

Mechanical Interaction between Vitamin E-Containing Ultrahigh Molecular Weight Polyethylene and Co-28Cr-6Mo Alloy in Water*

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Abstract

The mechanical interaction between ultrahigh molecular weight polyethylene (UHMWPE) and a Co-28Cr-6Mo alloy in water was examined in order to clarify the wear resistance mechanism of vitamin E-containing UHMWPE in knee prostheses. The sample UHMWPE was pressed and rubbed against the surface of the Co-28Cr-6Mo alloy in water by using a computer-controlled pin-on-disk wear test apparatus. The formation of a UHMWPE transfer film on the surface of the Co-28Cr-6Mo alloy was reduced by the addition of vitamin E to UHMWPE. The pull-away force between UHMWPE and the Co-28Cr-6Mo alloy was also reduced by the addition of vitamin E. These results suggest that vitamin E reduces the attraction between UHMWPE and the surface of the Co-28Cr-6Mo alloy.

Key words: Ultrahigh Molecular Weight Polyethylene (UHMWPE), Vitamin E (dl- α -Tocopherol), Wear, Transfer Film Formation, Pull-Away Force

1. Introduction

Ultrahigh molecular weight polyethylene (UHMWPE) is a material commonly used as a bearing surface in total joint arthroplasty due to its several excellent properties, such as chemical stability and high resistance to shock and wear. Despite all these advantages, UHMWPE implants impose limitations on the lifetime of artificial knee joints due to the occurrence of wear and delamination fractures^(1,2). In this regard, UHMWPE containing vitamin E (dl- α -Tocopherol), which is an antioxidant agent, was developed in order to prevent the appearance of delamination fractures, and is reported to prevent crack initiation at subsurface grain boundaries of UHMWPE⁽³⁾. Delamination fractures are a kind of fatigue failure accelerated by oxidation, and have often been observed in UHMWPE knee prosthesis components⁽⁴⁾.

On the other hand, it is believed that osteolysis and subsequent aseptic loosening are due to biological reactions involving UHMWPE wear debris^(5, 6). Therefore, the wear resistance of UHMWPE is an important property for extending the longevity of knee prostheses. We have reported that the wear volume of vitamin E-containing UHMWPE tested with a knee joint simulator was approximately 30% lower than that of virgin UHMWPE at 5 million cycles⁽⁷⁾. Performing wear resistance tests using a joint simulator is currently believed to be one of the appropriate methods for estimating the longevity of joint prostheses due to the implementation of biomimetic frictional settings for in-vitro wear, and thus we consider that the wear resistance of UHMWPE is improved by the addition of vitamin E. However, the wear resistance mechanism of vitamin E-containing UHMWPE has not yet been clarified.

UHMWPE wear in the body is a complex phenomenon affected by several mechanisms such as protein adsorption. However, the direct mechanical interaction between UHMWPE and the Co-28Cr-6Mo alloy might play an important role in the formation of wear particles. The formation of a transfer film is believed to be one of the dominant early-phase direct mechanical interactions contributing to the wear⁽⁸⁾, and the process is affected not only by the mechanical properties of the materials, but also by the attraction between the surfaces⁽⁹⁻¹¹⁾. The present study examined the effects of vitamin E addition on the formation of a UHMWPE transfer film at the Co-28Cr-6Mo alloy surface, as well as the pull-away force between UHMWPE and the Co-28Cr-6Mo alloy as a fundamental approach to clarifying the wear resistance mechanism of vitamin E-containing UHMWPE.

2. Materials and Methods

2.1. Preparation of specimens

UHMWPE resin powder (GUR1050, Ticona, USA) was mixed with vitamin E (dl- α -Tocopherol, Eisai, Japan) at 0.3 wt% using a screw cone mixer (LFS-GS-2J, Fukae Powtec, Japan). The vitamin E-containing UHMWPE board was manufactured using direct compression molding at 220 °C under 25 MPa for 30 min. The virgin UHMWPE board, which is used as the control material in this study, was manufactured in the same way without the addition of vitamin E. Conical pin specimens with a 1 mm diameter flat sliding surface were machined from the UHMWPE boards and were subjected to ultrasonic-immersion cleaning in isopropyl alcohol (50 vol%, Amakasu Chemical Industries, Japan) at room temperature for 15 minutes. In addition, disk specimens comprising a highly polished 8 mm diameter flat sliding surface ($R_a < 0.01 \mu\text{m}$), were machined from a Co-28Cr-6Mo alloy ingot and subjected to ultrasonic-immersion cleaning in acetone (99.5 vol%, Nacalai tesque, Japan) at room temperature for 15 minutes. All manufacturing and cleaning procedures were conducted in air, and no sterilization was carried out prior to the testing.

