

Evaluation of the Structural and Tribological
Performance of Ultrahigh Molecular Weight
Polyethylene Blended with Vitamin E

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Chapter 1

General Introduction

1.1 Vitamin E-Blended UHMWPE

Ultrahigh molecular weight polyethylene (UHMWPE) is a material commonly used in joint prostheses due to several of its excellent properties such as chemical stability and high resistance to shock and wear. Despite these advantages, UHMWPE implants impose limitations on the lifetime of artificial joints due to the occurrence of delamination fracture and wear [1,2]. Delamination fracture is a kind of fatigue failure accelerated by oxidation, and has often been observed in UHMWPE knee prosthesis components [3]. A photograph of a knee prosthesis is shown in Fig. 1.1, and an example of delamination fracture observed on a retrieved UHMWPE tibial component is shown in Fig. 1.2. UHMWPE blended with vitamin E (*dl*- α -Tocopherol) was developed in order to prevent the appearance of delamination fracture, and has been reported to prevent crack initiation at subsurface grain boundaries in UHMWPE under multidirectional deformation [4]. The manufacturing procedure of vitamin E-blended UHMWPE can be seen in Fig. 1.3.

Femoral component

- Co-28Cr-6Mo alloy
- Ti-6Al-4V alloy

Tibia component

- Ultrahigh molecular weight polyethylene (UHMWPE)

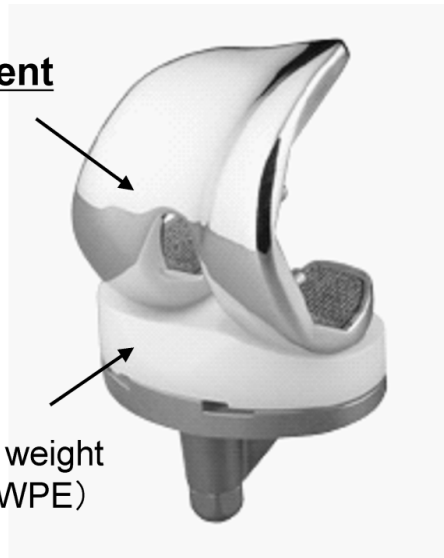
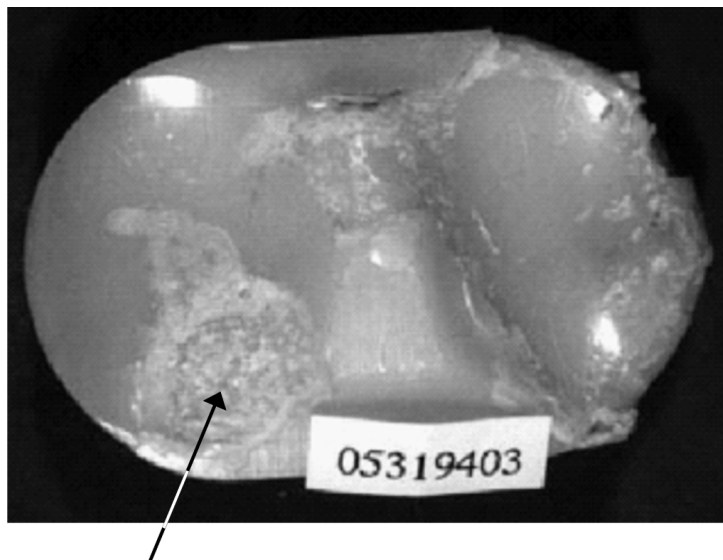


Fig. 1.1 Photograph of a knee prosthesis.



Delamination fracture

Fig. 1.2 Typical example of delamination fracture observed on a retrieved UHMWPE tibial component.

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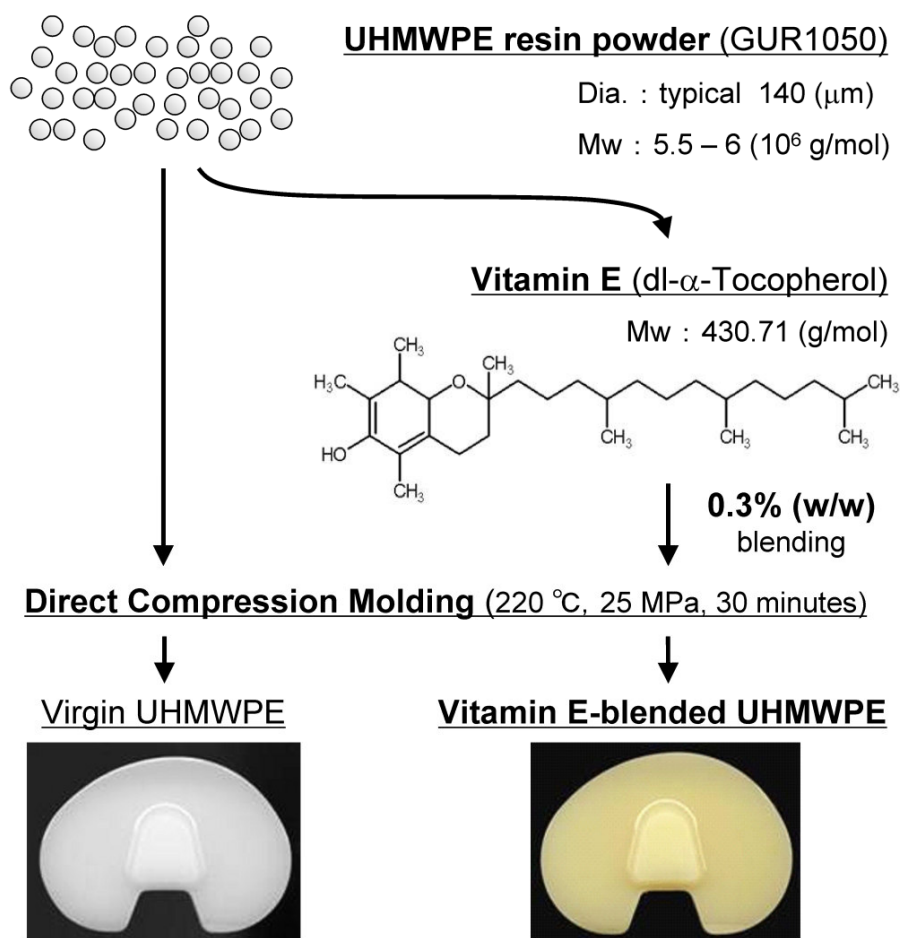


Fig. 1.3 Manufacturing procedure of vitamin E-blended UHMWPE knee component.

Additionally, it is currently believed that osteolysis and subsequent aseptic loosening are due to biological response involving UHMWPE wear debris [5-7]. The UHMWPE wear debris enter the periprosthetic tissue where they are phagocytosed by macrophages. The macrophages then release an array of cytokines and other mediators of inflammation that lead to the development of an inflamed granulomatous tissue adjacent to the bone. Eventually, osteoclasts are recruited and/or activated to resorb the bone leading to osteolysis and eventually loosening of the prosthesis (Fig. 1.4). Therefore, the wear performance of UHMWPE and the biological reactivity to wear debris from UHMWPE are essential properties for extending the longevity of joint prostheses. It has been reported that the wear volume of vitamin E-blended UHMWPE tested with a knee joint simulator was approximately 30% lower than that of virgin UHMWPE at 5 million cycles (Fig. 1.5) [8]. Due to the realistic settings of the joint simulator used in the aforementioned study, which included biomimetic frictional settings for in-vitro wear, we consider the results of this study to be significant and that the addition of vitamin E improves the wear resistance of UHMWPE. It has also been reported that primary human mononuclear cells cultured with debris from vitamin E-blended UHMWPE secreted significantly lower quantities of inflammatory cytokines such as TNF- α , IL-1 β and IL-6, compared to debris from virgin UHMWPE (Fig. 1.6) [9].

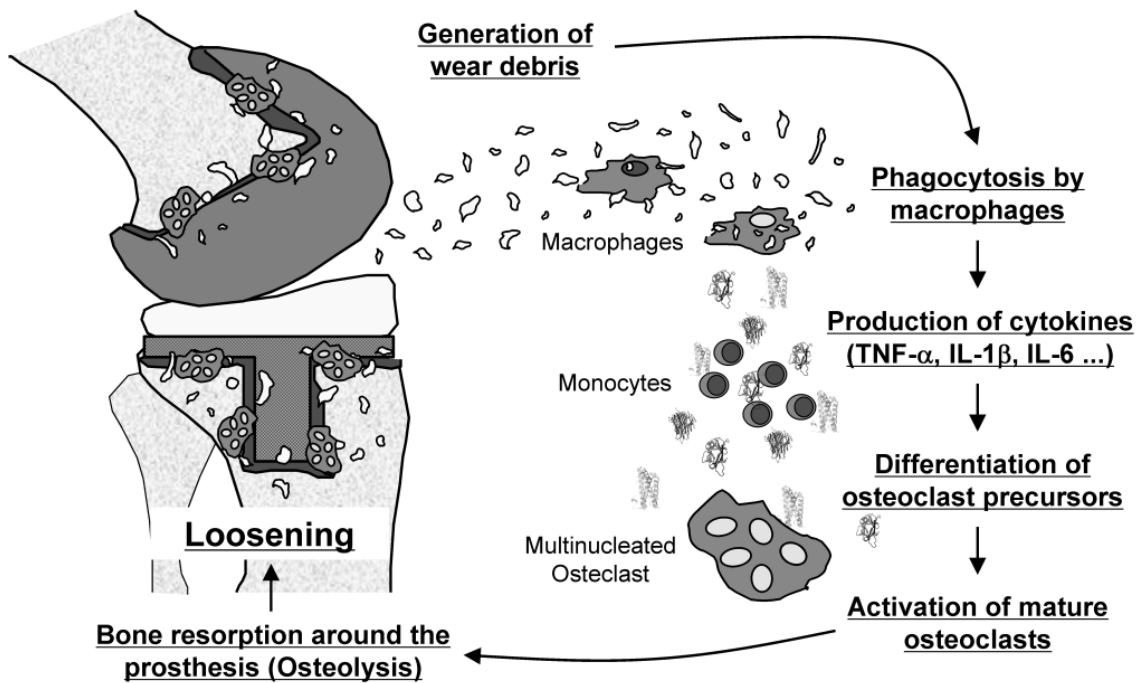


Fig. 1.4 Diagram of the biological response of UHMWPE wear debris on osteolysis and subsequent aseptic loosening.

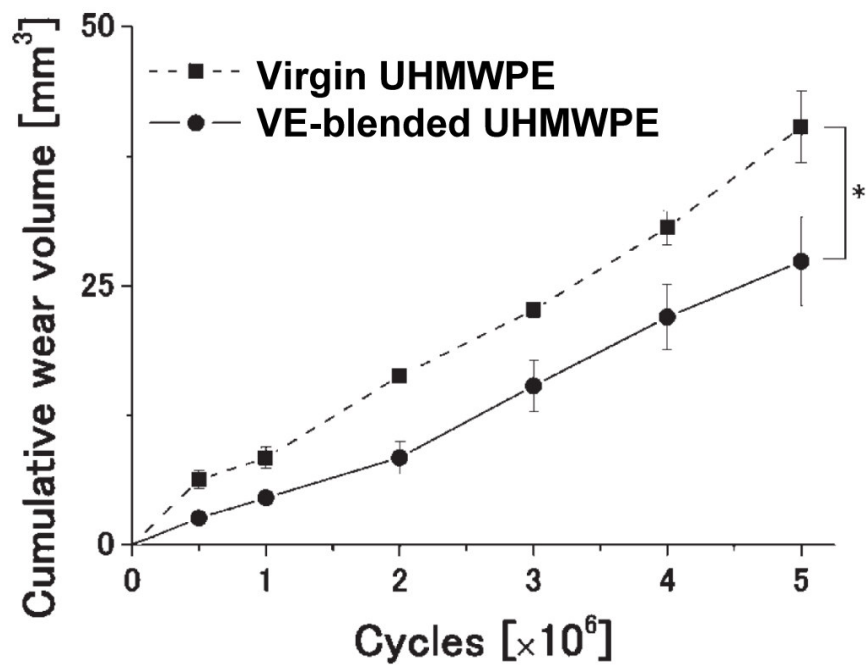


Fig. 1.5 Cumulative wear volume for virgin and vitamin E-blended UHMWPE tibial components ($n = 3$). Gravimetric wear decreased consistently with vitamin E addition. The error bars represent the standard deviation from the mean at each weighing interval [8].

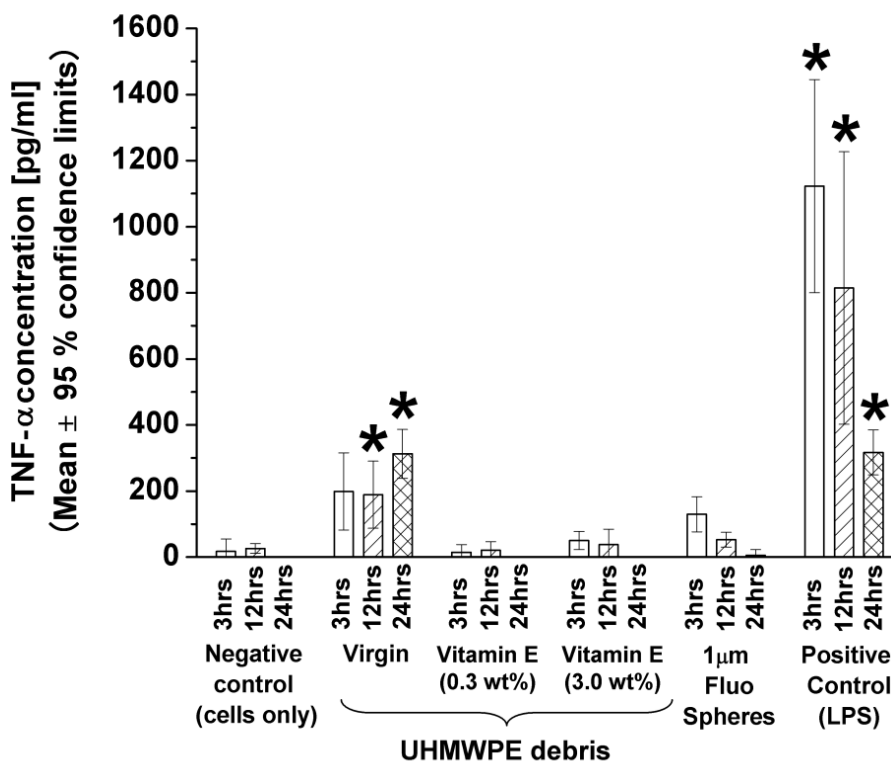


Fig. 1.6 TNF- α release from cells cultured with debris from vitamin E-blended and from virgin UHMWPE. Asterisk indicates statistically significant result against cells only group in same culture period [9].

1.2 Theme of Thesis

Vitamin E-blended UHMWPE exhibits several excellent properties for extending the longevity of knee prostheses compared with conventional UHMWPE, such as higher fatigue resistance, higher wear resistance, and lower biological reactivity. However, detailed mechanisms for these performance have not yet been clarified. In order to clarify the effects of the addition of vitamin E on the mechanism of wear resistance in UHMWPE, this study focused on issues related to the structural performance and the tribological performance. For structural performance, the strain-induced crystallization and orientation of molecular chains in the amorphous phase of vitamin E-blended UHMWPE was evaluated in Chapter 2. For tribological performance, the adhesive interaction between the surfaces of vitamin E-blended UHMWPE and Co-28Cr-6Mo alloy in water was evaluated in Chapter 3. In addition, the possibility of pressure-induced leaching of vitamin E from inside of vitamin E-blended UHMWPE and the effect of leached-vitamin E on adhesion were evaluated in Chapter 4. Furthermore, the frictional property of vitamin E-blended UHMWPE under serum lubricant was evaluated in Chapter 5. Finally, as one of the fundamental factors related to the biological reactivity to UHMWPE wear debris, the adsorption of serum proteins on the surface of vitamin E-blended UHMWPE was evaluated in Chapter 6.

This study is expected to provide useful information for clarifying the mechanisms that lead to wear and biological response of the vitamin E-blended UHMWPE for joint prostheses.

1.3 References

- [1] N. Shibata, S.M. Kurtz, N. Tomita, Recent advances of mechanical performance and oxidation stability in ultrahigh molecular weight polyethylene for total joint replacement: highly crosslinked and α -tocopherol doped, *Journal of Biomechanical Science and Engineering*, **1** (2006), 107-123.
- [2] S.M. Kurtz, O.K. Muratoglu, M. Evans, A.A. Edidin, Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty, *Biomaterials*, **20** (1999), 1659-1688.
- [3] P.S. Walker, G.W. Blunn, P.A. Lilley, Wear testing of materials and surfaces for total knee replacement, *Journal of Biomedical Materials Research, Part B: Applied Biomaterials*, **33** (1996), 159-175.
- [4] N. Tomita, T. Kitakura, N. Onmori, Y. Ikada, E. Aoyama, Prevention of fatigue cracks in ultrahigh molecular weight polyethylene joint components by the addition of vitamin E, *Journal of Biomedical Materials Research, Part B: Applied Biomaterials*, **48** (1999), 474-478.
- [5] M.J. Archibeck, J.J. Jacobs, K.A. Roebuck, T.T. Glant, The basic science of periprosthetic osteolysis, *The Journal of Bone and Joint Surgery (American)*, **82** (2000), 1478-1489.
- [6] E. Ingham, J. Fisher, Biological reactions to wear debris in total joint replacement, *Proceedings of the Institution of Mechanical Engineers, Part H: Journal of Engineering in Medicine*, **214** (2000), 21-37.
- [7] E. Ingham, J. Fisher, The role of macrophages in osteolysis of total joint replacement, *Biomaterials*, **26** (2005), 1271-1286.

- [8] S. Teramura, H. Sakoda, T. Terao, M.M. Endo, K. Fujiwara, N. Tomita, Reduction of wear volume from ultrahigh molecular weight polyethylene knee components by the addition of vitamin E, *Journal of Orthopaedic Research*, **26** (2007), 460-464.
- [9] S. Teramura, S. Russell, E. Ingham, J. Fisher, N. Tomita, K. Fujiwara, J.L. Tipper, Reduced biological response to wear particles from UHMWPE containing Vitamin E, *Proceedings of 55th Annual Meeting of Orthopaedic Research Society*, (2009), 2377.

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Chapter 2

Crystallization and Orientation of Molecular Chains

2.1 Introduction

It has been suggested that the wear rate of UHMWPE is affected by the mechanical properties such as ultimate tensile strength and breaking elongation [1]. However, these properties of the non-oxidized UHMWPE with and without vitamin E are almost the same [2]. On the other hand, it has been suggested that the lamellae crystals and molecular chains in amorphous phase of UHMWPE are preferentially aligned by uniaxial stretching, and this higher degree of orientation gives rise to greater wear resistance [3-5]. The purpose of this chapter was to evaluate the effects of the addition of vitamin E on the strain-induced crystallization and orientation of molecular chains in amorphous phase of UHMWPE as one of the fundamental approaches to clarifying the structural performance of vitamin E-blended UHMWPE.

2.2 Materials and Methods

2.2.1 Preparation of specimens

UHMWPE resin powder (GUR1050, Ticona, USA) was blended with vitamin E (0.3% and 3.0% w/w, *dl*- α -Tocopherol, Eisai, Japan) using a screw cone mixer (LFS-GS-2J, Fukae Powtec, Japan). The vitamin E-blended UHMWPE block was manufactured using direct compression molding at 220°C under 25 MPa for 30 min. The virgin UHMWPE block, which was used as the control material in this study, was manufactured similarly, but without the addition of vitamin E. The experimental specimens for the present study were manufactured from these UHMWPE blocks. All manufacturing procedures were conducted in air, and no sterilization was carried out prior to testing.

2.2.2 X-ray diffraction analysis

X-ray diffraction analyses were performed with a diffractometer (PW3050, Philips, Netherlands) using $\text{CuK}\alpha$ radiation operating at 40 kV and 50 mA (Fig. 2.1). The data were collected in the 2θ range of 5°–40° in steps of 0.02°. In a typical diffraction pattern of UHMWPE, two sharp peaks were located at $2\theta = 21.5^\circ$ and 23.8° , which were assigned to orthorhombic (110) and (200) reflections, and a broad halo was assigned to an amorphous reflection [6-8]. In the present study, the peak areas of the orthorhombic crystalline phase and amorphous phase for each UHMWPE were fitted from Gaussian function by using peak fitting simulation software (Origin, OriginLab, USA) as shown in Fig. 2.2, and the crystallinity was calculated by summing all the

peak area fractions of orthorhombic (110) and (200) crystals [6,8]. A schematic drawing of the UHMWPE specimen as well as the procedure for measuring the crystallinity of UHMWPE by X-ray diffraction analysis before and after applying the tensile strain is shown in Fig. 2.3. A dumbbell-shaped UHMWPE specimen was subjected to 30% tensile strain at a rate of 0.04 mm/s with an automatic tensile tester (EZ Graph, Shimadzu, Japan). Molecular chains in both the crystalline and amorphous regions were preferentially aligned parallel to the stretching direction [9,10]. In order to determine the crystallinity of UHMWPE specimens without any orientation influences after application of the tensile strain, X-ray diffraction data were collected from the range of 0° – 90° in steps of 5° , and the averaged value was defined as the crystallinity.

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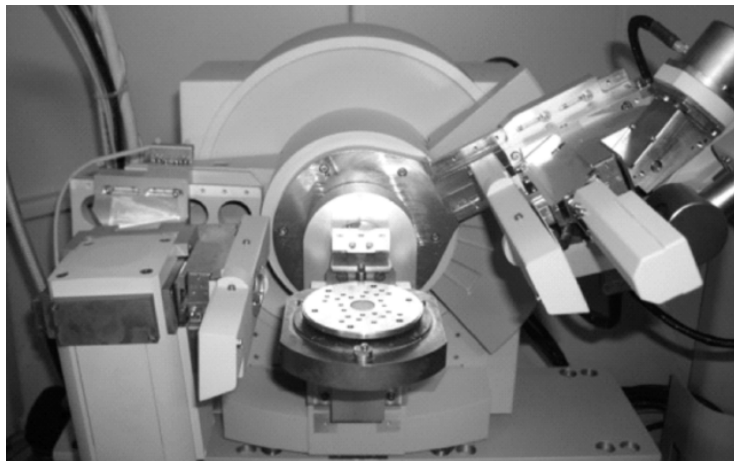


Fig. 2.1 X-ray diffractometer.

