

Relationship between Oxidation and Wear of Ultra-High Molecular Weight Polyethylene for Total Joint Arthroplasty

Kwon-Yong Lee[†]

School of Automotive, Industrial, and Mechanical Engineering, Taegu University

Abstract : The most widely-used orthopaedic grade polymer bearing liner material, ultrahigh molecular weight polyethylene (UHMWPE), for the total joint arthroplasty degrades after gamma-irradiation sterilization through the progressive oxidation in a shelf and in vivo. Oxidative degradation makes UHMWPE brittle and leads to decrease in mechanical properties. In this study the relationship between post-gamma-irradiation aging time and wear of UHMWPE was investigated. Six retrieved polyethylene hip liners implanted for 3-16 years and then stored in air for 1.5-6.5 years until tests were used. Two types of pin-on-disk wear testing were conducted by the uni-directional repeat pass rotating and by the linear reciprocating stainless steel disks against stationary polyethylene pins under 4Mpa at 1Hz with bovine serum lubrication in ambient environment. Wear of retrieved polyethylene hip liners does not have direct correlation with in vivo or total aging time. Linear reciprocal sliding motion generated more remarkable wear than uni-directional repeat pass sliding motion. It indicates that kinematic motion affects very crucially on the wear of aged UHMWPE having brittle white band region.

Key words : UHMWPE, wear, oxidation, aging time, brittleness, kinematic motion

Introduction

Charnley adopted the combination of metal head and polymer liner for total hip joint arthroplasty in early 1960s. Thereafter, PTFE, low density polyethylene (LDPE), high density polyethylene (HDPE), carbon-reinforced polyethylene, ultrahigh molecular weight polyethylene (UHMWPE), Ti-alloy, and alumina, etc., were tried for bearing liner materials, and stainless steel, Ti-alloy, CoCr-alloy, alumina, and zirconia were tried for femoral head materials. Recently, ceramic head is popular in European and Asian countries. For the special cases like young patients, metal-metal or ceramic-ceramic pairs has been tried. So far, however, UHMWPE bearing liner is a worldwide standard in total hip joint replacements.

Though total joint replacement provided enormous success to patients having end-stage joint problems, osteolysis in periprosthetic bone tissue and loosening of the implant components limit the longevity of total joint arthroplasty. Submicron size wear particles from UHMWPE component has been implicated as a major contributor to bone resorption and subsequent aseptic loosening [1-3]. Therefore, many efforts are on-going to prevent or reduce the wear particle generation from UHMWPE components.

Tribological issues in design of component, material pair, mechanisms of wear, surface roughness of femoral head, abrasion by 3rd body hard particles such as bone cement, metal debris from modular neck joint and porous coating, bone chip, etc., have been confirmed [4-8]. Additional issues of molecular

structural changes due to oxidation and progressive aging in UHMWPE during and after gamma -irradiation sterilization and the subsequent degradation in mechanical properties including wear resistance of UHMWPE have being also profoundly analyzed [9-13].

High-energy photons of gamma-ray during the sterilization process break the molecular chains in UHMWPE and generates free radicals. Some of free radicals react with the oxygen molecules diffused from the environment during irradiation. This is the initiation of oxidation in UHMWPE. Last of free radicals trapped inside are alive for a long time and continue to oxidise UHMWPE. This process results in thickening the oxidized surface layer as the aging time increases.

Gamma-irradiation not only causes oxidation but also increases the level of crosslinking in UHMWPE. The shorted molecular chains have more chance to be entangled physically and recombine with the same chain or neighboring chains resulting in chemical crosslinking. This increase of crosslinking improves the wear resistance in UHMWPE [14-16]. However, this increased level of crosslinking by the gamma-irradiation dramatically decreases after 5-6 years of post-irradiation aging time [13,17,18].