The surface roughness of the vitamin E-containing and virgin UHMWPE pin specimens were measured on the basis of international standards (JIS B 0601:2001). The roughness value (R_a) for these specimens was $0.077 \pm 0.014 \mu\text{m}$ and $0.094 \pm 0.011 \mu\text{m}$, respectively, where the comparison showed no statistically significant differences.

2.2. Pin-on-disk transfer test

The UHMWPE transfer test was carried out using a computer-controlled pin-on-disk wear test apparatus (Ys-TRIB-01, SANKI, Japan), as shown in Figure 1. All tests were conducted at room temperature inside the clean bench (Ys-Class5, SANKI, Japan), which provides an air cleanliness exceeding ISO Class 5 for the purpose of avoiding contamination with air dust particles. The pin specimens (vitamin E-containing or virgin UHMWPE) were kept within the holder. The load was applied to the pin holder through a

helical compression spring in order to avoid fluctuating loads and plastic deformation of the pin specimens during the wear tests. The contact stress on the sliding surface was consecutively set to 10, 20, and 30 MPa. The disk specimen, made of Co-28Cr-6Mo alloy, was kept within the holder fixed on the X-stage, and was set into linear reciprocating sliding motion for 5,000 cycles, with an amplitude of 1 mm and a frequency of 1 Hz. Ultrapure water (Arium611VF, Sartorius, Germany) was used as a lubricant. The lubricant bath was filled with 5 ml of lubricant, which was kept at a temperature of 37 °C and was replenished at a rate of 2 ml per 2,500 cycles during the tests due to its gradual evaporation. The tested disk specimen was subjected to an immersion-cleaning procedure in ultrapure water before observing the UHMWPE transfer film which formed on the disk surface after the transfer test. The actual micrograph of the Co-28Cr-6Mo alloy surface after the transfer test is shown in Figure 2.

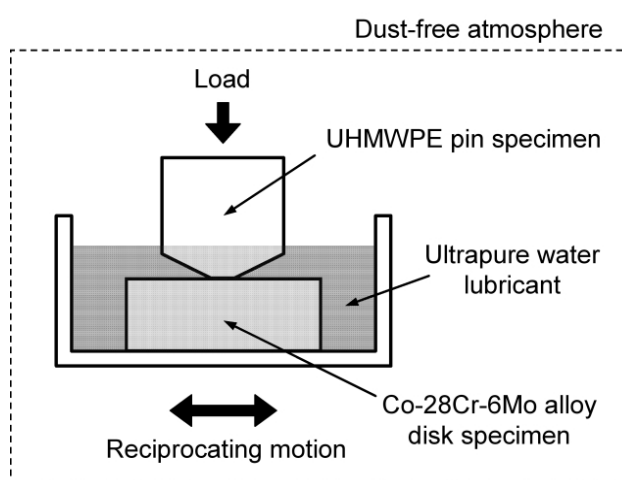


Fig. 1 A schematic drawing of the transfer test apparatus.

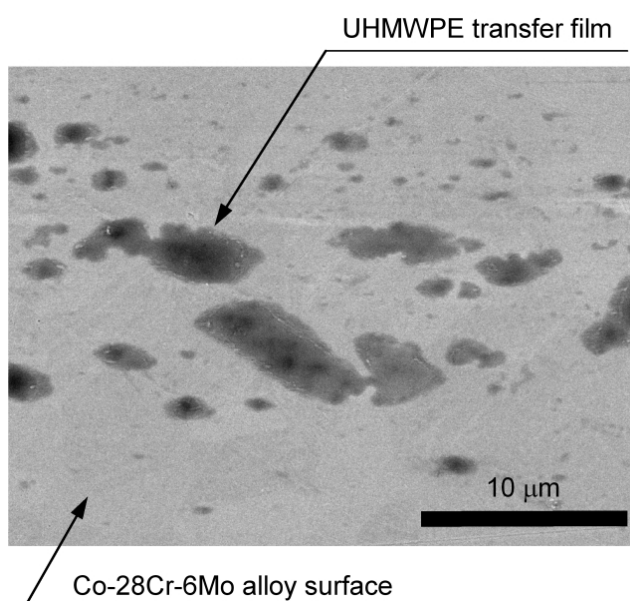


Fig. 2 Scanning electron micrograph of the Co-28Cr-6Mo alloy surface after the transfer test.