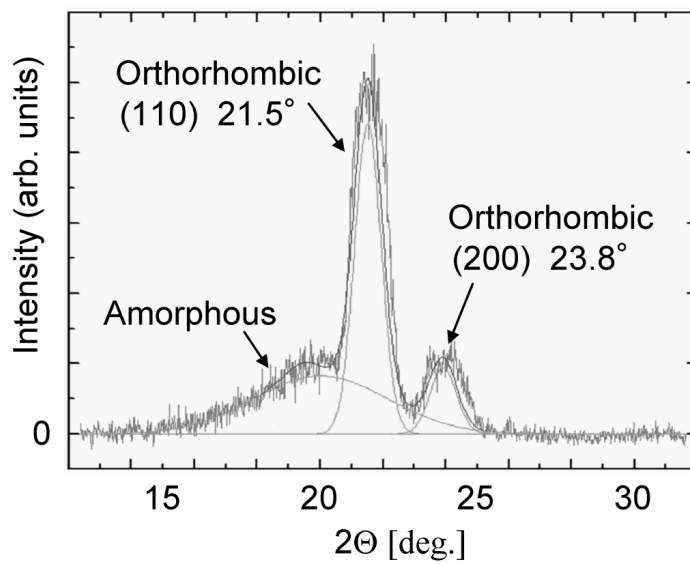


Fig. 2.2 Typical diffraction pattern of UHMWPE with peak fitting functions.

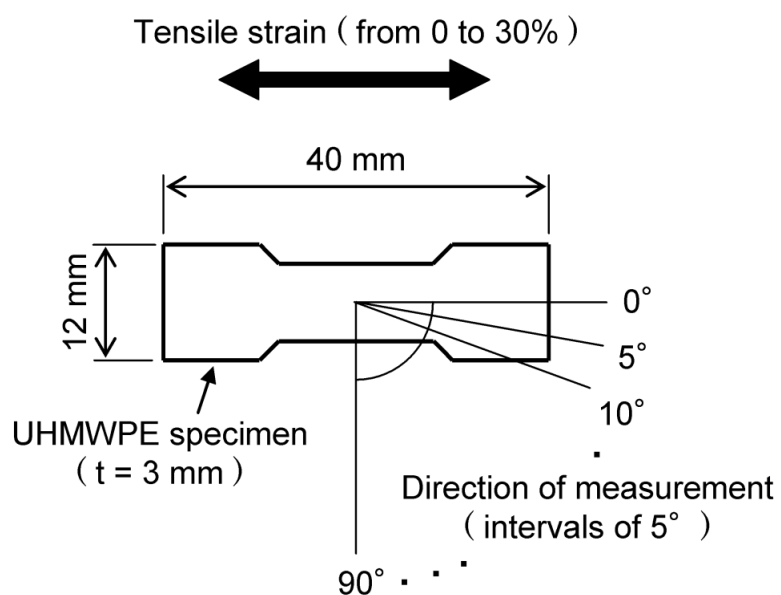


Fig. 2.3 Schematic drawing of UHMWPE specimen and procedure for measuring crystallinity by X-ray diffraction analysis

2.2.3 Raman spectroscopic analysis

The Raman spectrum of UHMWPE comprises three frequency regions: the skeletal C-C stretching vibration, the CH₂ twisting vibration, and the CH₂ bending vibration. The CH₂ twisting spectrum features the superposition of a narrow crystalline band at 1295 cm⁻¹ and a broad amorphous band with a maximum at 1303 cm⁻¹ (Fig. 2.4) [11-13]. In the present study, the crystalline and amorphous bands of the CH₂ twisting spectrum were fitted with a Gaussian function, and the integral intensities of these bands were calculated by using spectrum analysis software (Lab Spec, Horiba Jobin Yvon, France). The I_c value is an index of crystallinity and/or molecular chain orientation of UHMWPE, and is defined as

$$I_c = \frac{I_{1295}}{I_{1295} + I_{1303}} \quad (1)$$

where I_{1295} is the integral intensity of the narrow crystalline band and I_{1303} is the integral intensity of the amorphous band.

The UHMWPE specimen (thickness: 100 μm) was cut using a microtome and was fixed on the X-stage attached to the Raman spectrometer (Ramanor T64000, Horiba Jobin Yvon, France) as shown in Fig. 2.5. A schematic drawing of the UHMWPE specimen as well as the procedure for measuring the I_c value by Raman spectroscopic analysis before and after applying the tensile strain is shown in Fig. 2.6. Raman spectroscopy using an Ar⁺ laser (wavelength: 488 nm) operating at 200 mW with a focal spot size of 2 μm was performed before and after applying the 30% tensile strain at a rate of 0.04 mm/s. The 2,500 I_c values collected in the analytic region were averaged.

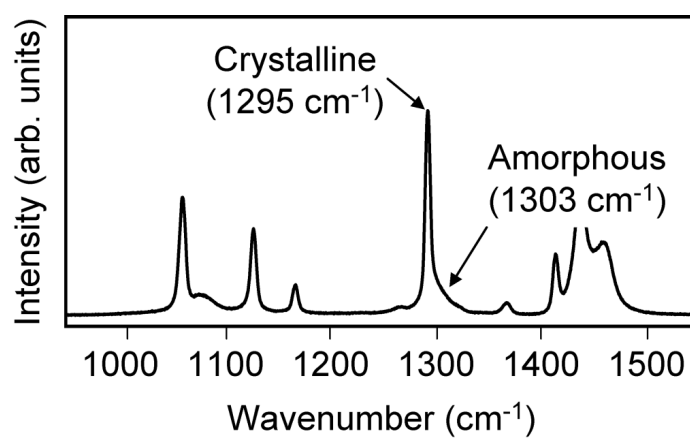


Fig. 2.4 Typical spectrum of UHMWPE by Raman Spectroscopy.

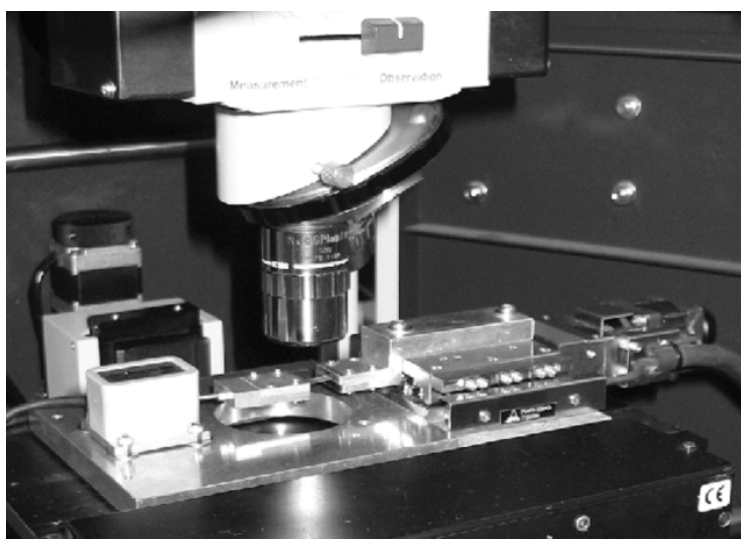


Fig. 2.5 Raman spectrometer with tensile testing machine

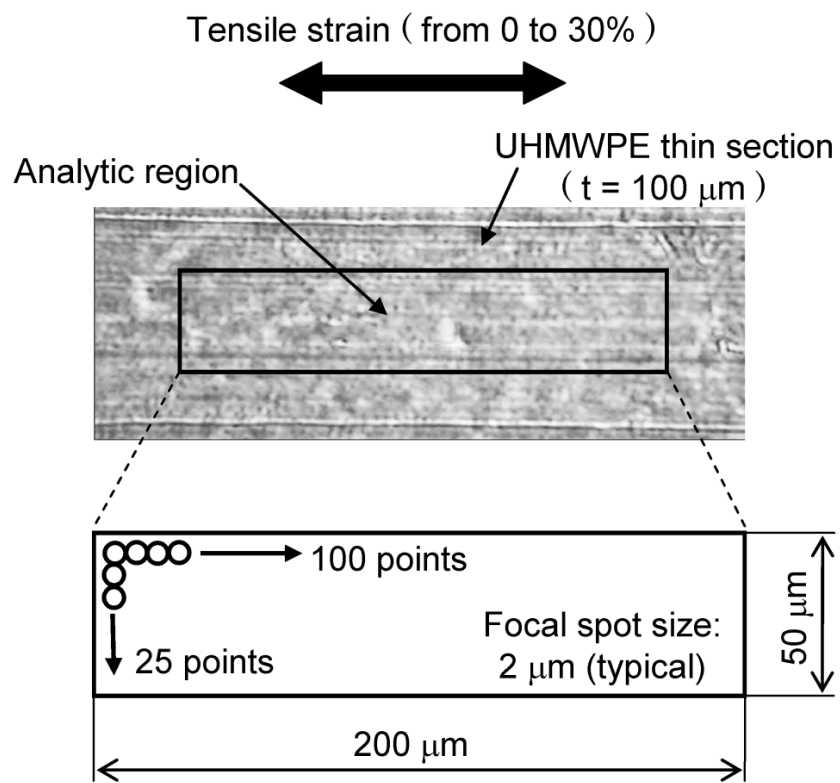


Fig. 2.6 Schematic drawing of UHMWPE specimen and procedure for measuring the I_c value by Raman spectroscopic analysis.

2.2.4 Image correlation analysis

The microscopic strain distribution of the material was measured using an image correlation technique [14-16]. In this technique, two or more images, one of which was undeformed and the others of which were deformed, were digitized and compared. The UHMWPE specimen (thickness: 100 μm) was fixed on the X-stage attached to the optical microscope (E600, Nikon, Japan) as shown in Fig. 2.7, and the 30% tensile strain was applied at a rate of 0.04 mm/s.

Surface images of the specimen before and after application of the tensile strain were photographed, and 8-bit gray levels are used for digitization of the light intensity in the black and white image. As for the undeformed image, 40 \times 30 grids were set in the analytic region as shown in Fig. 2.8(a), and the quadrilateral vertices (a, b, c, d) of each grid can be defined by the light intensity pattern of surrounding subsets. Then, the quadrilateral vertices of each grid in the deformed image (a', b', c', d') can be identified by finding the light intensity pattern of surrounding subsets. In the present study, the grid and subset consist of an array of 11 \times 11 pixels and 31 \times 31 pixels, respectively. The area of each grid in the analytic region was calculated by the vertex coordinate of the quadrilateral grid before and after tensile strain, as shown in Fig. 2.8(b) [15], and then the areal dilatation of each grid was obtained as

$$\frac{S'-S}{S} = \frac{dx(1+\varepsilon_x)dy(1+\varepsilon_y) - dxdy}{dxdy} = (1+\varepsilon_x)(1+\varepsilon_y) - 1 \quad (2)$$

where ε_x is strain parallel to the tensile direction and ε_y is strain perpendicular to the tensile direction.

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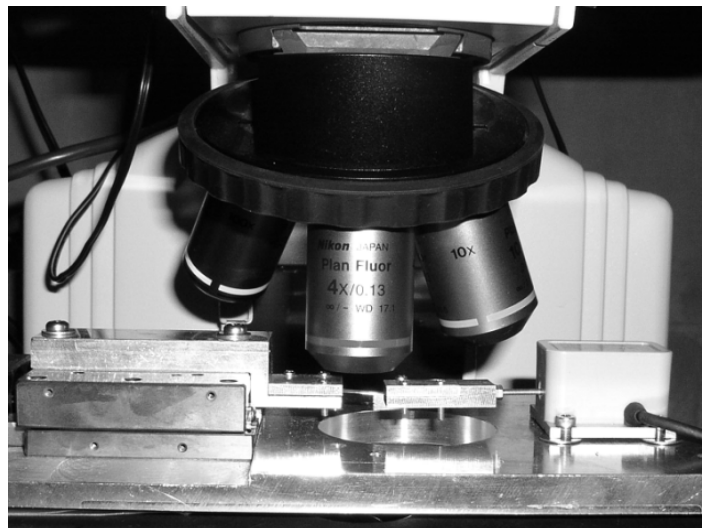
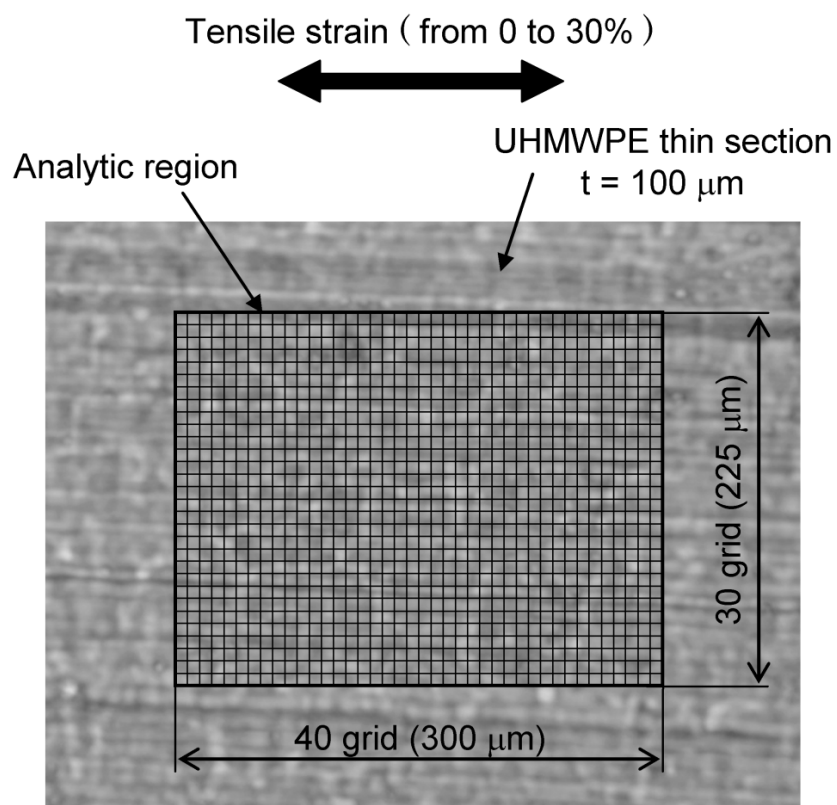
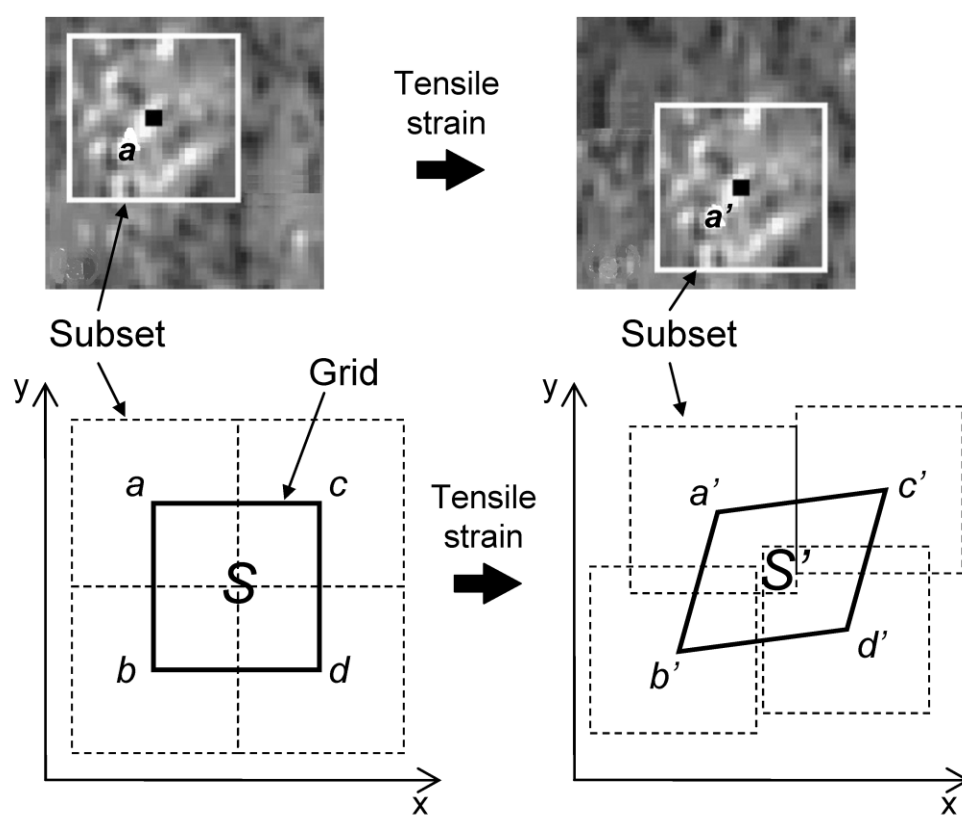


Fig. 2.7 Optical microscope with tensile testing machine for image correlation analysis.



(a)

Fig. 2.8 Schematic drawing of UHMWPE specimen and procedure for obtaining the areal dilatation by image correlation analysis. (a) Analytic region on UHMWPE specimen, (b) geometric diagram for calculating the area of each grid and subset on the analytic region [15]. S is area before tensile strain and S' is area after 30% tensile strain, and a, b, c, d are vertex coordinates of the quadrilateral grid.



(b)

2.2.5 Statistical methods

Effects of the vitamin E addition on the strain-induced crystallization were analyzed using one-way ANOVA followed by the Tukey test for post hoc comparisons.

2.3 Results

For vitamin E-blended (0.3% and 3.0% w/w) UHMWPE and virgin UHMWPE specimens, the difference in the crystallinity before and after applying 30% tensile strain is shown in Fig. 2.9. The difference in the I_c value for each UHMWPE specimen is shown in Fig. 2.10. The difference in the crystallinity for the vitamin E-blended specimens was significantly less than that for the virgin specimen, whereas the difference in the I_c value for the vitamin E-blended specimens was greater than that for the virgin specimen. Typical examples of the I_c value distribution for each type of UHMWPE specimen at 0% and 30% tensile strain, as observed by Raman spectroscopic analysis, are shown in Fig. 2.11. The I_c value distribution of vitamin E-blended UHMWPE tended to exhibit large shifts caused by the tensile strain in comparison with virgin UHMWPE.

Distributions of the negative areal dilatation for each type of UHMWPE specimen after 30% tensile strain are shown in Fig. 2.12. The vitamin E-blended UHMWPE had a larger percentage of negative areal dilatation after application of the 30% tensile strain in comparison with virgin UHMWPE, and this tendency was increased in proportion to the vitamin E concentration.

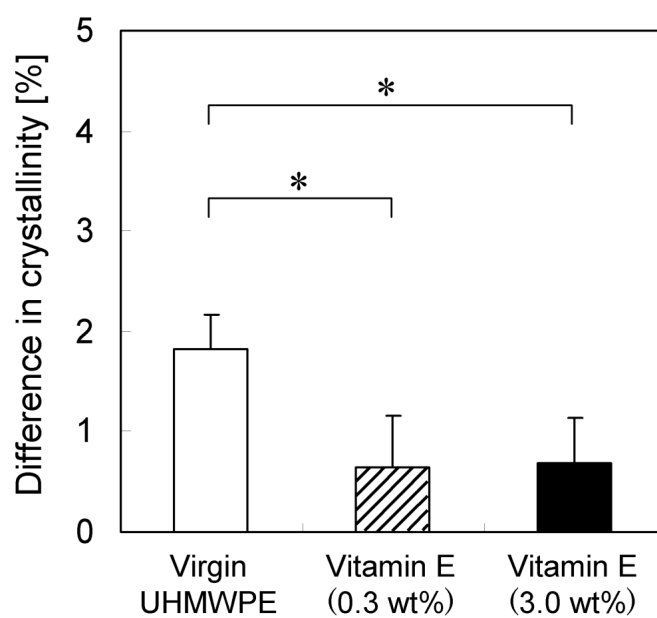


Fig. 2.9 Difference in crystallinity measured by X-ray diffractometer before and after 30% tensile strain for each UHMWPE specimen. Data represent mean \pm SD. Asterisk indicates a statistically significant difference (*; $P < 0.05$, $n = 3$).

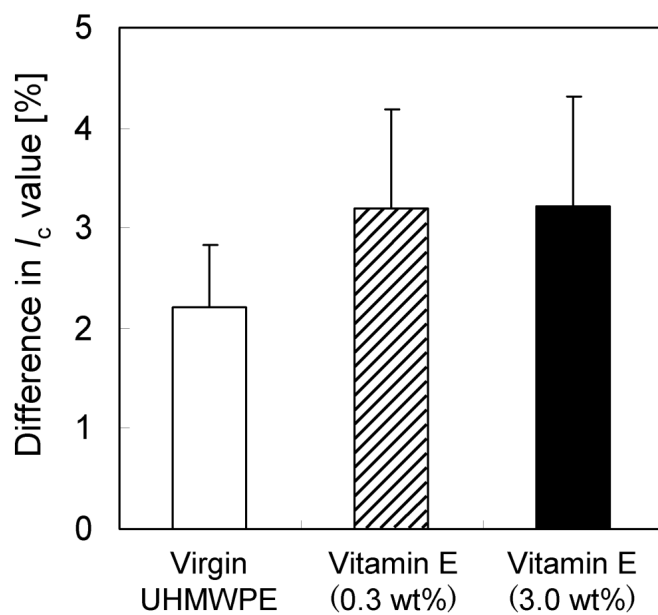


Fig. 2.10 Difference in I_c value measured by Raman spectrometer before and after 30% tensile strain for each UHMWPE specimen. Data represent mean \pm SD (n = 3).

