by pure water at room temperature. In the tests of the laminated materials, the unfilled layers were in contact with each other as the friction surface and the counterpart. The friction coefficient was calculated from the normal load and the average friction force.
4. Results

4.1. Compression test

The stress-strain curve of the unfilled PVA-H is shown in Fig. 7. Similar stress-strain curves were obtained from all other samples. Stress increased with increasing strain and decreased with increasing numbers of compressions. Figure 8 shows the relationship between the number of freeze–thaw cycles and the compressive modulus of the unfilled PVA-H, the \( \alpha \)-TCP–1.5 mass%–filled PVA-H, the \( \alpha \)-TCP–3 mass%–filled PVA-H, and the laminated material. In all samples, compressive modulus increased with increasing numbers of freeze–thaw cycles. The \( \alpha \)-TCP–3 mass%–filled PVA-H showed higher compressive modulus than the unfilled PVA-H in all freeze–thaw cycles. The modulus of the \( \alpha \)-TCP–1.5 mass%–filled PVA-H and the laminated material was higher than that of the unfilled PVA-H at 7 freeze–thaw cycles. These results suggest that filled \( \alpha \)-TCP may have a reinforcing effect. The details of this effect will be described in the Discussion section below. The modulus of the laminated material was lower than that of all single-layer samples at 3 freeze–thaw cycles, however, at 5 and 7 cycles, the modulus grew rapidly and increased to a point approximately equal to the moduli of the \( \alpha \)-TCP–filled PVA–Hs. The reason for this seems to be that the number of freeze–thaw cycles of the \( \alpha \)-TCP–filled layers of the second and third layers were less than the unfilled PVA-H of the first layer.

4.2. Friction test

4.2.1 Friction test with various counterparts

Stribeck curves obtained from the friction test between the laminated material and the chromium steel balls with diameters of 20 mm and 30 mm are shown in Figs. 9 and 10, respectively. The friction coefficient
against the chromium steel ball with a diameter of 20 mm was higher than that against the chromium steel ball with a diameter of 30 mm. The lubrication state of all samples seems to be a mixed lubrication because the Stribeck curves fall to the right. The Stribeck curves obtained from the test between the laminated materials are shown in Fig. 11. Since the friction coefficients draw downwardly convex curves, the lubrication state seems to shift from mixed lubrication to hydrodynamic lubrication. The radii of curvature of the chromium steel balls with diameters of 20 mm and 30 mm and the PVA-H sheet fixed to the pin are 10, 15, and 50 mm, respectively. It is considered that the contact area between a PVA-H sheet sample and a counterpart might be increased with increasing radius of curvature of the counterpart. Therefore, based on these results, increasing the contact area might yield hydrodynamic lubrication and a low friction coefficient. The laminated material that underwent 3 freeze–thaw cycles showed the lowest friction coefficient (approximately 0.03) with all counterparts. In the compression test, the laminated material that underwent 3 freeze–thaw cycles showed the lowest compressive modulus. Therefore, since this low modulus material might be easily deformed by an applied load and because the contact area could increase, the laminated material should show a low friction coefficient.

4.2.2 Friction test with PVA-H samples

Stribeck curves obtained from the friction test between identical materials are shown in Figs. 11-14. Since most Stribeck curves draw downwardly convex curves, the lubrication state of the PVA-H samples seems to be in a state between hydrodynamic lubrication and mixed lubrication. The friction coefficient of the laminated materials was approximately equal to the value of the unfilled PVA-H. Since an unfilled layer was used as the material of the friction surfaces in the friction test of both the single-layer unfilled PVA-Hs and the laminated materials, their friction conditions seemed to be similar. The laminated material that underwent 3 freeze–thaw
cycles showed the lowest friction coefficient at 0.024 to 0.057 (Fig. 11). In the compression test, the compressive modulus of the laminated material was lower than that of the unfilled PVA-H at 3 freeze–thaw cycles. Therefore, since the contact area of the laminated materials might be larger than that of the unfilled PVA-Hs, the laminated material should show a lower friction coefficient than the unfilled PVA-H, although the unfilled layers were in contact with each other in both friction tests. The α-TCP–filled PVA-H showed a higher friction coefficient than the unfilled PVA-H and the laminated material. Greater detail regarding the results of the α-TCP–filled PVA-H will be provided in the Discussion section below.