2.3. Quantification of the transfer film

The quantification of the UHMWPE transfer film formed on the disk specimen surface was performed as shown in Figure 3. The tested disk specimen was observed under a digital microscope (VHX-900, KEYENCE, Japan) at 300-fold magnification, and was photographed as an 8-bit grayscale image. The central part of the sliding region ($0.5 \times 0.5 \text{ mm}^2$ at a resolution of 500×500 pixels) was acquired, and all pixels were classified in accordance to their brightness value. The histogram took the form of a bell-shaped curve with a more gradual slope in the low brightness regions in comparison to the high brightness ones. This slightly more gradual slope was assumed to be the result of the adhesive substance produced by the reciprocating slide of the specimens, thus defined as the apparent transfer film. The apparent transfer film region and the background region were digitalized using the threshold value of brightness. The threshold value in the brightness histogram was determined by subtracting the difference of the mode value and the maximum value from the mode value. The quantification of the UHMWPE transfer film was defined as the ratio of the apparent transfer film region to the acquired whole image. In this study, ImageJ (NIH, Bethesda, MD) was used for the image processing.

2.4. Measurement of the pull-away force

The measurement of the pull-away force between UHMWPE and the Co-28Cr-6Mo alloy was carried out using the computer-controlled vertical force measuring apparatus (Ys-ADHES-01, SANKI, Japan) shown in Figure 4, and the actual output signal of the load cell during pull-away force measurement is shown in Figure 5. The vitamin E-containing and the virgin UHMWPE pin specimens were vertically pressed against the Co-28Cr-6Mo

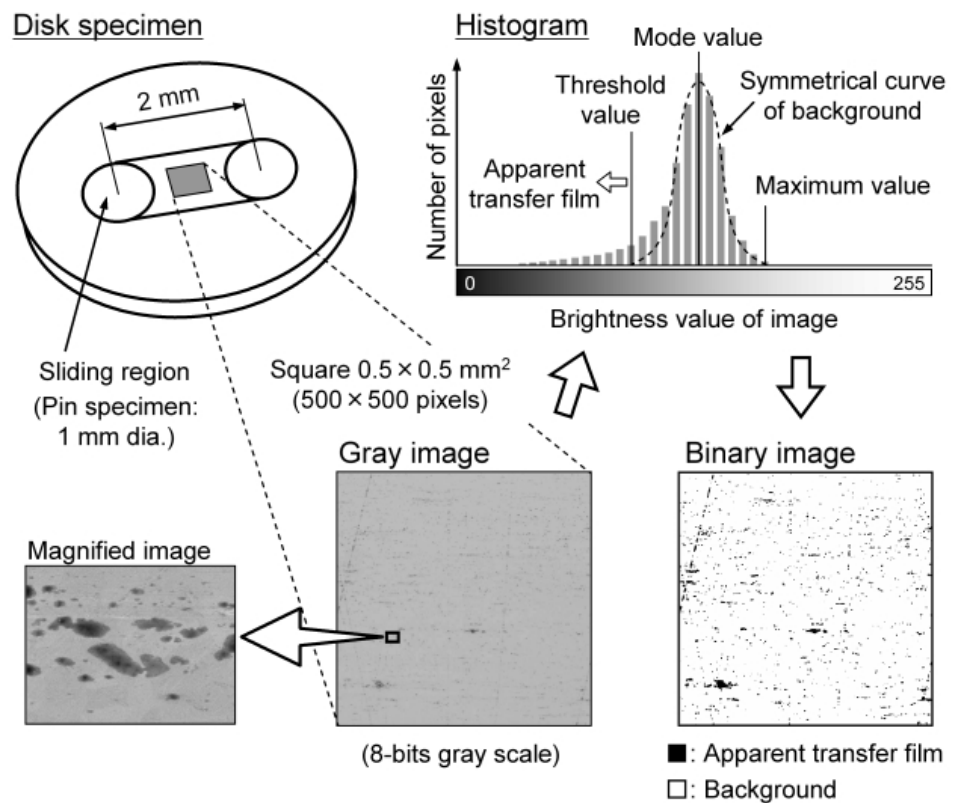


Fig. 3 Quantification procedure for the UHMWPE transfer film formed on the Co-28Cr-6Mo alloy surface.

alloy disk specimen in an ultrapure water droplet, and the pressing load was gradually increased until the contact stress reached 30 MPa. Thereafter, detection of the pull-away force by the load cell was initiated, and the pressing load was gradually decreased until the pin holder was separated from the base plate of the apparatus. The disk specimen was continuously pulled away at a velocity of 2.5 $\mu\text{m/s}$ until the pin and disk specimens were separated. At the moment of separation, the peak force was detected, and the deadweight of the pin specimen with the holder was measured at another moment. The pull-away force is determined as the difference of the peak force and the deadweight.