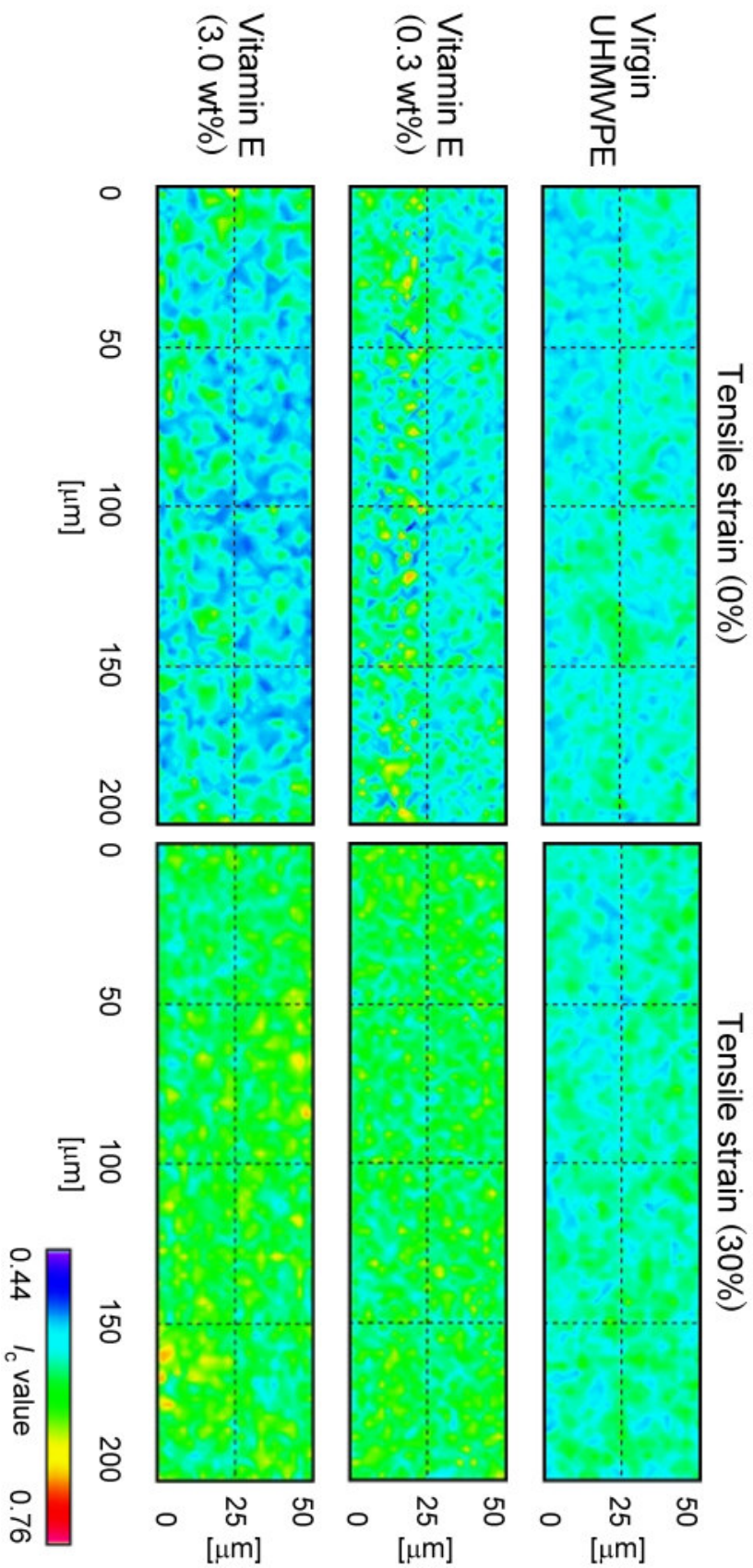


Fig. 2.11 Typical examples of l_c value distribution for each UHMWPE specimen at 0% and 30% tensile strain.

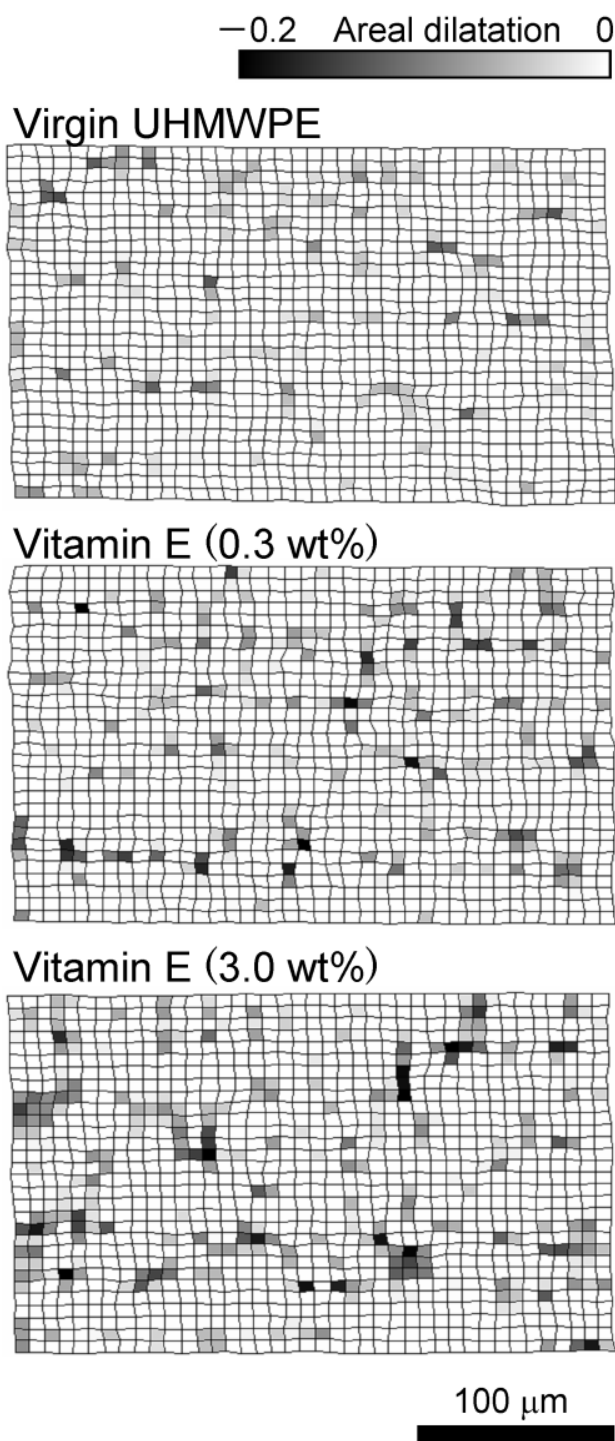


Fig. 2.12 Typical examples of distribution of negative areal dilatation for each UHMWPE specimen after 30% tensile strain.

2.4 Discussion

It has been suggested that vitamin E is present within the amorphous phase of UHMWPE [17,18], and that this inhibits crystallization because of the high affinity of vitamin E to polyethylene [19]. In fact, the present results showed that strain-induced crystallization was inhibited by the presence of vitamin E. In the Raman spectroscopic analysis, however, vitamin E-blended UHMWPE exhibited a larger increase in I_c value than virgin UHMWPE.

In principle, X-ray diffraction analysis data of UHMWPE is interpreted on the basis of two phase reflections: the orthorhombic reflection and the amorphous reflection. On the other hand, the Raman spectrum of UHMWPE can be described as a superposition of three components that originate from an orthorhombic crystalline phase, an amorphous phase, and an intermediate phase between the crystalline and amorphous phases, in which chain sections have lost lateral order, but have retained a stretched conformation [11-13]. It has also been suggested that the narrow crystalline band at 1295 cm^{-1} in the CH_2 twisting spectrum contains an orthorhombic crystalline phase and an intermediate phase [11].

In the image correlation analysis, the vitamin E-blended UHMWPE exhibited a larger percentage of negative areal dilatation upon application of the 30% tensile strain in comparison with the virgin UHMWPE. The strain-induced crystallization and/or orientation of the molecular chains were possibly associated with an increase of negative areal dilatation. These results suggest that the existence of vitamin E within the amorphous phase of UHMWPE enhances the mobility of the molecular chains present in the amorphous phase and increases the formation of the strain-induced

stretched conformation phase.

These results show that the addition of vitamin E to UHMWPE decreases the strain-induced crystallization and increases the strain-induced orientation of molecular chains present in amorphous phase. On the other hand, it has been suggested that the orientation of crystals and molecular chains of UHMWPE affects on the wear performance [3-5]. In order to clarify the relationship between the wear mechanism and molecular-chain structure of UHMWPE, it is necessary to distinguish between crystallinity and crystal orientation and molecular chain orientation in the amorphous phase.

2.5 Conclusion

The effects of vitamin E addition on the strain-induced structural changes of UHMWPE were examined. The vitamin E-blended UHMWPE showed lower strain-induced crystallization than virgin UHMWPE, whereas a higher I_c value was observed in the Raman spectroscopic analysis. The vitamin E-blended UHMWPE also exhibited a larger percentage of negative areal dilatation upon application of the tensile strain. These results suggest that the addition of vitamin E to UHMWPE decreases the strain-induced crystallization and increases the strain-induced orientation of molecular chains present in the amorphous phase.

2.6 Acknowledgments

UHMWPE blocks (vitamin E-blended and virgin) were supplied by Nakashima Medical Corporation. UHMWPE dumbbell-shaped specimens were machined by Yasojima Proceed Corporation.

2.7 References

- [1] A. Wang, D.C. Sun, C. Stark, J.H. Dumbleton, Wear mechanisms of UHMWPE in total joint replacements, *Wear*, **181-183** (1995), 241-249.
- [2] I. Sakuramoto, A. Mori, K. Nagata, N. Tomita, K. Kuramoto, S. Kawano, The effects of oxidative degradation on mechanical properties of UHMWPE for artificial knee joint, *Journal of the Japan Society of Mechanical Engineers A*, **67** (2001), 148-155 (in Japanese).
- [3] A. Wang, C. Stark, J.H. Dumbleton, Mechanistic and morphological origins of ultra-high molecular weight polyethylene wear debris in total joint replacement prostheses, *Proceedings of the Institution of Mechanical Engineers, Part H: Journal of Engineering in Medicine*, **210** (1996), 141-155.
- [4] C.R. Bragdon, D.O. O'Connor, J.D. Lowenstein, M. Jasty, W.D. Syniuta, The importance of multidirectional motion on the wear of polyethylene, *Proceedings of the Institution of Mechanical Engineers, Part H: Journal of Engineering in Medicine*, **210** (1996), 157-165.
- [5] A. Wang, A. Essner, V.K. Polineni, C. Stark, J.H. Dumbleton, Lubrication and

- wear of ultra-high molecular weight polyethylene in total joint replacements, *Tribology International*, **31** (1998), 17-33.
- [6] K.E. Russell, B.K. Hunter, R.D. Heyding, Polyethylenes revisited: WAXS and the phase structure, *European Polymer Journal*, **29** (1993), 211-217.
- [7] Y.L. Joo, O.H. Han, H.-K. Lee, J.K. Song, Characterization of ultra high molecular weight polyethylene nascent reactor powders by X-ray diffraction and solid state NMR, *Polymer*, **41** (2000), 1355-1368.
- [8] J.T. Yeh, S.C. Lin, C.W. Tu, K.H. Hsie, F.C.Chang, Investigation of the drawing mechanism of UHMWPE fibers, *Journal of Materials Science*, **43** (2008), 4892-4900.
- [9] S.H. Hyon, F. Horii, R. Kitamaru, Phase structure and molecular mobility of polyethylene fibers by broad-line NMR spectroscopy, *Bulletin of the Institute for Chemical Research, Kyoto University*, **55** (1977), 248-259.
- [10] N.A.J.A. Gerrits, Y. Tervoort, Deformation mechanisms during uniaxial drawing of melt-crystallized ultra-high molecular weight polyethylene, *Journal of Materials Science*, **27** (1992), 1385-1390.
- [11] G.R. Strobl, W. Hagedorn, Raman spectroscopic Method for determining the crystallinity of polyethylene, *Journal of Polymer Science*, **16** (1978), 1181-1193.
- [12] R. Mutter, W. Stille, G. Strobl, Transition regions and surface melting in partially crystalline polyethylene: A Raman spectroscopic study, *Journal of Polymer Science, Part B: Polymer Physics*, **31** (1993), 99-105.
- [13] P. Taddei, S. Affatato, C. Fagnano, B. Bordini, A. Tinti, A. Toni, Vibrational spectroscopy of ultra-high molecular weight polyethylene hip prostheses: influence of the sterilisation method on crystallinity and surface oxidation, *Journal of*

Molecular Structure, **613** (2002), 121-129.

[14] D. Choi, J.L. Thorpe, R.B. Hanna, Image analysis to measure strain in wood and paper, *Wood Science and Technology*, **25** (1991), 251-262.

[15] K. Murata, M. Masuda, M. Ichimaru, Analysis of radial compression behavior of wood using digital image correlation method, *Journal of the Japan Wood Research Society*, **45** (1999), 375-381 (in Japanese).

[16] Y. Niwa, S. Yamada, N. Shibata, Q.Q. Ni, M. Masuda, K. Murata, S. Teramura, H. Kobayashi, N. Tomita, Study on microscopic deformation behavior of ultra-high molecular weight polyethylene for knee prostheses, *Japanese Journal of Clinical Biomechanics*, **25** (2004), 363-368 (in Japanese).

[17] J. Mallegol, D.J. Carlsson, L. Deschenes, Post- γ -irradiation reactions in vitamin E stabilised and unstabilised HDPE, *Nuclear Instruments and Methods in Physics Research B*, **185** (2001), 283-293.

[18] E. Oral, K.K. Wannomaea, S.L. Rowella, O.K. Muratoglu, Diffusion of vitamin E in ultra-high molecular weight polyethylene, *Biomaterials*, **28** (2007), 5225-5237.

[19] E. Oral, E.S. Greenbaum, A.S. Malhi, W.H. Harris, O.K. Muratoglu, Characterization of irradiated blends of α -tocopherol and UHMWPE, *Biomaterials*, **26** (2005), 6657-6663.

Chapter 3

Adhesive Interaction with Smooth Metal Surface

3.1 Introduction

UHMWPE wear in the body is affected by several wear modes, such as abrasive wear and adhesive wear. For rough and hard corresponding surfaces, the dominant wear mode for UHMWPE will be abrasive wear. However, for extremely smooth corresponding surfaces, like joint prostheses, the dominant wear mode will be adhesive wear. In particular, the formation of transfer films is thought to be one of the essential factors involved in adhesive wear [1,2]. In this chapter, two fundamental approaches were used to evaluate the tribological performance of vitamin E-blended UHMWPE. First, the transfer film formation of vitamin E-blended UHMWPE on the Co-28Cr-6Mo alloy surface in water was examined. Additionally, the pull-away force between the surfaces of the vitamin E-blended UHMWPE and the Co-28Cr-6Mo alloy was measured.

3.2 Materials and Methods

3.2.1 Preparation of specimens

UHMWPE resin powder (GUR1050, Ticona, USA) was blended with vitamin E (0.3% w/w, *dl*- α -Tocopherol, Eisai, Japan) using a screw cone mixer (LFS-GS-2J, Fukae Powtec, Japan). The vitamin E-blended UHMWPE block was manufactured using direct compression molding at 220°C under 25 MPa for 30 min. The virgin UHMWPE block, 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 blocks as shown in Fig. 3.1. Then, the pin specimens were subjected to ultrasonic-immersion cleaning in isopropyl alcohol (50% v/v) at room temperature for 15 min. In addition, disk specimens comprising a highly polished 8 mm diameter flat sliding surface, were machined from a Co-28Cr-6Mo alloy ingot and subjected to ultrasonic-immersion cleaning in acetone (99.5% v/v) at room temperature for 15 min. 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-blended UHMWPE pin, the virgin UHMWPE pin and the Co-28Cr-6Mo alloy disk specimens were measured by stylus-type surface roughness tester (SE1200, Kosaka Laboratory, Japan) on the basis of international standards (JIS B 0601:2001). The roughness value (*Ra*) for these specimens was $0.077 \pm 0.014 \mu\text{m}$, $0.094 \pm 0.011 \mu\text{m}$ and $0.004 \pm 0.001 \mu\text{m}$, respectively. Data represent mean \pm SD ($n = 5$).

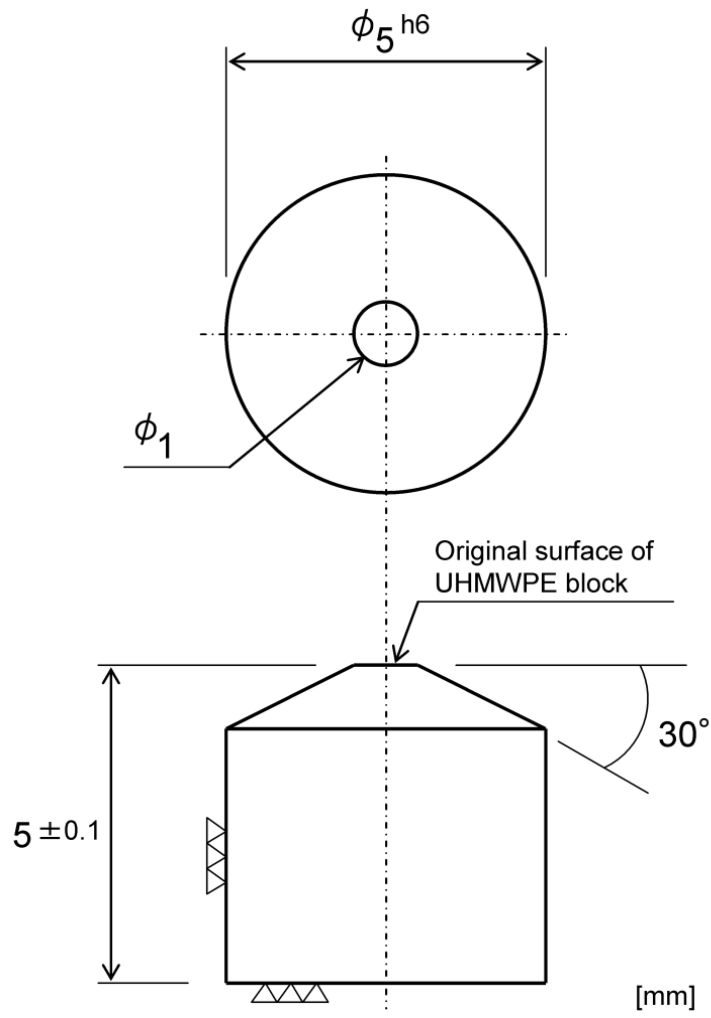
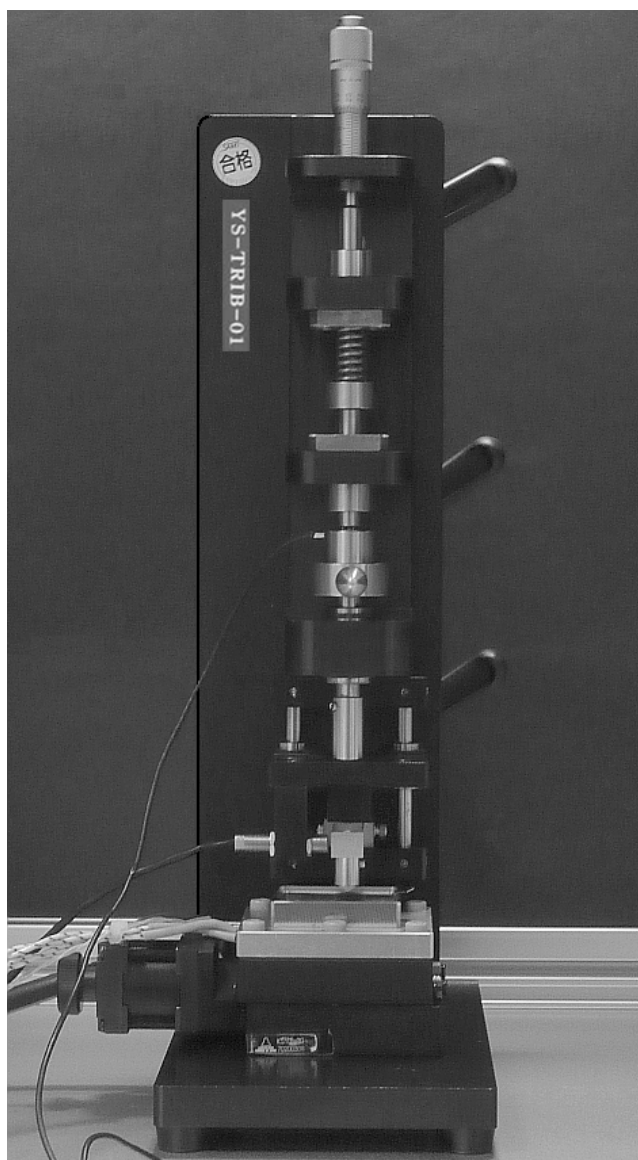


Fig. 3.1 Dimensional drawing of UHMWPE pin specimen.

3.2.2 Pin-on-disk transfer test

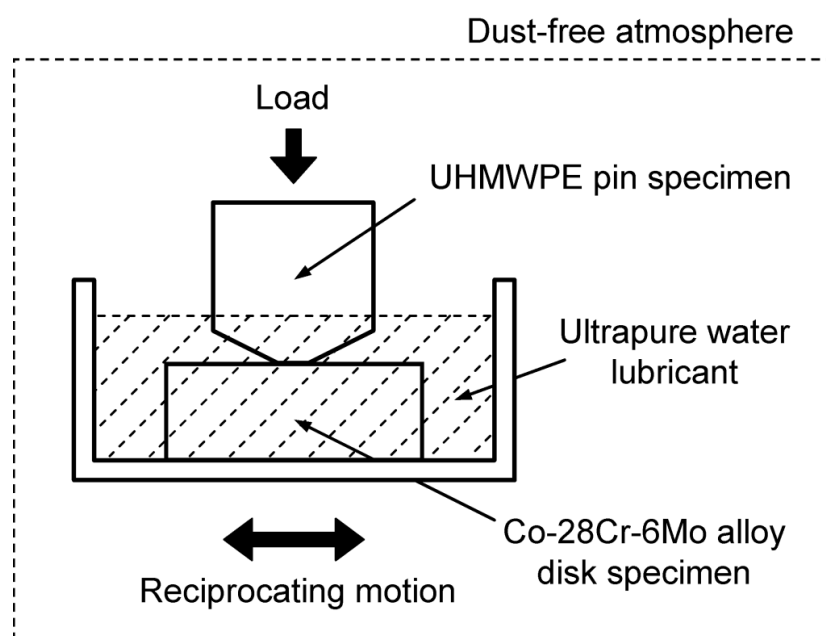
The UHMWPE transfer test was carried out using a computer-controlled pin-on-disk tribological test apparatus (Ys-TRIB-01, Sanki, Japan) as shown in Fig. 3.2. All tests were conducted at room temperature inside the clean bench (Ys-Class5, Sanki, Japan), which provides an air cleanliness exceeding ISO Class 5 for the purpose of avoiding contamination with air dust particles. The pin specimens (vitamin E-blended 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 load value was set as 8 N, 16 N or 24 N, and the nominal contact stress on the pin surface was 10 MPa, 20 MPa or 30 MPa, respectively. 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 specimens were carried out an immersion cleaning in ultrapure water and dried at room temperature inside a clean bench overnight. The actual micrograph of the Co-28Cr-6Mo alloy surface after the transfer test by using a field-emission-type scanning electron microscope (S-4500, Hitachi, Japan) without sputter coating is shown in Fig. 3.3.