5. Discussion

5.1. Effect of filling with α-TCP

The results of the compression tests suggest that filling with α-TCP is effective in reinforcing PVA-H. Because the interface between PVA-H and HAp transformed from α-TCP was not split, as shown in Fig. 4, PVA-H appears to be reinforced owing to its strong binding with the transformed α-TCP. However, at 3 and 5 freeze-thaw cycles, α-TCP–filled PVA-H showed no clear reinforcing effect. This lack of reinforcing effect might be attributed to α-TCP particles serving as defects in PVA-H when the compressive modulus of PVA-H is insufficient, thereby decreasing the strength of the material.

In the friction tests, the α-TCP–filled PVA-H showed higher friction coefficients than the unfilled PVA-H, possibly because α-TCP particles were exposed at the surface of PVA-H by wear and the particles might have scratched the counterpart. An SEM image of the surface of the α-TCP–filled PVA-H after the friction test is shown in Fig. 15. The upper part of the image is outside the wear track, while the lower part is inside the wear track. Outside the wear track, the surface of the material is covered by PVA-H. However, inside the wear track, the material has been worn and α-TCP particles are exposed at the surface.

As shown in Figs. 12-14, the tendencies of the Strubeck curves were affected by α-TCP concentrations. The inclinations of the curves of the unfilled PVA-H were smaller than those of the other samples; thus, the lubrication state of the unfilled PVA-H should be kept constant even when the load and the sliding speed of the friction surface change. The minima of the curves between the mixed lubrication and the hydrodynamic lubrication shifted, and the lubrication state appeared to change according to α-TCP concentrations. We assumed that these results might be caused by changes in the surface roughness, the contact area and the mechanical properties of PVA-H by filling with α-TCP, specifically, changes in the compressive modulus and the viscoelasticity. These results suggest that control of α-TCP concentration was effective in changing the friction properties of PVA-H. The real reason for the changes in the lubrication state could not be confirmed at the present study; further investigations are necessary to clarify the mechanism.

5.2. Effect of laminating

In the friction tests, the friction coefficient of the laminated materials was approximately equal to the value of the unfilled PVA-H. Moreover, in the compression tests, the compressive modulus of the samples that underwent 5 and 7 freeze–thaw cycles improved to a level approximately equal to that of the α-TCP–filled PVA-H. Therefore, laminating PVA-H was found to be effective in achieving both a low friction coefficient and a high compressive strength.

Finally, in the present study, pure water was used as the lubricant in the friction tests in order to avoid any influence of the lubricant on the water content ratio of the PVA-H. However, it is possible that the friction coefficient might be reduced if a high-viscosity liquid such as synovial fluid were used as the lubricant because a high-viscosity lubricant easily forms a fluid film and hydrodynamic lubrication could thus easily occur.

6. Conclusions

PVA-H and laminated composite materials were prepared with different numbers of freeze–thaw cycles and various concentrations of α-TCP to improve their mechanical and friction properties. Compression and friction tests were carried out. The conclusions reached in this study are as follows:

1. Laminated materials composed of PVA-Hs with different α-TCP concentrations were obtained.
2. Compressive modulus was found to increase with increasing numbers of freeze–thaw cycles.
3. The laminated materials showed the lowest friction coefficient of approximately 0.03.
4. Compressive modulus and the friction coefficient
were increased by filling the PVA-H with α-TCP. In the compression tests, filling the PVA-H with α-TCP was found to be an effective way of reinforcing the PVA-H. Additionally, the lamination of PVA-H layers with different α-TCP concentrations was found to be effective in achieving both a low friction coefficient and a high compressive strength.

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References