2.5. Statistical methods

Effects of vitamin E addition and contact stress on the UHMWPE transfer film formed on the Co-28Cr-6Mo alloy surface were analyzed using two-way ANOVA followed by post hoc comparisons.

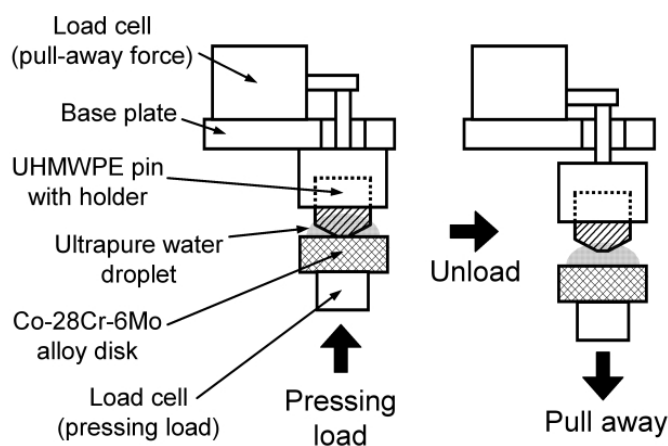


Fig. 4 A schematic drawing of the apparatus and the procedure for measuring the pull-away force between UHMWPE and the Co-28Cr-6Mo alloy.

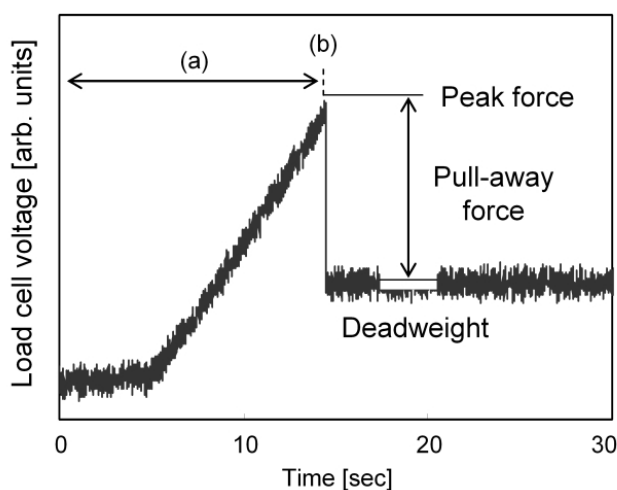


Fig. 5 A typical example of an actual output signal of the load cell during pull-away force measurement between a UHMWPE pin and the Co-28Cr-6Mo alloy disk. The disk specimen is pulled away within (a), and the pin and disk specimens are separated at (b).

3. Results

The apparent region ratio of vitamin E-containing UHMWPE and virgin UHMWPE transfer film formed on the Co-28Cr-6Mo alloy surface at different values for the contact stress are shown in Figure 6. Transfer film formation was increased in accordance with contact stress between 10 MPa and 20 MPa in both specimens. The vitamin E-containing UHMWPE specimen tended to exhibit a transfer film formation approximately 20 to 30% lower than that for the virgin UHMWPE specimen for all contact stress values, and a statistically significant difference was seen at 10 MPa loading.

The pull-away force between vitamin E-containing UHMWPE and the Co-28Cr-6Mo alloy was 4.9 ± 1.7 mN, and that of the virgin UHMWPE was 7.3 ± 2.5 mN (Figure 7). The vitamin E-containing UHMWPE specimen showed a pull-away force which was approximately 30% lower than that for the virgin UHMWPE specimen, and a comparison showed a statistically significant difference.