These progressive changes in molecular structure during aging cause the variation in mechanical properties. Highly oxidized subsurface layer, called the white band, showed a remarkable decrease in elongation and ultimate tensile strength of UHMWPE [19]. Previous wear study on the shelf-aged UHMWPE reported that oxidation progressed and decreased the level of crosslinking accompanying with the existence of white bands and brittle cracking, and in turn it did the wear

[†]Corresponding author; Tel: 82-53-850-6683, Fax: 82-53-850-6549
E-mail: kwonlee@Taegu.ac.kr

resistance with aging [20,21]. Therefore, recently new processing and sterilization methods for preventing oxidation and improving the level of crosslinking in UHMWPE have been developed [22,23].

For the retrieved acetabular cups, other report showed no detrimental effect of aging time on the wear performance [24]. Comparing in vivo aging with shelf aging, additional effect of mechanical loading will be involved in the changes of the molecular structure. In this study, by using the post-irradiation in vivo aged (retrieved) UHMWPE hip liners, the relationship between post-irradiation aging and the wear of UHMWPE was investigated. And the effect of kinematic motion on the wear of aged brittle UHMWPE was also studied.

Method

Specimen

Six retrieved polyethylene hip acetabular liners, which were gamma-irradiated, aged in vivo for 3-16 years and then stored in air for 1.5-6.5 years, were used and listed in an order of total aging time in Table 1. All liners were cored by a hollow punch (10 mm diameter) and machined to right angle cylindrical pin specimens. Two pin specimens were prepared for each liner. Each of two pins was used in two different kinematic motions, respectively. When all aged liners were cored, macro-scale cracks near the punched holes and subsurface white bands were observed on the three liners (#1, #3, #6). This brittle layer was almost removed during machining them to right angle cylindrical pins. Each pin was tested against orthopaedic grade stainless steel flat disks. Six disk specimens were highly polished ($R_a = 0.02 \mu\text{m}$) with silicon carbide abrasive papers and alumina powder.

Wear Testing

Two types of wear tests with polyethylene pin-on-stainless steel flat disk contact were conducted under an uni-directional repeat pass sliding motion and a linear reciprocal sliding motion (Figure 1). A nominal contact pressure of 4Mpa was applied to the each pair of contact specimens by a lever arrangement and dead weights. The disc moved along a distance of 63 mm per each cycle at 1Hz, thereby producing a sliding velocity of 63 mm/s at a center of the pin specimen. Both kinematic motions of an uni-directional repeat pass sliding and a linear reciprocal sliding provide an equal sliding distance per each cycle. Bovine serum diluted with 1% sodium azide solution at a volume ratio of 2 : 1 (serum:solution) was

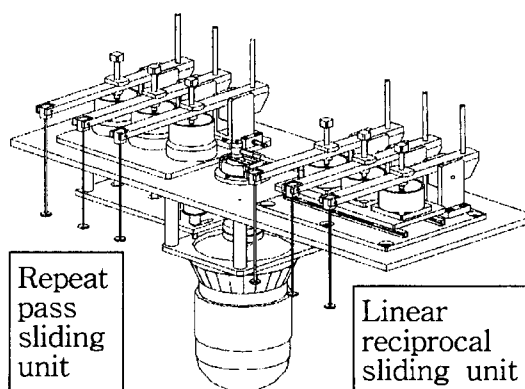


Fig. 1. Schematic diagram of the multi- functions and multi-stations pin-on-disk wear testing apparatus.

used as a lubricant at room temperature.

All tests were interrupted after every 100 thousands cycles, the UHMWPE pin was cleaned with acetone and deionized water by an ultrasonic cleaner, dried with a tissue, and weighed with a microbalance (sensitivity of 0.01 mg). Wear testing continued during a total of 500 thousand cycles of sliding for all pin specimens from retrieved UHMWPE liners. The wear amount of UHMWPE pin specimen was determined by weight loss of each specimen, which was corrected for the weight gain that was obtained from a soak control test.