(a)

Fig. 3.2 Experimental apparatus for transfer test. (a) Photograph of whole apparatus, (b) Schematic drawing of sliding section.

Evaluation of the Structural and Tribological Performance of Ultrahigh Molecular Weight Polyethylene Blended with Vitamin E



(b)

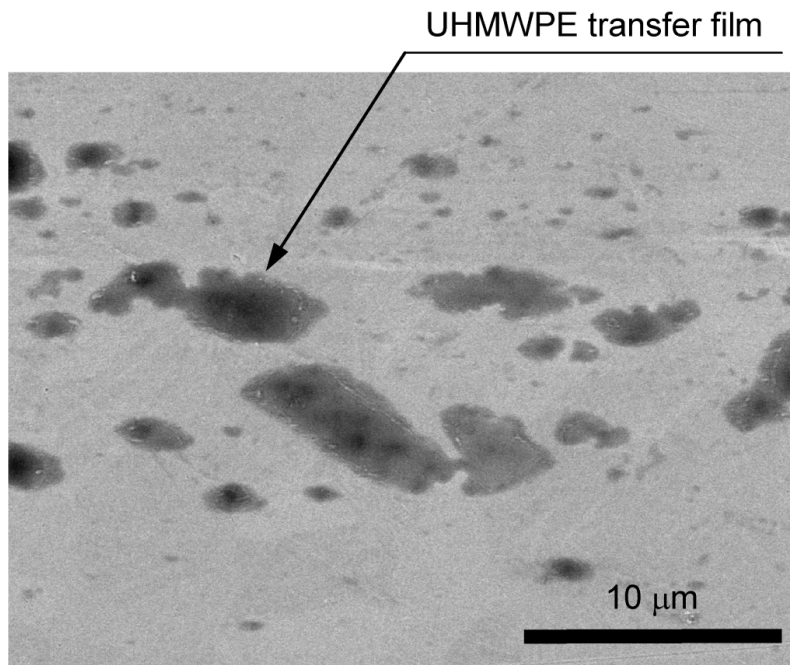


Fig. 3.3 Scanning electron micrograph of Co-28Cr-6Mo alloy surface after transfer test.

3.2.3 Quantification of transfer film

The quantification of the UHMWPE transfer film formed on the disk specimen surface was performed as shown in Fig. 3.4. 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 for the brightness histogram was determined as the opposite side of the maximum value in the symmetrical curve. 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.

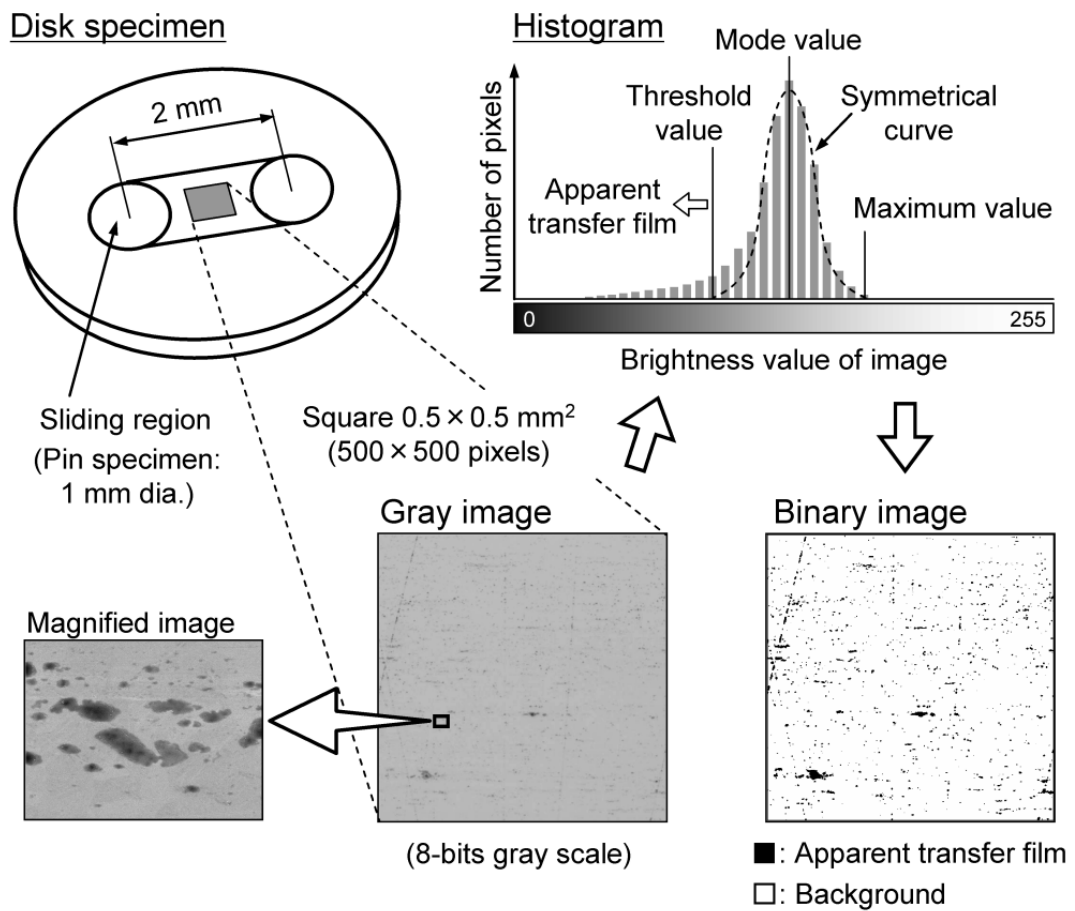
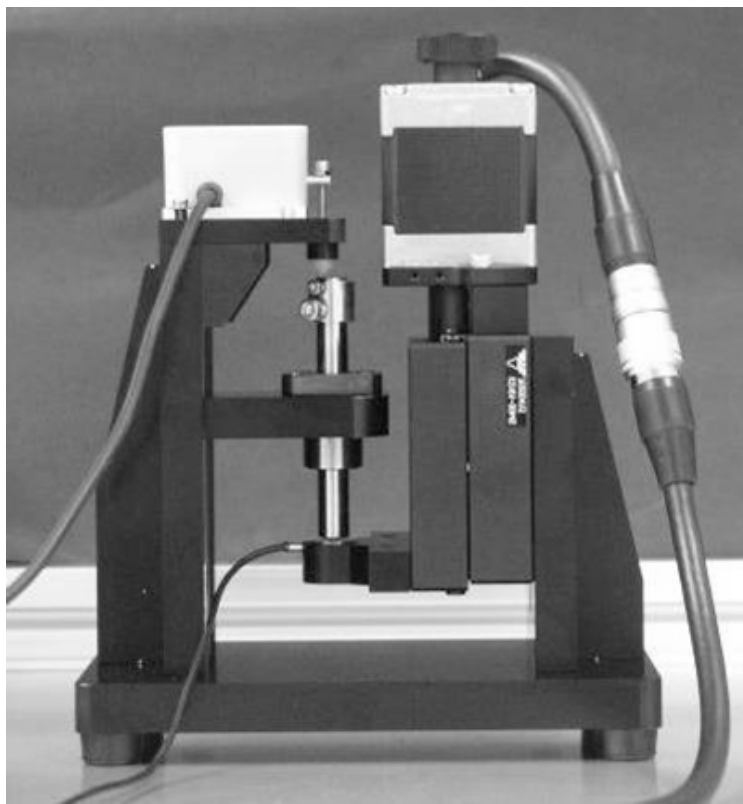


Fig. 3.4 Quantification procedure for UHMWPE transfer film formed on Co-28Cr-6Mo alloy surface.

3.2.4 Measurement of 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) as shown in Fig. 3.5, and the actual output signal of the load cell during pull-away force measurement is shown in Fig. 3.6. The vitamin E-blended and the virgin UHMWPE pin specimens were vertically pressed against the Co-28Cr-6Mo 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.

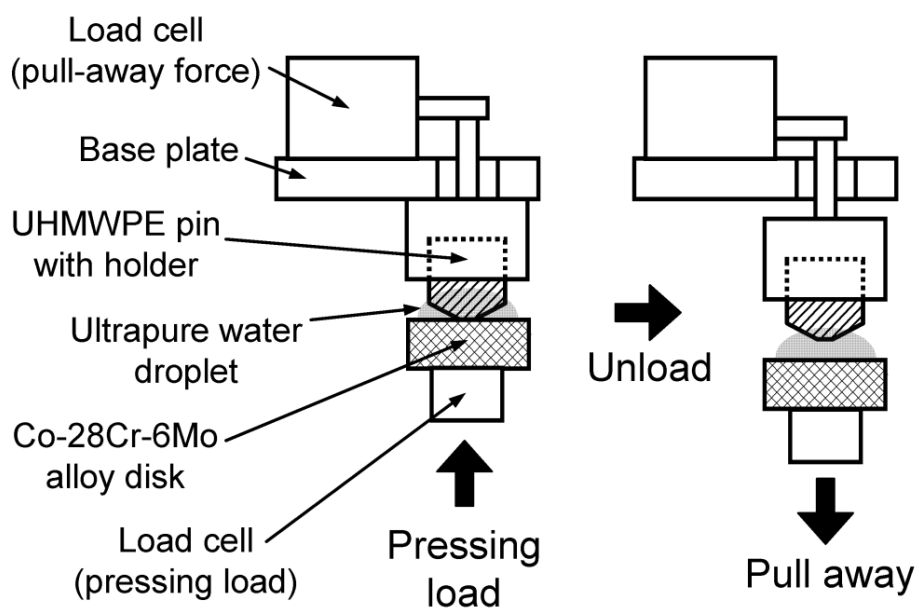
It is considered that the apparatus for measuring the pull-away force detects not only the attractive force between the surfaces, but also the breaking force of the UHMWPE junction at the real contact points. Since scanning electron microscope images confirmed that there were no UHMWPE fragments on the counterface after the pull-away force measurements, we assume that the breaking force contributes very little to the measurement results.



(a)

Fig. 3.5 Experimental apparatus for measuring pull-away force between UHMWPE and Co-28Cr-6Mo alloy. (a) Photograph of whole apparatus, (b) Schematic drawing of measuring section and procedure for measurement.

Evaluation of the Structural and Tribological Performance of Ultrahigh Molecular Weight Polyethylene Blended with Vitamin E



(b)

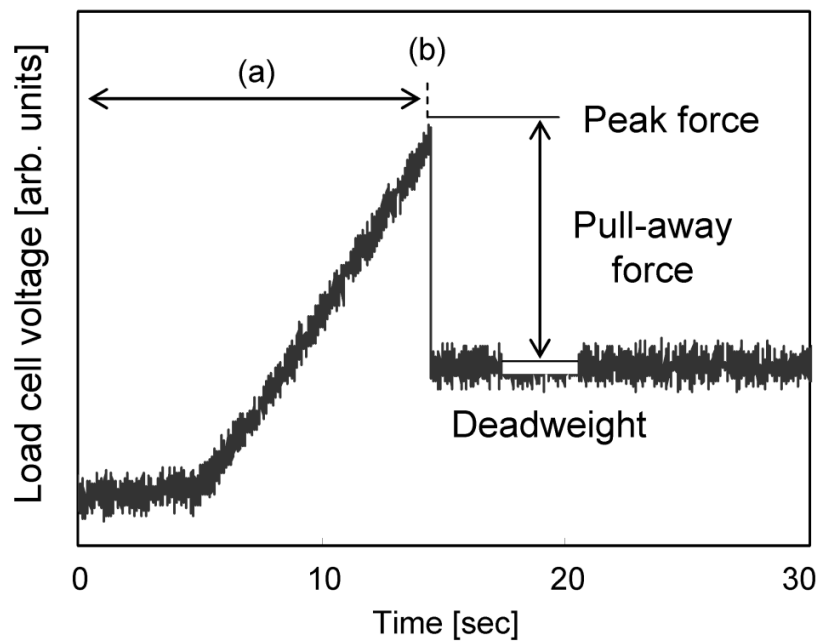


Fig. 3.6 Typical example of actual output signal of load cell during pull-away force measurement between UHMWPE pin and Co-28Cr-6Mo alloy disk. Disk specimen is gradually pulled away within (a), pin and disk specimens are separated at (b).

3.2.5 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 the Tukey test for post hoc comparisons.

3.3 Results

The apparent region ratio of vitamin E-blended UHMWPE and virgin UHMWPE transfer film formed on the Co-28Cr-6Mo alloy surface at different values for the contact stress are shown in Fig. 3.7. Transfer film formation was increased in accordance with contact stress between 10 MPa and 20 MPa in both specimens. The vitamin E-blended 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-blended 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 (Fig. 3.8). The vitamin E-blended 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.

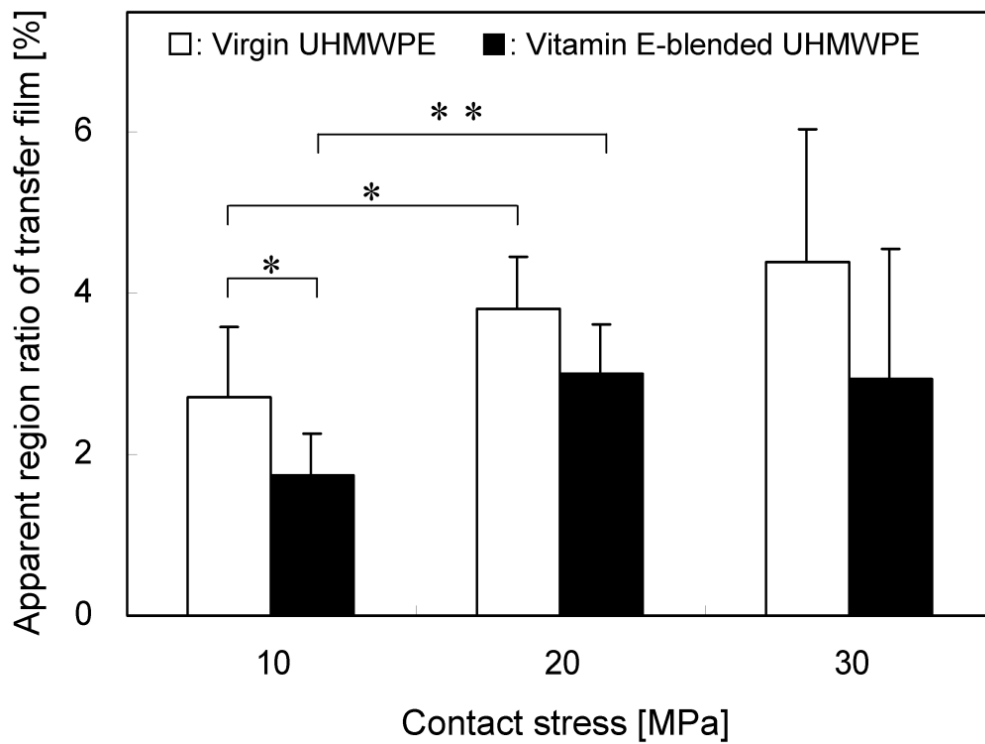


Fig. 3.7 Apparent region ratio of UHMWPE transfer film formed on Co-28Cr-6Mo alloy surface at different contact stress values. Data represent mean \pm SD. Asterisks indicate statistically significant differences (*; $P < 0.05$, **; $P < 0.01$, $n = 6$).

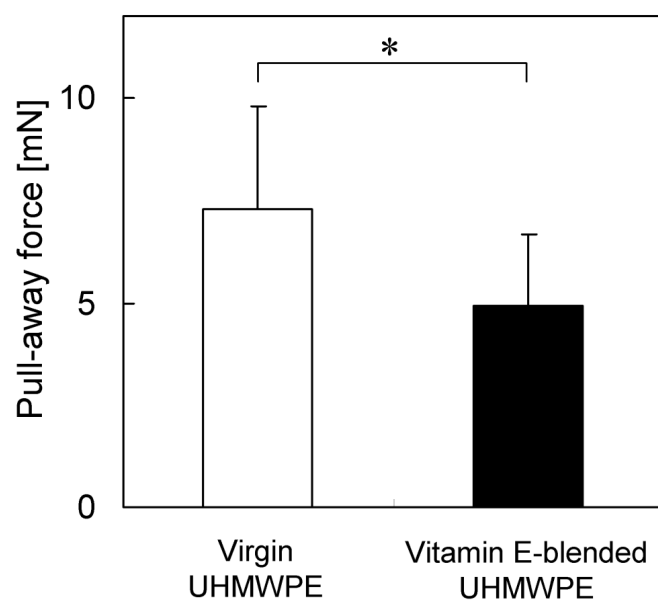


Fig. 3.8 Pull-away force between UHMWPE and Co-28Cr-6Mo alloy. Data represent mean \pm SD. Asterisk indicates a statistically significant difference (*; $P < 0.05$, $n = 8$, Student's t-test).

3.4 Discussion

Our results showed that the formation of UHMWPE transfer films on the surface of the Co-28Cr-6Mo alloy was reduced by the addition of vitamin E to UHMWPE. The transfer process is affected not only by the bulk properties of materials, but also by the surface phenomena [3-5]. As the mechanical properties of non-oxidized UHMWPE with or without vitamin E are almost the same [6], it is likely that some kind of interaction between the surfaces of UHMWPE and Co-28Cr-6Mo alloy is changed by the addition of vitamin E. In terms of the surface issues, we have suggested two possible mechanisms for the reduction in transfer film formation of vitamin E-blended UHMWPE. One possibility is that vitamin E inhibits the continuous oxidation of UHMWPE, thus reducing the attraction between UHMWPE and Co-28Cr-6Mo alloy. Another possibility is that vitamin E leaches from inside of vitamin E-blended UHMWPE under compressive load, and inhibits adhesion between UHMWPE and Co-28Cr-6Mo alloy.

In the former mechanism, UHMWPE is thought to be oxidized by a cyclic oxidation process known as Bolland's cycle, producing hydroperoxides [7]. This continuous oxidation process is terminated by lack of oxygen and/or the formation of relatively stable radicals, such as those of vitamin E [8-10]. In addition, it has also been reported that the hydroperoxide concentration in vitamin E-doped UHMWPE remains unchanged under aging conditions [10]. It is well known that oxidation is one of the main factors related to wear. Since the increase in attraction between UHMWPE and Co-28Cr-6Mo alloy by formation of hydroperoxides on the UHMWPE surface is inhibited by vitamin E blending, the anti-oxidant effects of vitamin E are

thought to be one mechanism for the reduction in the transfer film formation and/or in the pull-away force.

However, the latter mechanism, namely, pressure-induced leaching of vitamin E from inside of UHMWPE, has not yet been investigated. In the next chapter, we examined the possibility of pressure-induced leaching of vitamin E from inside of vitamin E-blended UHMWPE and the inhibiting effects of leached-vitamin E on the formation of a UHMWPE transfer film on the Co-28Cr-6Mo alloy surface.

It is generally known that UHMWPE transfer films could not be observed on the opposite side of sliding surfaces when serum solution was used as lubricant [11-13]. However, it has been suggested that the partial dry contact at asperity levels of UHMWPE under serum lubrication is induced by increasing the contact stress [14]. Our hypothetic model of formation of UHMWPE transfer film onto the surface of Co-28Cr-6Mo alloy in serum lubricant is shown in Fig. 3.9. The present study evaluated the UHMWPE transfer film formed on the Co-28Cr-6Mo alloy in water as a first step toward solving the wear resistance mechanism of UHMWPE. Further experiments in serum lubricant are necessary to elucidate this point.

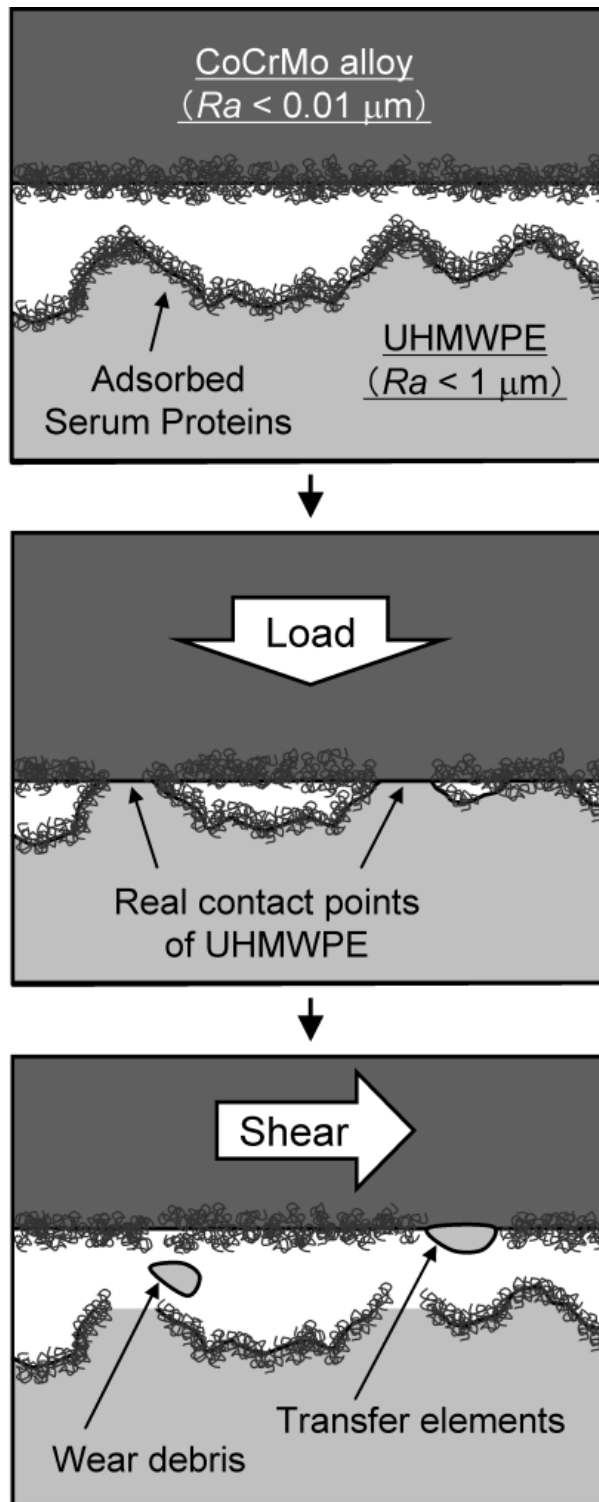


Fig. 3.9 Hypothetic model of formation of UHMWPE transfer film in serum lubricant.