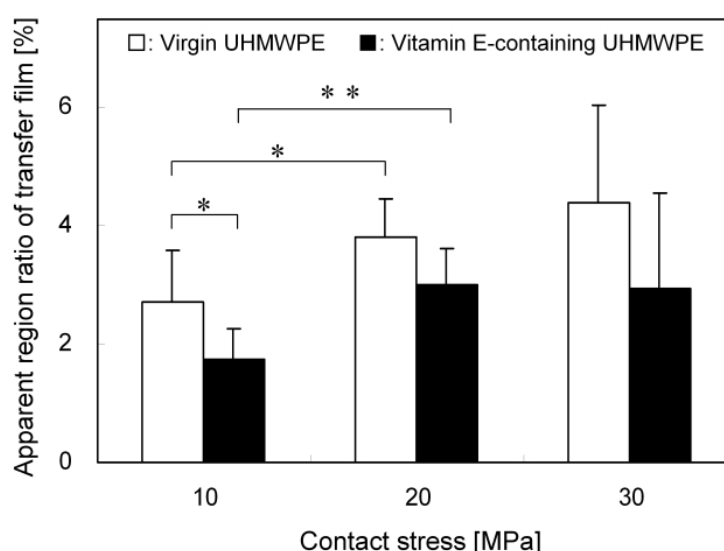


Fig. 6 Apparent region ratio of the UHMWPE transfer film formed on the Co-28Cr-6Mo alloy surface at different contact stress values. Data represent mean \pm SD. Asterisks indicate a statistically significant difference (*; $P < 0.05$, **; $P < 0.01$, $n = 6$).

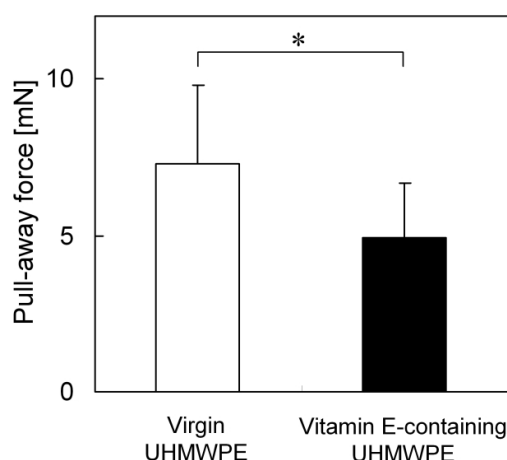


Fig. 7 Pull-away force between UHMWPE and the Co-28Cr-6Mo alloy. Data represent mean \pm SD. Asterisk indicates a statistically significant difference (*; $P < 0.05$, $n = 8$, by student's t -test).

4. Discussion

Our results showed that the formation of a UHMWPE transfer film on the surface of the Co-28Cr-6Mo alloy was reduced by the addition of vitamin E to UHMWPE, regardless of the fact that the surfaces were cleaned by ultrasonic-immersion in isopropyl alcohol. The formation of the transfer film is believed to be one of the dominant early-phase direct mechanical interactions contributing to wear, where the process is affected not only by the mechanical properties of the materials, but also by surface interactions. As the mechanical properties of non-oxidized UHMWPE with or without vitamin E are almost the same⁽¹²⁾, it is likely that some kind of attraction between UHMWPE and the surface of the Co-28Cr-6Mo alloy is changed by the addition of vitamin E.

On the other hand, the oxidation of UHMWPE caused by the combination of free radicals with oxygen, is a well-known process for producing peroxides in UHMWPE. This continuous oxidation process ends due to lack of oxygen and/or as a result of the presence of relatively stable radicals, such as those of vitamin E^(13, 14). If the peroxides on the UHMWPE surface are reduced by the addition of vitamin E, the reduction of the pull-away force between UHMWPE and the Co-28Cr-6Mo alloy might be explained by the effect of vitamin E on the continuous oxidation process.

However, it is considered that the apparatus for measuring the pull-away force detects not only the attractive force between the surfaces, but also the breaking force of the UHMWPE junction at the real contact points. Since scanning electron microscope images confirmed that there were no UHMWPE fragments on the counterface after the pull-away force measurements, we assume that the breaking force contributes very little to the measurement results. It is also possible that vitamin E seeped onto the surface as a result of the applied loading. Further experiments are warranted in order to elucidate this point.

5. Conclusion

The formation of UHMWPE transfer film on the surface of Co-28Cr-6Mo alloy was reduced by the addition of vitamin E to UHMWPE. The pull-away force between UHMWPE and the Co-28Cr-6Mo alloy was also reduced by the addition of vitamin E. These results suggest that vitamin E reduces the attraction between the surfaces of UHMWPE and the Co-28Cr-6Mo alloy.

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