3.5 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 Co-28Cr-6Mo alloy.

3.6 Acknowledgments

UHMWPE blocks (vitamin E-blended, virgin) and the Co-28Cr-6Mo alloy ingot were supplied by Nakashima Medical Corporation. UHMWPE pin specimens were machined by Yasojima Proceed Corporation. Co-28Cr-6Mo alloy disk specimens were polished by Sanki Corporation. The pin-on-disk tribological test apparatus, the vertical force measuring apparatus and the clean bench were developed by Sanki Corporation. The author is grateful to Mr. Sadamu Kinoshita, Graduate School of Engineering, Kyoto University, for SEM observation.

3.7 References

- [1] T. Sasada, Frictional damage in solid surfaces: with special reference to the adhesive wear, *Journal of the Japan Society of Mechanical Engineers*, **75** (1972), 905-912 (in Japanese).
- [2] N.K. Myshkin, M.I. Petrokovets, A.V. Kovalev, Tribology of polymers: Adhesion, friction, wear, and mass-transfer, *Tribology International*, **38** (2005), 910-921.
- [3] A. Chanda, A.K. Mukhopadhyay, D. Basu, S. Chatterjee, Wear and friction behaviour of UHMWPE-alumina combination for total hip replacement, *Ceramic International*, **23** (1997), 437-447.
- [4] T.A. Blanchet, F.E. Kennedy Jr, The development of transfer films in ultra-high molecular weight polyethylene/stainless steel oscillatory sliding, *Tribology Transactions*, **32** (1989), 371-379.
- [5] S.A. Karpe, The frictional behavior of unlubricated polyethylene, *Tribology Transactions*, **25** (1982), 537-545.
- [6] I. Sakuramoto, A. Mori, K. Nagata, N. Tomita, K. Kuramoto, S. Kawano, The effects of oxidative degradation on mechanical properties of UHMWPE for artificial knee joint, *Journal of the Japan Society of Mechanical Engineers A*, **67** (2001), 148-155 (in Japanese).
- [7] S.M. Kurtz, UHMWPE Biomaterials Handbook (Second Edition), Academic press, (2009) 312.
- [8] K. Katsuyama, T. Inoue, T. Takahashi, T. Kai, Synergistic effect of vitamin E related additives on antioxidation of polyolefin resin, *Journal of the Japan Petroleum Institute*, **49** (2006), 121-126 (in Japanese).

- [9] E. Oral, S.L. Rowell, O.K. Muratoglu, The effect of α -tocopherol on the oxidation and free radical decay in irradiated UHMWPE, *Biomaterials*, **27** (2006), 5580-5587.
- [10] P. Bracco, V. Brunella, M. Zanetti, M.P. Luda, L. Costa, Stabilisation of ultra-high molecular weight polyethylene with Vitamin E, *Polymer Degradation and Stability*, **92** (2007), 2155-2162.
- [11] H. McKellop, I.C. Clarke, K.L. Markolf, H.C. Amstutz, Wear Characteristics of UHMW polyethylene: A method for accurately measuring extremely low wear rates, *Journal of Biomedical Materials Research*, **12** (1978), 895-927.
- [12] J.R. Cooper, D. Dowson, J. Fisher, The effect of transfer film and surface roughness on the wear of lubricated ultra-high molecular weight polyethylene, *Clinical Materials*, **14** (1993), 295-302.
- [13] A. Wang, A. Essner, C. Stark, J.H. Dumbleton, Comparison of the size and morphology of UHMWPE wear debris produced by a hip joint simulator under serum and water lubricated conditions, *Biomaterials*, **17** (1995), 865-871.
- [14] A. Wang, A. Essner, R. Klein, Effect of contact stress on friction and wear of ultra-high molecular weight polyethylene in total hip replacement, *Proceedings of the Institution of Mechanical Engineers, Part H: Journal of Engineering in Medicine*, **215** (2001), 133-139.

Chapter 4

Leaching of Vitamin E under Compressive Load

4.1 Introduction

The formation of UHMWPE transfer film on the surface of the Co-28Cr-6Mo alloy was reduced by the addition of vitamin E to UHMWPE as shown in Chapter 3. We have suggested two possible mechanisms for the reduction in transfer film formation of vitamin E-blended UHMWPE. One possibility is that vitamin E inhibits the continuous oxidation of UHMWPE, thus reducing the attraction between UHMWPE and Co-28Cr-6Mo alloy. Another possibility is that vitamin E leaches from inside of UHMWPE under compressive load, and inhibits adhesion between UHMWPE and Co-28Cr-6Mo alloy. The purpose of this chapter was to evaluate the possibility of pressure-induced leaching of vitamin E from inside of vitamin E-blended UHMWPE and the inhibiting effects of leached-vitamin E on the formation of UHMWPE transfer film on the Co-28Cr-6Mo alloy surface.

4.2 Materials and Methods

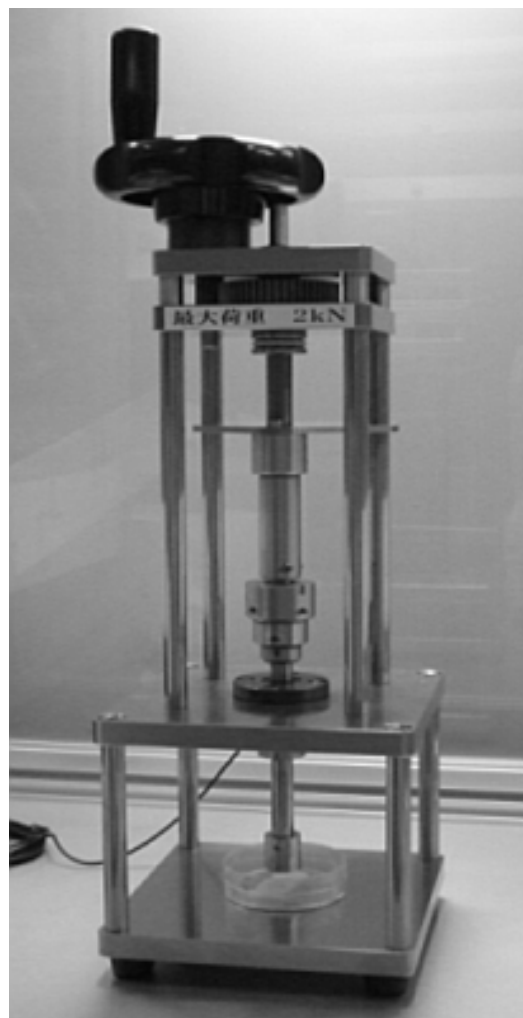
4.2.1 Preparation of specimens

UHMWPE resin powder (GUR1050, Ticona, USA) was blended with vitamin E (0.3% w/w, *dl*- α -Tocopherol, Eisai, Japan) using a screw cone mixer (LFS-GS-2J, Fukae Powtec, Japan). The vitamin E-blended UHMWPE block was manufactured using direct compression molding at 220°C under 25 MPa for 30 min. The virgin UHMWPE block, which is used as the control material in this study, was manufactured similarly, but without the addition of vitamin E. The thin section specimens for the vitamin E leaching tests (thickness: 100 μ m) were cut from UHMWPE blocks using a microtome and subjected to ultrasonic immersion cleaning in isopropyl alcohol (50% v/v) at room temperature for 15 min. Then, the specimens were stored in ultrapure water at 37°C. The pin specimens for the transfer tests were machined from a virgin UHMWPE block. The pin geometry was a flat-ended conical cylindrical shape (ϕ 5 \times 5 mm) with a tip diameter of ϕ 1 mm ($Ra < 0.1 \mu$ m). Then, specimens were subjected to ultrasonic immersion cleaning in isopropyl alcohol (50% v/v) at room temperature for 15 min. In addition, disk specimens with a highly polished flat sliding surface and a diameter of 8 mm ($Ra < 0.01 \mu$ m) were machined from a Co-28Cr-6Mo alloy ingot and subjected to ultrasonic immersion cleaning in acetone (99.5% v/v) at room temperature for 15 min. All manufacturing and cleaning procedures were conducted in air, and no sterilization was carried out prior to the testing.

4.2.2 Test for vitamin E leaching

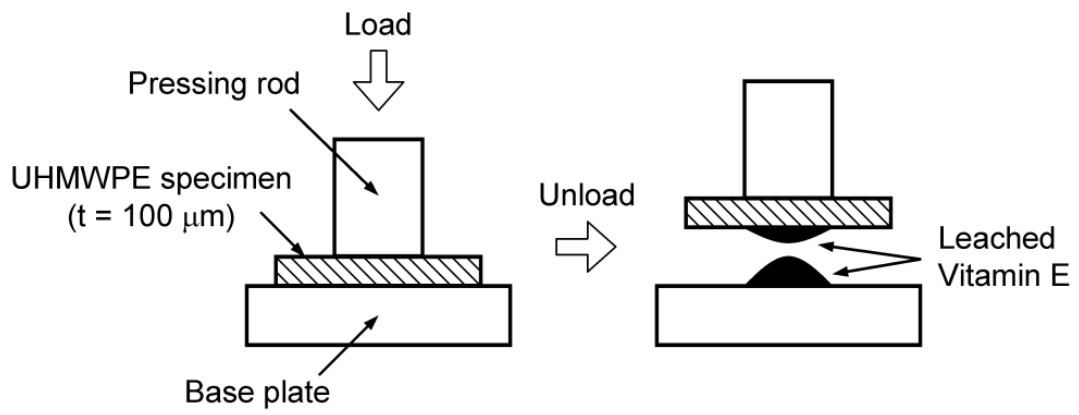
The test for vitamin E leaching from inside of vitamin E-blended UHMWPE was carried out using a press (Ys-Press-01, Sanki, Japan), as shown in Fig. 4.1. A vitamin E-blended UHMWPE specimen was fixed on the base plate, and a vertical compressive load was applied to the specimen with a metal cylindrical rod. The load value was set as 150 N or 1,500 N, and the nominal contact stress on the rod surface was 3 MPa or 30 MPa, respectively. The load was applied for 1 min and then released. Then, vitamin E that was present between the specimen and base plate was dissolved in washing ethanol solvent (99.5% v/v).

In addition, this dissolved procedure using the specimen and base plate without compressive load was carried out as the control experiment. Similar experiments were carried out using virgin UHMWPE specimens.



(a)

Fig. 4.1 Experimental apparatus for test of vitamin E leaching from inside of vitamin E-blended UHMWPE under compressive load. (a) Photograph of whole apparatus, (b) Schematic drawing of compressive section and procedure for testing.



(b)

4.2.3 Quantification of vitamin E

The vitamin E dissolved in the washing ethanol solvent was quantified with a fluorescence spectrophotometer (F-3000, Hitachi, Japan). It has been shown that the excitation and emission wavelengths of vitamin E (α -Tocopherol) are 295 nm and 320 nm, respectively [1,2]. Typical fluorescence spectra of vitamin E in ethanol are shown in Fig. 4.2. The Raman signal of the ethanol solvent, which appears around 320 nm, was subtracted from the original output signal. The amount of vitamin E (L_e) was defined as

$$L_e = V_e - V_v \quad (1)$$

where V_e is the difference obtained by subtracting the fluorescence intensity of the vitamin E-blended UHMWPE under no compressive load from the fluorescence intensity of the specimen under a load of 3 MPa or 30 MPa for fluorescence emissions at wavelengths from 315 nm to 325 nm, and V_v is the fluorescence intensity of virgin UHMWPE. A preliminary experiment revealed that the fluorescence intensity of vitamin E in this range of wavelengths was positively correlated with vitamin E concentration on a standard curve.

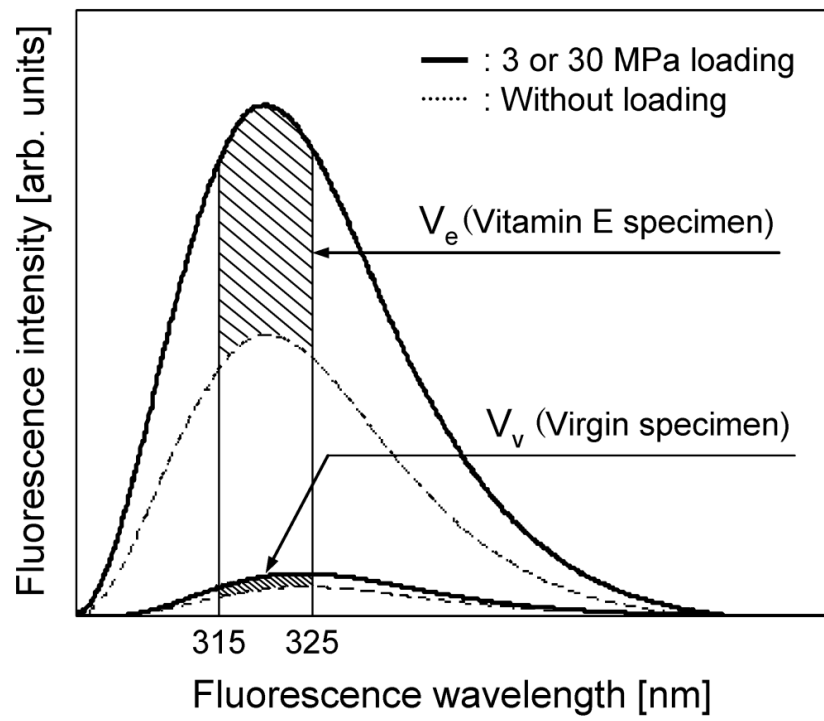


Fig. 4.2 Typical fluorescence spectra of ethanol solutions after leaching test.

4.2.4 UHMWPE transfer test

The UHMWPE transfer test was carried out using a computer-controlled pin-on-disk tribological test apparatus (Ys-TRIB-01, Sanki, Japan), as shown in Fig. 4.3. All tests were conducted at room temperature inside a clean bench (Ys-Class5, Sanki, Japan) that provided air with cleanliness exceeding ISO Class 5 in order to avoid contamination with air dust particles. Vitamin E solution (200 ng/ml) was prepared by dissolving vitamin E in ethanol, and 0.5 μl of solution was placed on the tip of the virgin pin specimen. After evaporation of ethanol, the amount of vitamin E residue on the tip of the pin specimen was about 10 ng/cm^2 . Next, the pin specimen was placed within the holder. The load was set to 8 N, and the nominal contact stress on the pin surface was 10 MPa. The disk specimen was placed within a holder fixed on the X-stage and underwent linear reciprocating sliding motion for 5,000 cycles, with an amplitude of 1 mm and a frequency of 1 Hz. The lubricant bath was filled with 5 ml of ultrapure water, 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 to compensate for gradual evaporation. The tested disk specimen was subjected to immersion cleaning in ethanol (99.5% v/v) before observing the UHMWPE transfer film that formed on the disk surface. The quantification of the UHMWPE transfer film formed on the disk specimen surface was performed as previously shown in Chapter 3 (Fig. 3.4).

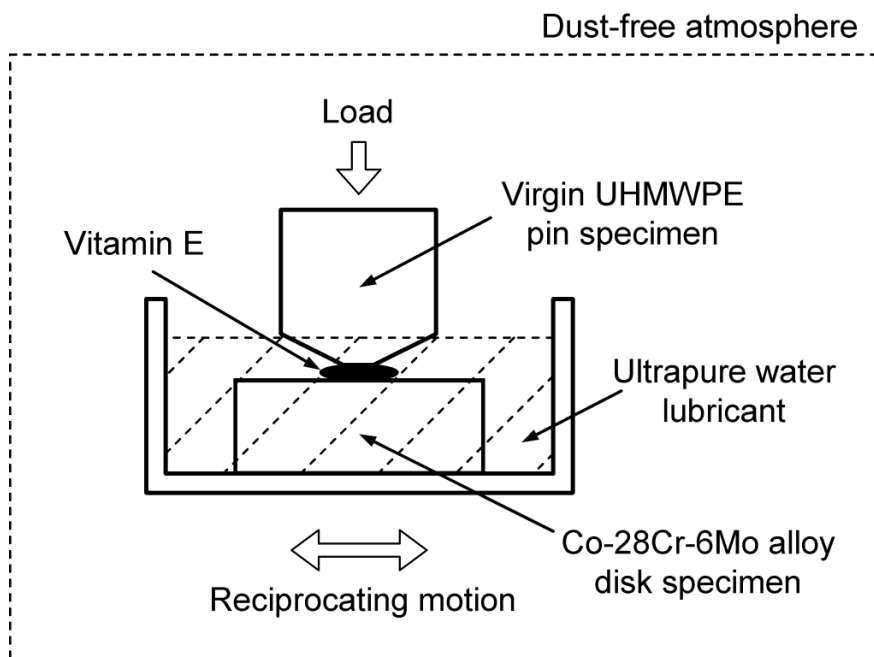


Fig. 4.3 Schematic of apparatus used in transfer tests

4.3 Results

The amount of vitamin E dissolved in the washing ethanol solvent at different contact stress values is shown in Fig. 4.4. The amount of vitamin E had positive correlation with a contact stress. Typical microscope images of the Co-28Cr-6Mo alloy surface after transfer tests without and with the application of vitamin E onto the surface of the virgin UHMWPE pin specimen are shown in Fig. 4.5. It was observed that the decreasing trend of the adhesive substance on the Co-28Cr-6Mo alloy surface by the application of vitamin E. The apparent region ratio of UHMWPE transfer film that formed on the Co-28Cr-6Mo alloy surface without and with the application of vitamin E is shown in Fig. 4.6. The extent of UHMWPE transfer film formation was significantly decreased by the application of vitamin E onto the surface of the virgin UHMWPE pin specimen.

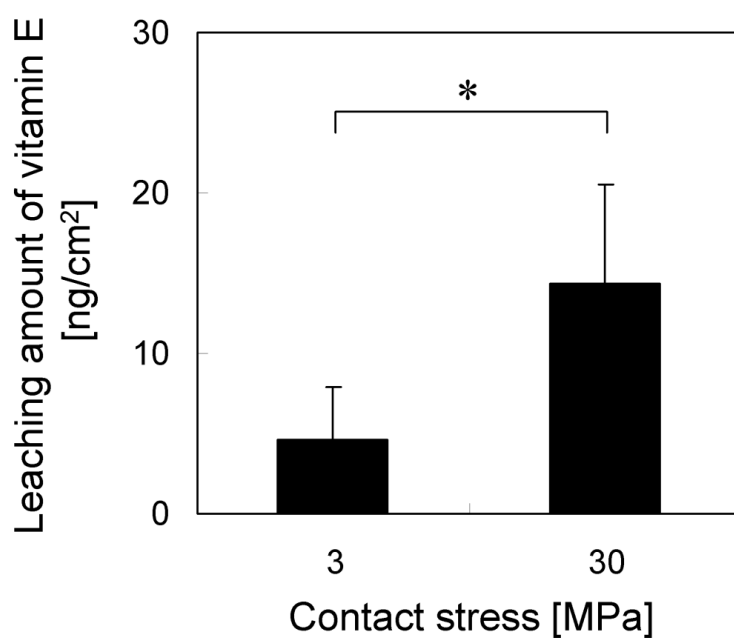


Fig. 4.4 Amount of vitamin E dissolved in the washing ethanol solvent at different contact stress values. Data represent mean \pm SD. Asterisk indicates a statistically significant difference (*; $P < 0.05$, $n = 5$, Student's t-test).

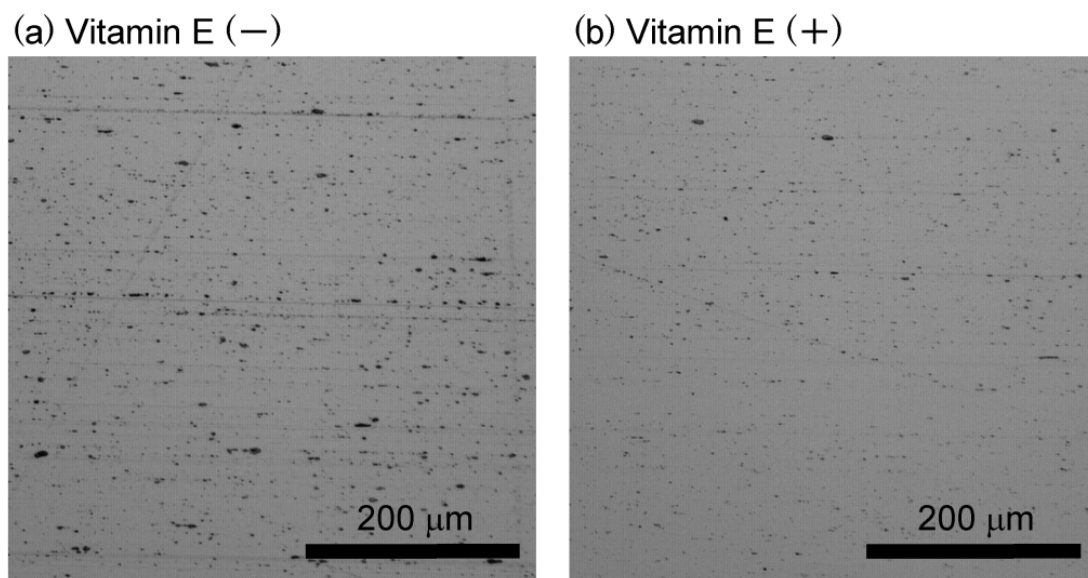


Fig. 4.5 Typical microscope images of Co-28Cr-6Mo alloy surface after transfer tests. (a) without and (b) with application of vitamin E.

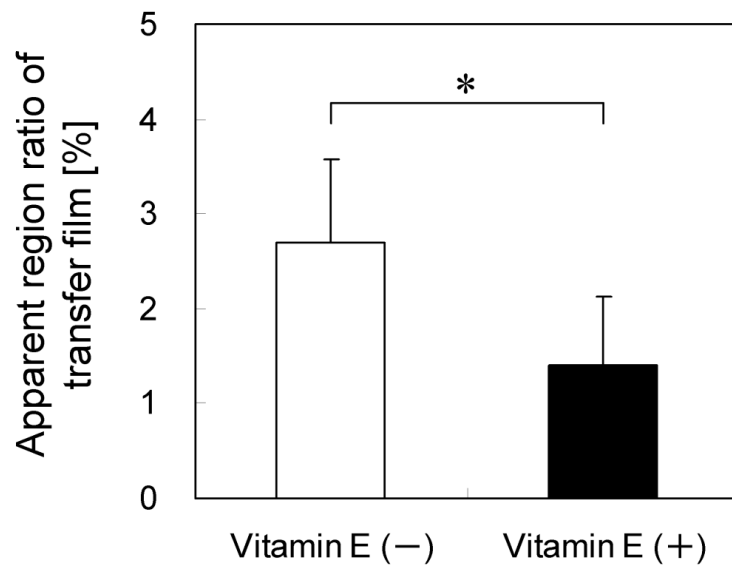


Fig. 4.6 Apparent region ratio of virgin UHMWPE transfer film formed on Co-28Cr-6Mo alloy surface without and with application of vitamin E. Data represent mean \pm SD. Asterisk indicates a statistically significant difference (*; $P < 0.05$, $n = 6$, Student's t-test).

4.4 Discussion

The present results showed that the amount of vitamin E dissolved in the washing ethanol solvent had positive correlation with the applied load to vitamin E-blended UHMWPE, and the extent of UHMWPE transfer film formation on a Co-28Cr-6Mo alloy surface is significantly reduced by the application of vitamin E onto the surface of the virgin UHMWPE pin specimen. These results strongly suggested that the vitamin E leached from vitamin E-blended UHMWPE by those high pressures contributed to the inhibition of UHMWPE transfer film formation on the Co-28Cr-6Mo alloy surface. Although the application of vitamin E to the virgin UHMWPE at the onset of the sliding test differs from the leaching of vitamin E from inside of vitamin E-blended UHMWPE during the sliding test, these results suggest that adhesion between UHMWPE and Co-28Cr-6Mo alloy is reduced by the presence of vitamin E.

Regarding the biological response involving UHMWPE wear debris, it has been reported that cells cultured in the presence of debris from vitamin E-blended UHMWPE secreted significantly lower quantities of inflammatory cytokines compared with cells exposed to virgin UHMWPE [3]. This improved biological response is consistent with the proposed leaching mechanism, as vitamin E (α -Tocopherol) has been shown to decrease the release of inflammatory cytokines from monocytes [4], and the cell morphology changes correlated with macrophage activation has been shown to be induced by oxidative degradation of UHMWPE [5]. Both the leaching and the anti-oxidant effects of vitamin E may be involved in the mechanism for not only increased wear resistance but also improved biological reactivity to vitamin E-blended UHMWPE.

4.5 Conclusion

It was suggested that vitamin E leached from inside of vitamin E-blended UHMWPE under compressive load, and the amount of vitamin E that leached was positively correlated with the applied load. In addition, the extent of UHMWPE transfer film formation was significantly decreased by the application of vitamin E onto the surface of the virgin UHMWPE pin specimen.

4.6 Acknowledgments

UHMWPE blocks (vitamin E-blended, virgin) and the Co-28Cr-6Mo alloy ingot were supplied by Nakashima Medical Corporation. UHMWPE pin specimens were machined by Yasojima Proceed Corporation. Co-28Cr-6Mo alloy disk specimens were polished by Sanki Corporation. The pressing apparatus was developed by Sanki Corporation. The author is grateful to Dr. Nobuaki Shirai, Industrial Research Center of Shiga prefecture, for his technical comments in the fluorescence detection of vitamin E.

4.7 References

- [1] J.N. Thompson, P. Erdody, W.B. Maxwell, Simultaneous fluorometric determinations of vitamins A and E in human serum and plasma, *Biochemical Medicine*, **8** (1973), 403-414.
- [2] K. Abe, G. Katsui, Fluorometric determination of tocopherol in serum, *Journal of the Japanese Society of Nutrition and Food Science*, **28** (1975), 277-280 (in Japanese).
- [3] S. Teramura, S. Russell, E. Ingham, J. Fisher, N. Tomita, K. Fujiwara, J.L. Tipper, Reduced biological response to wear particles from UHMWPE containing Vitamin E, *Proceedings of 55th Annual Meeting of Orthopaedic Research Society*, (2009), 2377.
- [4] S. Devaraj, I. Jialal, α -tocopherol decreases interleukin-1 β release from activated human monocytes by inhibition of 5-lipoxygenase, *Arteriosclerosis, Thrombosis, and Vascular Biology*, **19** (1999), 1125-1133.
- [5] M. Bosetti, L. Zanardi, P. Bracco, L. Costa, M. Cannas, In vitro evaluation of the inflammatory activity of ultra-high molecular weight polyethylene, *Biomaterials*, **24** (2003), 1419-1426.

Chapter 5

Frictional Property in Serum Lubricant

5.1 Introduction

Regarding the interaction between UHMWPE and another material, it has been suggested that vitamin E reduces the adhesion between the surfaces of UHMWPE and Co-28Cr-6Mo alloy as shown in Chapter 3. In addition, the possibility of pressure-induced leaching of vitamin E from inside of vitamin E-blended UHMWPE has been suggested in Chapter 4. On the other hand, in regard to the interaction between UHMWPE and a lubricant, a considerable number of friction studies concerning serum lubricant have been conducted in order to provide useful information in clarifying the mechanisms that lead to UHMWPE wear [1-5]. The purpose of this chapter was to evaluate the effects of the addition of vitamin E on the frictional property of UHMWPE in serum lubricant as one of the fundamental approaches to clarifying the tribological performance of vitamin E-blended UHMWPE.

5.2 Materials and Methods

5.2.1 Preparation of specimens

UHMWPE resin powder (GUR1050, Ticona, USA) was blended with vitamin E (0.3% w/w, *dl*- α -Tocopherol, Eisai, Japan) using a screw cone mixer (LFS-GS-2J, Fukae Powtec, Japan). The vitamin E-blended UHMWPE block was manufactured by direct compression molding at 220°C and 25 MPa for 30 min. The virgin UHMWPE block, which was used as the control material in this study, was manufactured similarly, but without the addition of vitamin E. The pin specimens for the friction tests were machined from these UHMWPE blocks. The pin geometry was a flat-ended conical cylindrical shape ($\phi 5 \times 5$ mm) with a tip diameter of $\phi 1$ mm ($Ra < 0.1$ μm). Then, pin specimens were subjected to ultrasonic immersion cleaning in isopropyl alcohol (50% v/v) at room temperature for 15 min. In addition, disk specimens with a highly polished flat sliding surface and diameter of 8 mm ($Ra < 0.01$ μm) were machined from a Co-28Cr-6Mo alloy ingot and cleaned by ultrasonication in acetone (99.5% v/v) at room temperature for 15 min. All manufacturing and cleaning procedures were conducted in air, and no sterilization was carried out prior to the testing.

5.2.2 Pin-on-disk friction test

Friction tests were carried out using a computer-controlled pin-on-disk tribological test apparatus (Ys-TRIB-01, Sanki, Japan), as shown in Fig. 5.1. The pin specimen was mounted vertically at the tip of the leaf spring. A load of 2.4 N or 24 N

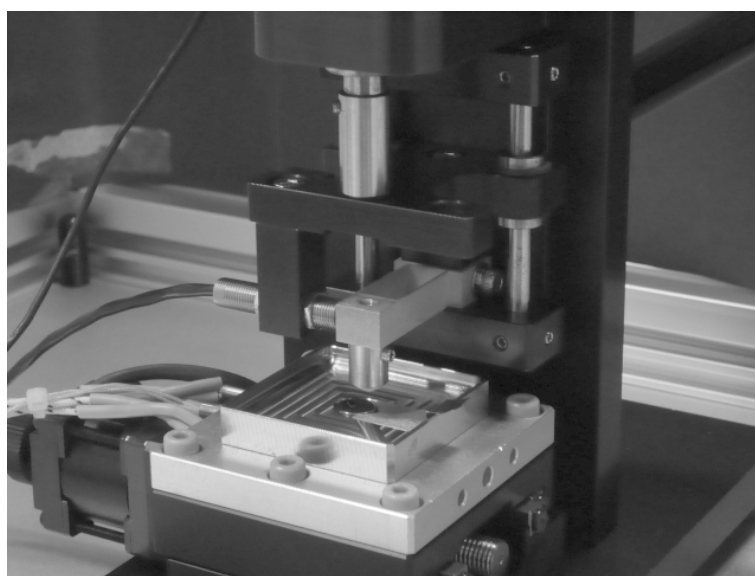
was applied to the pin specimen; the nominal contact stress on the pin surface was 3 MPa or 30 MPa, respectively. The disk specimen was fixed within the lubricant bath on the X-stage, and set into linear reciprocating sliding motion for 2,000 cycles with amplitude of 1 mm and frequency of 0.3 Hz. The lubricant bath was filled with 5 ml of bovine calf serum (SAFC Biosciences, USA), which was kept at 37°C and replenished at a rate of 1 ml per 500 cycles during the tests to compensate for its gradual evaporation.

5.2.3 Application of vitamin E to pin surface

Vitamin E solution (30 µg/ml) was prepared by dissolving vitamin E in ethanol (99.5% v/v), and 0.5 µl of solution was placed on the tip of the virgin pin specimen. After evaporation of ethanol, the amount of vitamin E residue on the tip of the pin specimen was about 1.5 µg/cm². Next, the pin specimen was mounted on the leaf spring, and the friction test was carried out.

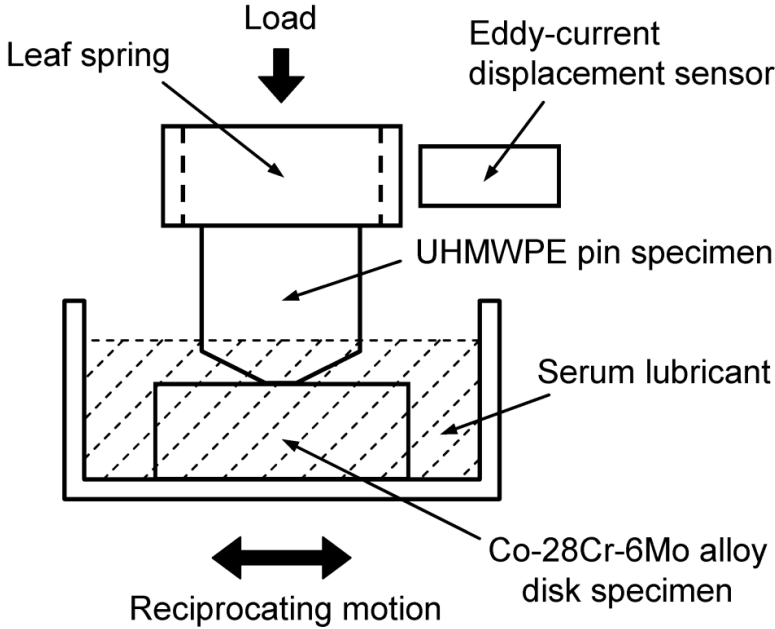
5.2.4 Definition of friction force

The friction force between the UHMWPE pin and the Co-28Cr-6Mo alloy disk was calculated from the displacement of the leaf spring during the sliding motion. A typical example of the output signal of the eddy-current displacement sensor during friction force measurements is shown in Fig. 5.2. The positive and negative friction forces indicate the opposite sliding directions during the linear reciprocating motion. The friction force was defined as the average value of dynamic friction force within the central area of 1 mm on the sliding trajectory.



(a)

Fig. 5.1 Experimental apparatus for friction test. (a) Photograph of sliding section, (b) Schematic drawing of sliding section.



(b)

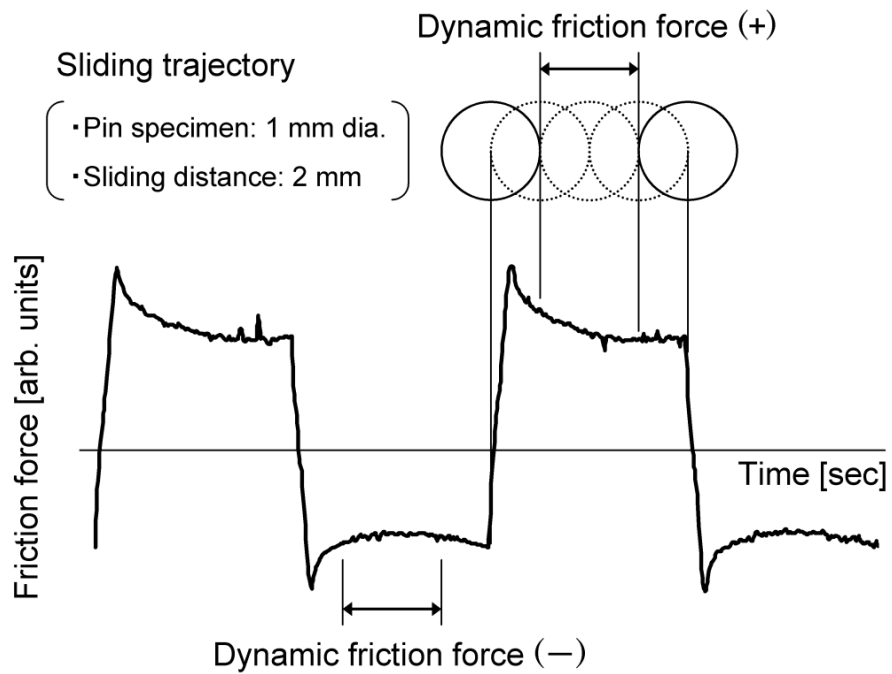


Fig. 5.2 Typical example of output signal from eddy-current displacement sensor during friction force measurement between UHMWPE pin and Co-28Cr-6Mo alloy disk.

5.2.5 Quantification of serum-derived residue

After friction tests, the Co-28Cr-6Mo alloy disk specimens were cleaned by immersion in ultrapure water and then dried at room temperature inside a clean bench over night. The actual micrograph of the Co-28Cr-6Mo alloy surface after the friction test is shown in Fig. 5.3. A considerable amount of residue was distributed over the entire sliding region on the Co-28Cr-6Mo alloy surface. Given the experimental conditions, it is concluded that these residues were substance derived from serum proteins. The quantification of the serum-derived residues on the disk specimen surface was performed as previously shown in Chapter 3 (Fig. 3.4). The apparent region ratio of the serum-derived residues was defined as the ratio between the area of the apparent residue and the area of the entire acquired image.

5.2.6 Statistical methods

The effects of vitamin E addition on the serum-derived residues on the Co-28Cr-6Mo alloy surface were analyzed using one-way ANOVA followed by the Tukey test for post hoc comparisons.

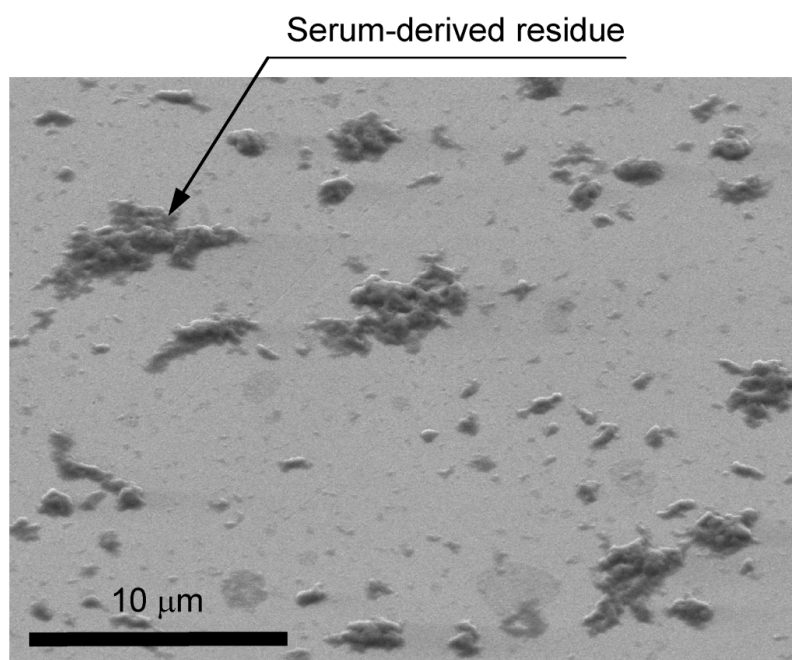


Fig. 5.3 Scanning electron micrograph of Co-28Cr-6Mo alloy surface after friction test.

5.3 Results

The friction behavior of vitamin E-blended UHMWPE in serum lubricant tended to be similar to that of virgin UHMWPE under 3 MPa loading, as shown in Fig. 5.4. Under 30 MPa loading, the friction behavior of vitamin E-blended UHMWPE in serum lubricant exhibited three features that were not observed for virgin UHMWPE, as shown in Fig. 5.5. Firstly, the friction force was lower in the initial stage of friction tests (sliding distance: 0-2 m); secondly, the variability of the friction force was less in the transition process (2-5 m); and thirdly, friction force was significantly higher in the steady state sliding (5-8 m). The friction behavior of virgin UHMWPE in serum lubricant was altered by the application of vitamin E to the sliding surface, as shown in Fig. 5.6. The friction behavior of vitamin E-applied UHMWPE was similar to that of vitamin E-blended UHMWPE.

The apparent region ratio of serum-derived residues on the Co-28Cr-6Mo alloy surface after friction tests for the vitamin E-blended, vitamin E-applied and virgin UHMWPE pin specimens are shown in Fig. 5.7. For vitamin E-blended UHMWPE, a significantly larger amount of serum-derived residues were observed in comparison with virgin UHMWPE. For virgin UHMWPE, a trend of increasing the serum-derived residues was observed with the application of vitamin E to the sliding surface.

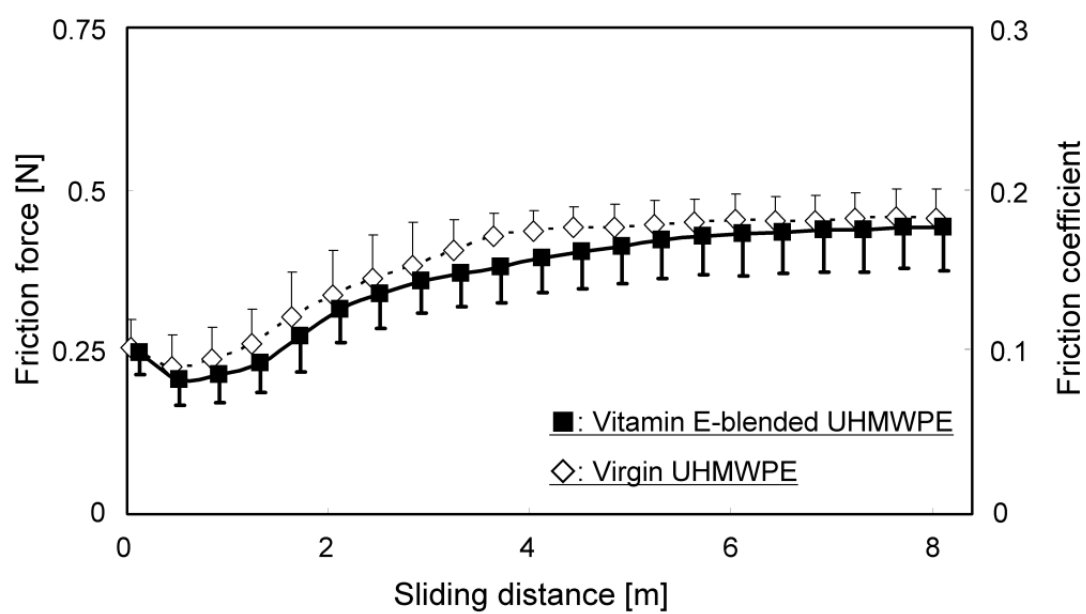


Fig. 5.4 Friction behavior of vitamin E-blended UHMWPE and virgin UHMWPE in serum lubricant under 3 MPa loading. Data represent mean \pm SD (n = 6).

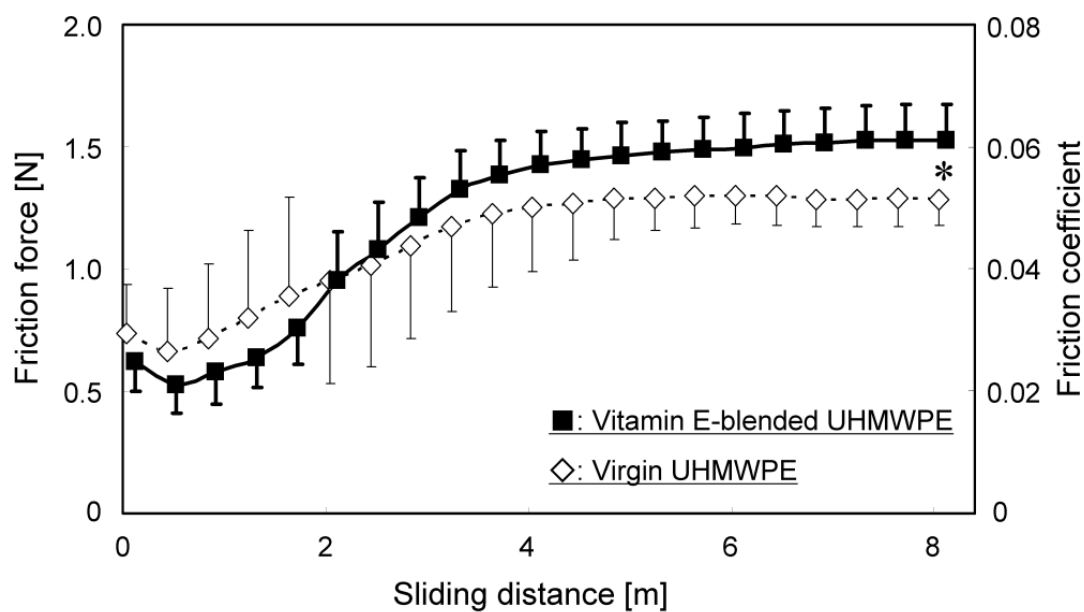


Fig. 5.5 Friction behavior of vitamin E-blended UHMWPE and virgin UHMWPE in serum lubricant under 30 MPa loading. Data represent mean \pm SD. Asterisk indicates a statistically significant difference (*; $P < 0.01$, $n = 6$, Student's t-test).

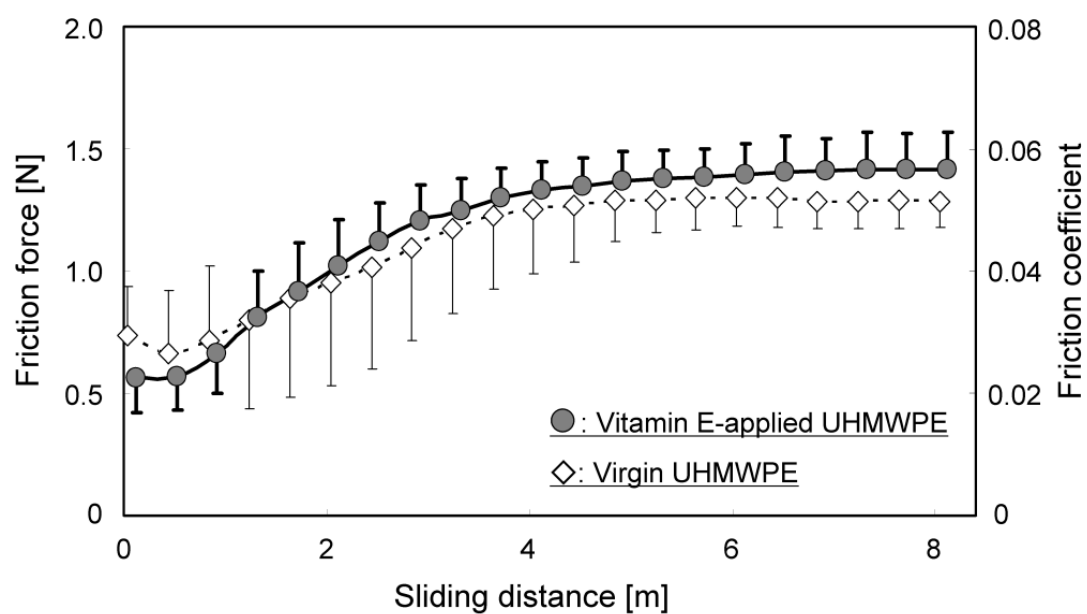


Fig. 5.6 Friction behavior of vitamin E-applied UHMWPE and virgin UHMWPE in serum lubricant under 30 MPa loading. Data represent mean \pm SD (n = 6).

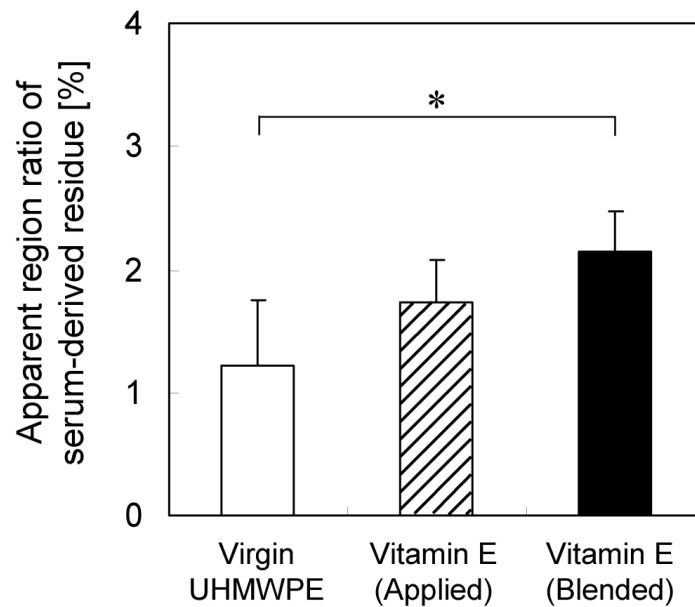


Fig. 5.7 Apparent region ratio of serum-derived residues formed on Co-28Cr-6Mo alloy surface after friction tests under 30 MPa loading for each type of UHMWPE specimen. Data represent mean \pm SD. Asterisk indicates a statistically significant difference (*; $P < 0.05$, $n = 5$).

5.4 Discussion

The frictional property of vitamin E-blended UHMWPE in serum lubricant differed from that of virgin UHMWPE under 30 MPa loading, while there was little difference under 3 MPa loading. These results suggest that the effects of vitamin E on the frictional property of UHMWPE in serum lubricant depend on the compressive load on the sliding surface. One explanation for these results is that the bulk properties of UHMWPE were altered by the addition of vitamin E. Two phenomena have been suggested to change the bulk properties of UHMWPE. Firstly, vitamin E in the amorphous phase of UHMWPE might decrease strain-induced crystallization and increase the strain-induced orientation of molecular chains in the amorphous phase as shown in Chapter 2. Secondly, the prevention of oxidation chain reactions (radical reactions) by vitamin E might affect the performance of γ -irradiated UHMWPE [6]. However, the materials used in this study were not subjected to γ -irradiation, and the mechanical properties of the non-oxidized UHMWPE with and without vitamin E are almost the same [7].

Therefore, we have investigated an alternative mechanism, that is, vitamin E leaching from inside of vitamin E-blended UHMWPE under compressive load. We have found that blended vitamin E migrates to the surface of UHMWPE under compressive load, and the amount is positively correlated with the applied load, as shown in Chapter 4. The friction behavior of the vitamin E-blended UHMWPE at the initial stage of the frictional test is likely affected by the presence of vitamin E on the sliding surface. The friction force of vitamin E-blended UHMWPE tended to be lower in the first 2 m and higher in the steady state (5-8 m), compared with that for

virgin UHMWPE. Our results also show that the friction force of virgin UHMWPE in the first 1 m is decreased by the application of vitamin E to the sliding surface. Although the application of vitamin E to virgin UHMWPE at the onset of the friction test differs from the leaching of vitamin E from inside of vitamin E-blended UHMWPE during the friction test, this result suggests that the friction force of UHMWPE in the initial stage of friction tests is decreased by the presence of vitamin E on the sliding surface. However, it is unlikely that vitamin E leaches from inside of vitamin E-blended UHMWPE over the entire testing period, and vitamin E that leaches during the initial stage is considered to disperse gradually into the lubricant as the sliding distance increases. Another feature of the friction test on the vitamin E-blended UHMWPE is that the friction force exhibited less variability in the first 5 m, and the amount of serum-derived residues on the Co-28Cr-6Mo alloy surface after friction tests was significantly larger than that on the virgin UHMWPE surface. Since the friction force and the serum-derived residues were increased by the application of vitamin E to the sliding surface of virgin UHMWPE, this finding suggests that the significantly higher friction force of vitamin E-blended UHMWPE in the steady state of the friction test can be attributed to the substances generated by the interaction between vitamin E and serum proteins on the sliding surface. Moreover, this interaction would be considered as one of the possible factors that lead to lower variability of the friction force of vitamin E-blended UHMWPE in the transition process.

Among the interactions between vitamin E and proteins, it is well known that the intricate secondary and tertiary structures of globular proteins become unfolded in aqueous solution via interaction with oil [8]. In relation to friction, it has been suggested that unfolded proteins preferentially adsorb onto hydrophobic surfaces

and/or other unfolded proteins due to strong hydrophobic interactions, and consequently efficient hydration of the frictional interface is decreased [9]. However, the effects of serum proteins on the friction and wear performance of UHMWPE encompasses complex phenomena affected by many high-energy processes, for example, the extremely high pressure at the real contact area; thus, further experiments are necessary to elucidate these effects.

In the present study, the friction force of vitamin E-blended UHMWPE had a lower initial value and a higher value in the steady state, compared with that of virgin UHMWPE. In actual walking cycles, however, contact stress over 30 MPa on the UHMWPE tibial component occurs only for short time intervals, and serum proteins are subsequently metabolized. Our results suggest that the friction force after the high compressive contact between UHMWPE and Co-28Cr-6Mo alloy is decreased temporarily by the presence of vitamin E on the sliding surface. Although, these mechanisms might be contribute to the improved wear resistance of vitamin E-blended UHMWPE observed in knee simulator testing, further study should be done for the effects on the artificial hip joints where multi-directional sliding movement will be applied continuously.

5.5 Conclusion

The load-dependent frictional property of vitamin E-blended UHMWPE in serum lubricant was evaluated using unidirectional pin-on-disk apparatus. The friction force of vitamin E-blended UHMWPE had a lower initial value and a higher value in the steady state, and the variability of friction force in the transition process was relatively small. Friction behavior similar to that of vitamin E-blended UHMWPE was observed as a result of applying vitamin E to the sliding surface of virgin UHMWPE. These results suggest that the frictional property of vitamin E-blended UHMWPE in serum lubricant is affected by the presence of vitamin E on the sliding surface under high compressive load.

5.6 Acknowledgments

UHMWPE blocks (vitamin E-blended, virgin) and the Co-28Cr-6Mo alloy ingot were supplied by Nakashima Medical Corporation. UHMWPE pin specimens were machined by Yasojima Proceed Corporation. Co-28Cr-6Mo alloy disk specimens were machined and polished by Sanki Corporation. The author is grateful to Mr. Sadamu Kinoshita, Graduate School of Engineering, Kyoto University, for SEM observation.

5.7 References

- [1] H. McKellop, I.C. Clarke, K.L. Markolf, H.C. Amstutz, Wear Characteristics of UHMW polyethylene: A method for accurately measuring extremely low wear rates, *Journal of Biomedical Materials Research*, **12** (1978), 895-927.
- [2] Y. Sawae, T. Murakami, J. Chen, Effect of synovia constituents on friction and wear of ultra-high molecular weight polyethylene sliding against prosthetic joint materials, *Wear*, **216** (1998), 213-219.
- [3] M.R. Widmer, M. Heuberger, J. Voros, N.D. Spencer, Influence of polymer surface chemistry on frictional properties under protein-lubrication conditions: implications for hip-implant design, *Tribology Letters*, **10** (2001), 111-116.
- [4] M.P. Gispert, A.P. Serro, R. Colaco, B. Saramago, Friction and wear mechanisms in hip prosthesis: Comparison of joint materials behaviour in several lubricants, *Wear*, **260** (2006), 149-158.
- [5] H.W. Fang, M.C. Hsieh, H.T. Huang, C.Y. Tsai, M.H. Chang, Conformational and adsorptive characteristics of albumin affect interfacial protein boundary lubrication: From experimental to molecular dynamics simulation approaches, *Colloids and Surfaces B*, **68** (2009), 171-177.
- [6] N. Shibata, S.M. Kurtz, N. Tomita, Recent advances of mechanical performance and oxidation stability in ultrahigh molecular weight polyethylene for total joint replacement: highly crosslinked and α -tocopherol doped, *Journal of Biomechanical Science and Engineering*, **1** (2006), 107-123.
- [7] I. Sakuramoto, A. Mori, K. Nagata, N. Tomita, K. Kuramoto, S. Kawano, The effects of oxidative degradation on mechanical properties of UHMWPE for

artificial knee joint, *Journal of the Japan Society of Mechanical Engineers A*, **67** (2001), 148-155 (in Japanese).

- [8] G. Meng, J.C.K. Chan, D. Rousseau, E.C.Y. Li-Chan, Study of protein-lipid interactions at the bovine serum albumin/oil interface by Raman microspectroscopy, *Journal of Agricultural and Food Chemistry*, **53** (2005), 845-852.
- [9] M.P. Heuberger, M.R. Widmer, E. Zobeley, R. Glockshuber, N.D. Spencer, Protein-mediated boundary lubrication in arthroplasty, *Biomaterials*, **26** (2005), 1165-1173.

Evaluation of the Structural and Tribological Performance of
Ultrahigh Molecular Weight Polyethylene Blended with Vitamin E

Chapter 6

Adsorption of Serum Proteins

6.1 Introduction

Protein adsorption is known to be the very first stage of blood-surface interaction [1], and most of the adsorbed proteins on polyethylene particles in-vivo have been identified as albumin, and heavy-chain and light-chain γ -globulin [2]. It is well known that Fc γ receptors present on the macrophage interact with Fc domain of human immunoglobulin G (IgG) bound to pathogens, and that macrophages secrete several proinflammatory cytokines, such as tumor necrosis factor- α (TNF- α) and interleukin-1 β (IL-1 β), as well as initiate phagocytosis of pathogens [3,4]. In addition, macrophages long-term adhesion on the polymer surface seems to be mediated by IgG and its fragments [5]. Although albumin is not known to be involved in phagocytosis by macrophages, it has been suggested that the albumin adsorbed onto the surface of hydrophobic polymer materials increases hemocompatibility and decreases the adsorption of other serum proteins [1,6]. The purpose of this chapter was to evaluate the adsorbed amount of γ -globulin and albumin onto the surface of vitamin E-blended

UHMWPE as one of the fundamental approaches to clarifying the mechanism for the biological response to vitamin E-blended UHMWPE debris.

6.2 Materials and Methods

6.2.1 Preparation of specimens

UHMWPE resin powder (GUR1050, Ticona, USA) was mixed with vitamin E (0.3% w/w, *dl*- α -Tocopherol, Eisai, Japan) using a screw cone mixer (LFS-GS-2J, Fukae Powtec, Japan). The vitamin E-blended UHMWPE block was manufactured using direct compression molding at 220°C under 25 MPa for 30 min. The virgin UHMWPE block, which was used as the control material in this study, was manufactured in the same manner, but without the addition of vitamin E. The experimental specimens (ϕ 8 mm, thickness: 100 μ m) were cut from UHMWPE blocks using a microtome. Following this, the specimens were subjected to ultrasonic immersion cleaning in isopropyl alcohol (50% v/v) at room temperature for 15 minutes. All manufacturing and cleaning procedures were conducted in air, and no sterilization was carried out prior to testing.

6.2.2 Measurement of surface properties

The surface properties of vitamin E-blended and virgin UHMWPE are listed in Table 6.1. The contact angle of each specimen against 4 μ l of ultrapure water was determined by the sessile drop method using CA-Z2 (Kyowa Interface Science, Japan)

at room temperature. The ζ -potential of each specimen was measured using ELS-7000AS with the cell unit for flat plate samples (Otsuka Electronics, Japan) in 10 mM NaCl at 25°C. The pH of the streaming solution was adjusted to 7.4 by mixing HCl and NaOH aqueous solutions. The roughness value (Ra) of each specimen was measured by stylus-type surface roughness tester (SE1200, Kosaka Laboratory, Japan) on the basis of international standards (JIS B 0601:2001).

6.2.3 Preparation of fluorescently-labeled proteins

Human γ -globulin (G4386, Sigma-Aldrich, USA) dissolved in 50 mM sodium borate buffer (pH 8.5) and fluorescent dye (DyLight 488, Pierce, USA) dissolved in dimethylformamide were mixed well and incubated at room temperature for 1 hour. The molar ratio of protein and fluorescent dye was determined as one to one. Fluorescently-labeled γ -globulin was selectively dissolved in PBS solution using the desalting column (Pierce, USA), and the protein concentration in the solution was regulated at about 2 mg/ml. Human albumin (A9511, Sigma-Aldrich, USA) labeled with fluorescent dye was made similarly, and was regulated at a protein concentration of about 8 mg/ml. A mixed solution of γ -globulin and albumin was prepared by dissolving non-labeled albumin in fluorescently-labeled γ -globulin solution, and the albumin concentration was regulated at about 8 mg/ml.

6.2.4 Quantification of adsorbed proteins

UHMWPE specimens were covered with each protein solution and incubated for 1 hour at 37°C. Adsorbed proteins were collected by incubating specimens with 2%

sodium dodecyl sulfate (SDS) solution for 4 hours at room temperature. The quantification of proteins was carried out using a fluorescence spectrophotometer (F-3000, Hitachi, Japan), at excitation and emission wavelengths of 493 nm and 518 nm, respectively. Typical spectra of fluorescently-labeled proteins in SDS solution is shown in Fig. 6.1. The peak value of fluorescence intensity of proteins was positively correlated with protein concentration on the standard curve, and thus the amount of adsorbed protein was defined by the integral value of the fluorescence intensity in the interval of fluorescence wavelength from 513 nm to 523 nm.

6.2.5 Statistical methods

The effects of vitamin E and albumin on the adsorption of γ -globulin onto UHMWPE surface were analyzed using two-way ANOVA followed by the Tukey test for post hoc comparisons.

Table. 6.1 Surface properties of vitamin E-blended and virgin UHMWPE. Data represent mean \pm SD, (a): n = 10, (b): n = 3 , (c): n = 10.

UHMWPE type	Contact angle ^(a) (deg)	ζ -potential ^(b) (mV)	Roughness ^(c) (μm)
Virgin	85.5 \pm 5.7	-47.9 \pm 8.0	2.45 \pm 0.46
Vitamin E	93.3 \pm 4.6	-45.8 \pm 4.4	2.20 \pm 0.57

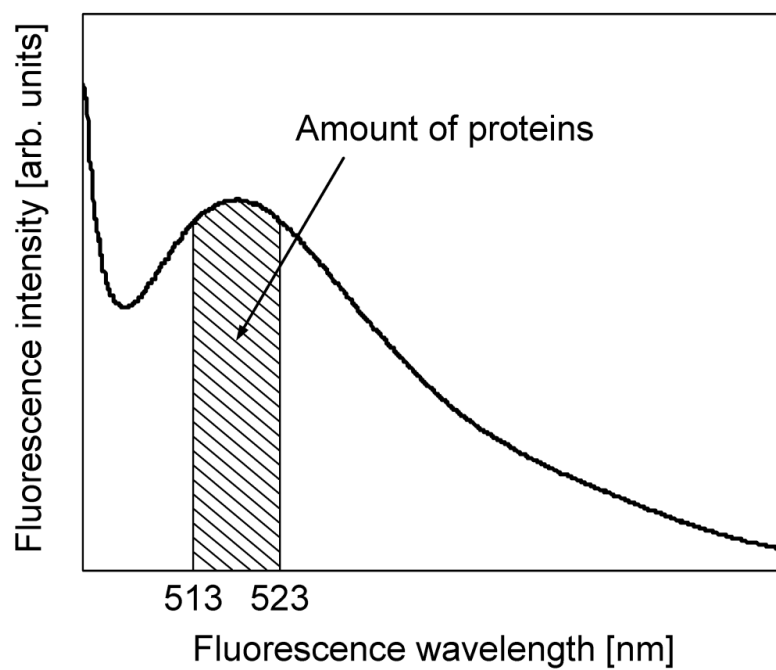


Fig. 6.1 Typical spectra of fluorescently-labeled proteins in SDS solution.

6.3 Results

The adsorbed amount of γ -globulin onto the surface of vitamin E-blended UHMWPE was almost the same in comparison to virgin UHMWPE, as shown in Fig. 6.2. The adsorbed amount of albumin on the surface of vitamin E-blended UHMWPE was approximately 50% lower than that for the virgin UHMWPE, as shown in Fig. 6.3.

The adsorbed amounts of γ -globulin on the surfaces of vitamin E-blended and virgin UHMWPE were significantly reduced by the mixture of albumin into the γ -globulin solution. In addition, there were no differences in the adsorbed amount of γ -globulin between vitamin E-blended and virgin UHMWPE regardless of the presence of albumin as shown in Fig. 6.4.

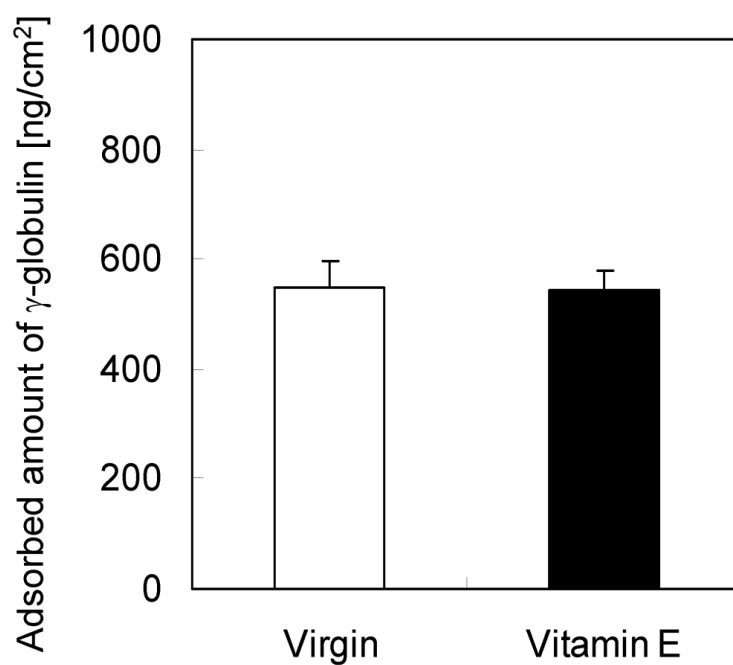


Fig. 6.2 Adsorbed amount of γ -globulin on vitamin E-blended and virgin UHMWPE surfaces. Data represent mean \pm SD (n = 6).

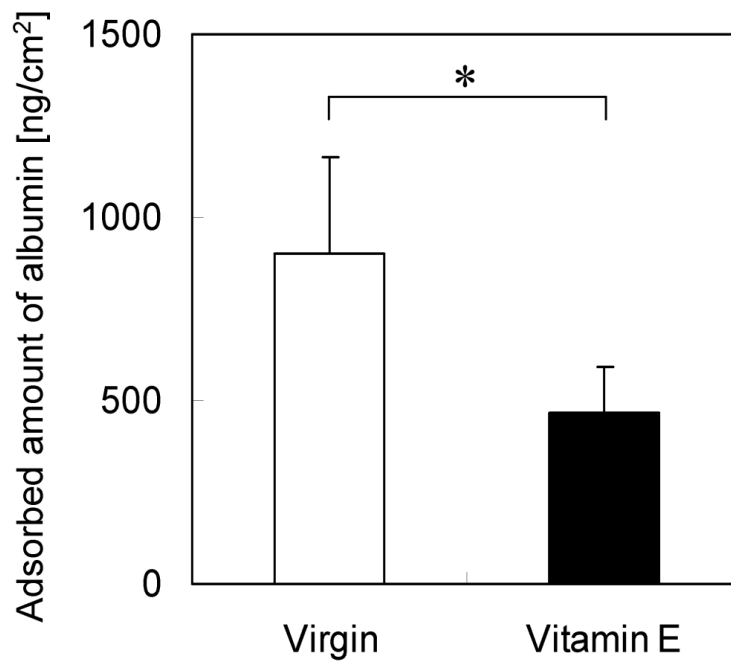


Fig. 6.3 Adsorbed amount of albumin on vitamin E-blended and virgin UHMWPE surfaces. Data represent mean \pm SD. Asterisk indicates a statistically significant difference (*; $P < 0.01$, $n = 6$, Student's t-test).

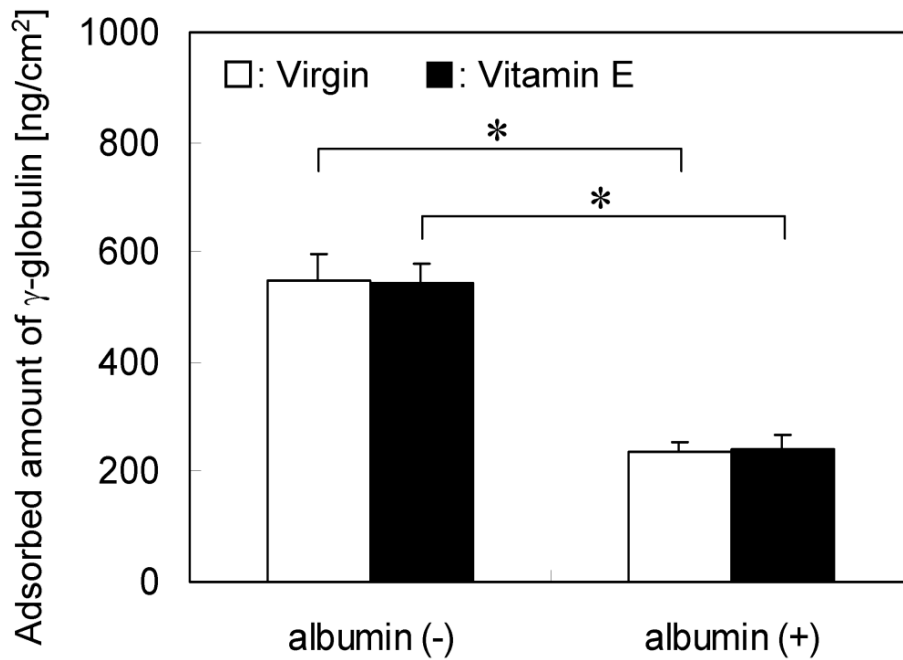


Fig. 6.4 Adsorbed amount of γ -globulin on vitamin E-blended and virgin UHMWPE surfaces with and without albumin mixture in γ -globulin solution. Data represent mean \pm SD. Asterisk indicates a statistically significant difference (*; $P < 0.001$, $n = 6$).

6.4 Discussion

It has been reported that primary human mononuclear cells cultured with wear debris from vitamin E UHMWPE secreted very low levels of osteolytic cytokines as shown in Fig. 1.6. The biological response of the mononuclear cells to the UHMWPE wear debris is thought to be affected by several direct and/or indirect effects of vitamin E such as anti-inflammation, anti-oxidation, and radical scavenging. If some amount of vitamin E exists in the lubricant, the release of inflammatory cytokines such as, TNF- α and IL-1 β from monocytes [7,8], can be reduced, thus the direct effect of vitamin E can be considered as one of the factors. The anti-oxidation effect of vitamin E may alter cell morphology relating to macrophage activation [9], as well as granulocyte activation relating to the inflammatory response directed at implants [10]. It has been reported that the oxidation degree of bulk UHMWPE was decreased by the addition of vitamin E [11,12], and thus the anti-oxidant effect of vitamin E can also be considered as one of factors. Additionally, UHMWPE is thought to be oxidized by a cyclic oxidation process known as Bolland's cycle, producing hydroperoxides [13]. This continuous oxidation process is terminated by lack of oxygen and/or the formation of relatively stable radicals, such as those of vitamin E [14,15]. The inhibition of producing hydroperoxides on the UHMWPE surface could also be one factor in reducing the biological response to debris.

The adsorption of γ -globulin onto the surface of UHMWPE wear debris is thought to be a factor directly involved in macrophage phagocytosis due to observed opsonin activity [3,4]. However, the adsorbed amount of γ -globulin on the surface of the vitamin E-blended UHMWPE was almost the same in comparison to the virgin

UHMWPE. In contrast, the adsorbed amount of albumin on the surface of the vitamin E-blended UHMWPE was approximately half the amount for the virgin UHMWPE. It has been suggested that albumin adsorbed onto the surface of hydrophobic polymer materials affects the adsorption of other serum proteins [1,6]. Our results showed that the adsorbed amount of γ -globulin on the surfaces of vitamin E-blended and virgin UHMWPE were significantly decreased by the mixture of albumin into the γ -globulin solution. However, there was no difference in the amount of adsorbed γ -globulin between vitamin E-blended and virgin UHMWPE in the presence of albumin. These results suggest that the difference in the adsorbed amount of albumin between vitamin E-blended and virgin UHMWPE plays no role in the mechanism for reducing the biological response to vitamin E-blended UHMWPE debris. On the other hand, we have suggested that pressure-induced leaching of vitamin E from inside of vitamin E-blended UHMWPE occurs during joint function in the knee prosthesis, as shown in Chapter 4. This suggests that vitamin E on the surface of UHMWPE may play a role in the adsorption of γ -globulin. Further experiments are necessary to clarify this point.

6.5 Conclusion

The adsorption of γ -globulin onto the surface of vitamin E-blended UHMWPE was almost the same in comparison to virgin UHMWPE. The adsorption of albumin was approximately 50% lower than that for the virgin UHMWPE. There was no difference in the amount of adsorbed γ -globulin between vitamin E-blended and virgin UHMWPE in the mixture containing both albumin and γ -globulin.

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6.7 References

- [1] V.I. Sevastianov, Role of protein adsorption in blood compatibility of polymers, *CRC Critical Reviews in Biocompatibility*, **4** (1988), 109-130.
- [2] T. Ojima, Effect of serum protein binding on the phagocytosis of polyethylene particles by macrophages, *Journal of Juzen Medical Society*, **108** (1999), 371-380 (in Japanese).
- [3] J.G.J. van de Winkel, P.J.A. Capel, Human IgG Fc receptor heterogeneity: Molecular aspects and clinical implication, *Immunology Today*, **14** (1993),

215-221.

- [4] M.L. Refici, D.W. Metzger, B.P. Arulanandam, M.R. Lennartz, D.J. Loegering, Fc γ -receptor signaling augments the LPS-stimulated increase in serum tumor necrosis factor- α levels, *American Journal of Physiology-Regulatory, Integrative and Comparative Physiology*, **280** (2001), R1037-R1044.
- [5] C.R. Jenney, J.M. Anderson, Adsorbed IgG: A potent adhesive substrate for human macrophages, *Journal of Biomedical Materials Research, Part B: Applied Biomaterials*, **50** (2000), 281-290.
- [6] K. Ogawara, K. Furumoto, S. Nagayama, K. Minato, K. Higaki, T. Kai, T. Kimura, Pre-coating with serum albumin reduces receptor-mediated hepatic disposition of polystyrene nanosphere: implications for rational design of nanoparticles, *Journal of Controlled Release*, **100** (2004), 451-455.
- [7] I. Jialal, S. Devaraj, N. Kaul, The effect of α -tocopherol on monocyte proatherogenic activity, *American Society of Nutritional Science*, **131** (2001), 389S-394S.
- [8] S. Devaraj, I. Jialal, α -tocopherol decreases interleukin-1 β release from activated human monocytes by inhibition of 5-lipoxygenase, *Arteriosclerosis, Thrombosis, and Vascular Biology*, **19** (1999), 1125-1133.
- [9] M. Bosetti, L. Zanardi, P. Bracco, L. Costa, M. Cannas, In vitro evaluation of the inflammatory activity of ultra-high molecular weight polyethylene, *Biomaterials*, **24** (2003), 1419-1426.
- [10] F. Reno, F. Lombardi, M. Cannas, UHMWPE oxidation increases granulocytes activation: a role in tissue response after prosthesis implant, *Biomaterials*, **24** (2003), 2895-2900.

- [11] S. Teramura, N. Tomita, S. Kawashima, K. Fujita, M. Aoki, T. Isu, Oxidation resistance of vitamin E additive ultra high molecular weight polyethylene for an artificial knee joint, *Journal of the Surface Science Society*, **25** (2004), 568-572 (in Japanese).
- [12] N. Shibata, N. Tomita, The anti-oxidative properties of α -tocopherol in γ -irradiated UHMWPE with respect to fatigue and oxidation resistance, *Biomaterials*, **26** (2005), 5575-5762.
- [13] S.M. Kurtz, UHMWPE Biomaterials Handbook (Second Edition), Academic press, (2009) 312.
- [14] E. Oral, S.L. Rowell, O.K. Muratoglu, The effect of α -tocopherol on the oxidation and free radical decay in irradiated UHMWPE, *Biomaterials*, **27** (2006), 5580-5587.
- [15] P. Bracco, V. Brunella, M. Zanetti, M.P. Luda, L. Costa, Stabilisation of ultra-high molecular weight polyethylene with Vitamin E, *Polymer Degradation and Stability*, **92** (2007), 2155-2162.

Evaluation of the Structural and Tribological Performance of
Ultrahigh Molecular Weight Polyethylene Blended with Vitamin E

Chapter 7

Summary

The wear performance of ultrahigh molecular weight polyethylene (UHMWPE) and the biological reactivity to UHMWPE wear debris are essential properties for extending the longevity of joint prostheses. The UHMWPE blended with vitamin E (*dl- α -Tocopherol*) has exhibited the higher wear resistance and lower biological reactivity compared with conventional UHMWPE. However, detailed mechanisms for these performance have not yet been clarified.

In this study, the effects of the addition of vitamin E on the structural and tribological performance of UHMWPE were evaluated in order to clarify the mechanism of wear resistance of vitamin E-blended UHMWPE (Chapter 2-5). Additionally, the adsorption of serum proteins onto the surface of vitamin E-blended UHMWPE was evaluated in order to clarify the mechanism for the biological response to vitamin E-blended UHMWPE debris (Chapter 6).

The summary of each chapter is shown in the following:

Chapter 2

The effects of the addition of vitamin E on the strain-induced crystallization and molecular chain orientation of UHMWPE were evaluated. The structure changes of vitamin E-blended UHMWPE before and after tensile strain were analyzed by X-ray diffraction, Raman spectroscopy and image correlation method. The vitamin E-blended UHMWPE exhibited lower strain-induced crystallization than virgin UHMWPE but a higher I_c value in Raman spectroscopic analysis. The vitamin E-blended UHMWPE also exhibited a larger percentage of negative areal dilatation under tensile strain. These results suggest that the addition of vitamin E to UHMWPE decreases the strain-induced crystallization and increases the strain-induced orientation of the molecular chains present in the amorphous phase.

Chapter 3

The effects of the addition of vitamin E on the adhesive interaction between the surfaces of UHMWPE and Co-28Cr-6Mo alloy in water was evaluated. UHMWPE specimens were 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 significantly decreased 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 Co-28Cr-6Mo alloy in water.

Chapter 4

The possibility of pressure-induced leaching of vitamin E from inside of vitamin E-blended UHMWPE was evaluated. UHMWPE specimens were pressed against a base plate, and leached vitamin E was dissolved in ethanol. The quantification of vitamin E in ethanol was carried out by fluorescence spectrophotometry. It was suggested that vitamin E leached from inside of vitamin E-blended UHMWPE under compressive load. In addition, the amount of vitamin E that leached was positively correlated with the applied load. The extent of UHMWPE transfer film formation was significantly decreased by the application of vitamin E onto the surface of the virgin UHMWPE.

Chapter 5

The effects of the addition of vitamin E on the frictional property of UHMWPE in serum lubricant was evaluated. UHMWPE specimens were slid against the surface of Co-28Cr-6Mo alloy by using a pin-on-disk friction test apparatus. The friction behavior of vitamin E-blended UHMWPE differed from that of virgin UHMWPE under 30 MPa loading, while little difference was observed under 3 MPa loading. The friction force of vitamin E-blended UHMWPE showed a lower value in initial friction and a higher value in steady state friction, and the variability of friction force in the transition process was relatively small. Friction behavior similar to that of the vitamin E-blended UHMWPE was observed as a result of applying vitamin E to the sliding surface of virgin UHMWPE. These results suggest that the frictional property of vitamin E-blended UHMWPE in serum lubricant is affected by the presence of vitamin E on the sliding surface under high compressive load.

Chapter 6

The amounts of γ -globulin and albumin adsorbed onto the surface of vitamin E-blended UHMWPE were evaluated. UHMWPE specimens were covered with each fluorescently-labeled protein solution, and adsorbed proteins on the surface of specimen were collected by incubation in sodium dodecyl sulfate (SDS) solution. The quantification of proteins in SDS solution was carried out by fluorescence spectrophotometry. The adsorption of γ -globulin onto the surface of vitamin E-blended UHMWPE was almost the same in comparison to virgin UHMWPE. The adsorption of albumin was approximately 50% lower than that for the virgin UHMWPE. There was no difference in the amount of adsorbed γ -globulin between vitamin E-blended and virgin UHMWPE in the solution containing both albumin and γ -globulin.

List of Publications

1 Original Papers

- [1] Y. Okubo, S. Mori, K. Yamamoto, D. Hamada, H. Kohno, K. Fujiwara, M. Hashimoto, K. Ikeuchi, N. Tomita, Mechanical interaction between vitamin E-containing ultrahigh molecular weight polyethylene and Co-28Cr-6Mo alloy in water, *Journal of Biomechanical Science and Engineering*, **4 (2)**, (2009), 166-173.
- [2] Y. Okubo, S. Teramura, Y. Niwa, K. Ibaraki, K. Murata, S.H. Hyon, G. Pezzotti, N. Tomita, Strain-induced crystallization and orientation of vitamin E-blended ultrahigh molecular weight polyethylene, *Bio-Medical Materials and Engineering*, **19 (6)**, (2009), 431-439.
- [3] Y. Okubo, S. Mori, K. Yamamoto, N. Tomita, Confirmation of pressure-induced leaching of vitamin E from inside of ultrahigh molecular weight polyethylene, *Journal of Biomechanical Science and Engineering*, **5 (2)**, (2010), 154-162.

- [4] Y. Okubo, D. Hamada, K. Yamamoto, S. Mori, K. Ikeuchi, N. Tomita, Load-dependent frictional performance of vitamin E-blended ultrahigh molecular weight polyethylene in serum lubricant, *Tribology Online*, **5** (2), (2010), 96-101.
- [5] Y. Okubo, H. Higashi, S. Mori, D. Hamada, N. Tomita, Adsorption of serum proteins on the surface of vitamin E-blended ultrahigh molecular weight polyethylene, *in preparation*.

2 Proceedings

2.1 International conferences

- [1] Y. Okubo, D. Hamada, K. Yamamoto, S. Mori, K. Fujiwara, K. Ikeuchi, N. Tomita, Effects of serum and load conditions on the frictional property of vitamin E-blended UHMWPE, *Proceedings of 4th International Meeting, UHMWPE for Arthroplasty*, (2009), 29-30. Torino, ITALY.
- [2] Y. Okubo, S. Teramura, Y. Niwa, K. Ibaraki, K. Murata, S.H. Hyon, G. Pezzotti, N. Tomita, Strain-induced crystallization and orientation of vitamin E-blended ultrahigh molecular weight polyethylene, *Proceedings of 56th Annual Meeting of Orthopaedic Research Society*, (2010), 2296. New Orleans, Louisiana, USA.

The others

- [3] S. Mori, Y. Okubo, K. Yamamoto, D. Hamada, H. Kohno, K. Fujiwara, M. Hashimoto, K. Ikeuchi, N. Tomita, Mechanical interaction between vitamin E-containing ultrahigh molecular weight polyethylene and Co-28Cr-6Mo alloy in water, *Proceedings of 4th World Tribology Congress*, (2009), 645. Kyoto, JAPAN.
- [4] S. Mori, Y. Okubo, K. Yamamoto, D. Hamada, K. Fujiwara, K. Ikeuchi, N. Tomita, Transfer film formation of vitamin E-blended UHMWPE on Co-28Cr-6Mo alloy surface, *Proceedings of 4th International Meeting, UHMWPE for Arthroplasty*, (2009), 31-32. Torino, ITALY.
- [5] D. Hamada, Y. Okubo, K. Yamamoto, S. Mori, K. Fujiwara, K. Ikeuchi, N. Tomita, Effect of loading and serum proteins on the frictional property of vitamin E-containing ultrahigh molecular weight polyethylene, *Proceedings of 22nd International Society for Technology in Arthroplasty*, (2009), A722. Big Island, Hawaii, USA.
- [6] H. Higashi, Y. Okubo, D. Hamada, K. Yamamoto, S. Mori, K. Ikeuchi, N. Tomita, Load-dependent interaction between vitamin E-blended UHMWPE and serum conformation, *Proceedings of 56th Annual Meeting of Orthopaedic Research Society*, (2010), 2298. New Orleans, Louisiana, USA.

2.2 Domestic conferences

- [1] Y. Okubo, S. Mori, S. Teramura, K. Matsumura, S.H. Hyon, S. Tsutsumi, K. Fujiwara, N. Tomita, Effects of dl- α -tocopherol addition on wear mechanism of ultra-high molecular weight polyethylene for artificial knee joint, *Proceedings of Tribology Conference, the Japanese Society of Tribologists*, (2007), 511-512 (in Japanese). Saga.
- [2] Y. Okubo, S. Mori, S. Teramura, K. Fujiwara, N. Tomita, Protein adsorption on the surface of vitamin E added ultra-high molecular weight polyethylene, *Proceedings of 38th Annual Meeting of the Japanese Society for Replacement Arthroplasty*, (2008), 231 (in Japanese). Okinawa.
- [3] Y. Okubo, S. Mori, D. Hamada, H. Kohno, K. Fujiwara, N. Tomita, Investigation of wear resistant mechanism of vitamin E-containing UHMWPE -The transfer film formation-, *Proceedings of 39th Annual Meeting of the Japanese Society for Replacement Arthroplasty*, (2009), 284 (in Japanese). Tokyo.
- [4] Y. Okubo, S. Mori, K. Yamamoto, N. Tomita, Load-dependent weeping of vitamin E inside the UHMWPE for artificial knee joint, *Proceedings of 36th Annual Meeting of the Japanese Society for Clinical Biomechanics*, (2009), 130 (in Japanese). Ehime.

- [5] Y. Okubo, S. Teramura, Y. Niwa, K. Ibaraki, S.H. Hyon, N. Tomita, Strain-induced crystallization and orientation of vitamin E-containing UHMWPE, *Proceedings of 31st Annual Meeting of the Japanese Society for Biomaterials*, (2009), 246 (in Japanese). Kyoto.

The others

- [6] S. Mori, Y. Okubo, D. Hamada, K. Fujiwara, H. Kohno, N. Tomita, Effects of vitamin E addition on adhesion of ultra-high molecular weight polyethylene for artificial knee joint, *Proceedings of Mechanical Engineering Congress, the Japan Society of Mechanical Engineers*, (2008), (5) 97-98 (in Japanese). Kanagawa.
- [7] D. Hamada, Y. Okubo, K. Yamamoto, S. Mori, K. Fujiwara, K. Ikeuchi, N. Tomita, Effect of vitamin E addition on the frictional property of ultrahigh molecular weight polyethylene, *Proceedings of Mechanical Engineering Congress, the Japan Society of Mechanical Engineers*, (2009), (6) 297-298 (in Japanese). Iwate.
- [8] D. Hamada, Y. Okubo, K. Yamamoto, S. Mori, K. Fujiwara, K. Ikeuchi, N. Tomita, Effects of serum proteins and loading on the frictional property of vitamin E-blended ultrahigh molecular weight polyethylene, *Proceedings of 22nd Bioengineering Conference, Annual Meeting of Bioengineering Division, the Japan Society of Mechanical Engineers*, (2010), 342 (in Japanese). Okayama.

- [9] D. Hamada, Y. Okubo, K. Yamamoto, S. Mori, K. Fujiwara, K. Ikeuchi, N. Tomita,
Investigation of the frictional property of vitamin E-blended UHMWPE,
*Proceedings of 40th Annual Meeting of the Japanese Society for Replacement
Arthroplasty*, (2010), 350 (in Japanese). Okinawa.

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DOCTORAL THESIS

博士（工学） 学位論文

Evaluation of the Structural and Tribological Performance of

Ultrahigh Molecular Weight Polyethylene Blended with Vitamin E

ビタミンEを混合した超高分子量ポリエチレンの

構造的およびトライボロジー的特性の評価

Department of Mechanical Engineering and Science

Graduate School of Engineering

Kyoto University

京都大学 大学院工学研究科 機械理工学専攻

From 2006 to 2010

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