Results

White Band and Brittleness

When all retrieved acetabular liners were cored by a hollow punch, three (liner #1, #3, #6) of them were so brittle that many macro-scale cracks formed near the edge of punched hole (Figure 2). These brittle liners have the white bands at the subsurface, and the 1-2 mm thick surface layer from the articulating concave surface of each punched pins were easily separated by brittle fracture and fragmentation. Last three liners (#2, #4, #5) showed no crack and white band. The

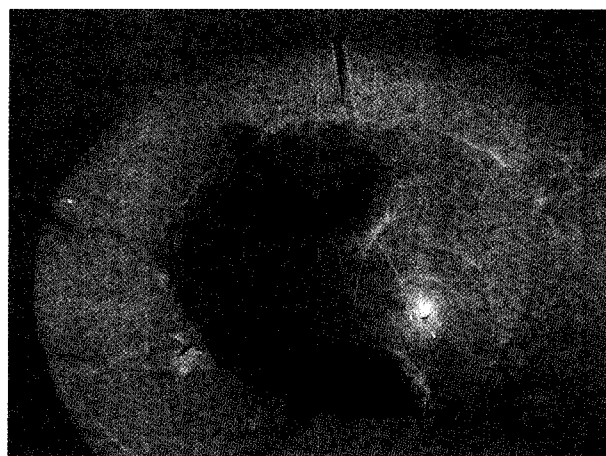


Fig. 2. Photograph showing brittle macro-cracks near the punched hole of liner #1.

Table 1. Aging time of hip liners before the wear tests

liner	in vivo	shelf	total
#1	3yrs 1mn	4yrs 3mns	7yrs 4mns
#2	4yrs 4mns	6yrs 8mns	11yrs
#3	10yrs 2mns	2yrs 1mn	12yrs 3mns
#4	13yrs	1yr 7mns	14yrs 7mns
#5	12yrs 9mns	2yrs 1mn	14yrs 10mns
#6	16yrs	2yrs 1mn	18yrs 1mn

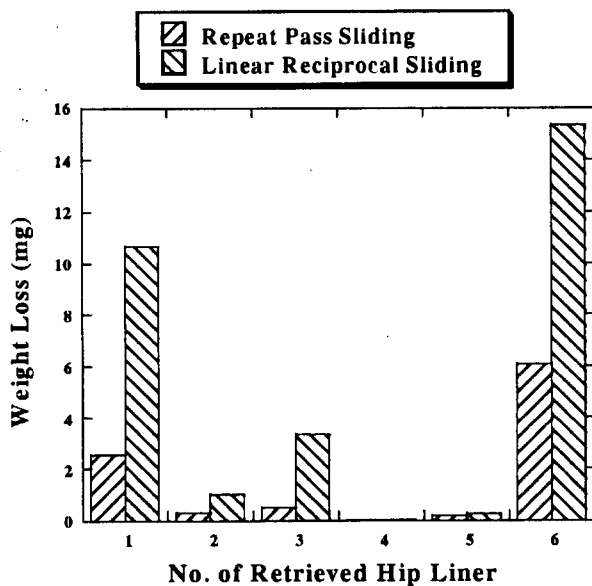


Fig. 3. Wear of retrieved liners under both kinematic motions in the order of total aging time.

degree of brittleness of each liner was not directly correlated with the aging (in vivo or total) time.

Effects of Aging Time and Kinematic Motion

The mean wear amounts of all aged UHMWPE pins against stainless steel disks moving in both kinematic motions of uni-directional repeat pass sliding and linear reciprocal sliding after 500 thousand cycles were plotted in an order of total aging time in Figure 3. Liner #1 and #6 shows very high wear, while liner #2 and #5 do very low wear and liner #4 does no wear. Wear of three liners having brittle cracks and white bands was much higher than wear of last three liners having no crack. No correlation between wear and total aging time was observed.

Wear under the linear reciprocal sliding motion was higher than wear under the uni-directional repeat pass sliding motion for all liners. The difference in wear under both kinematic motions become larger for a group of liners having brittle cracks and white bands than for the other group of liners having no crack.

The mean wear amount of all aged UHMWPE pins were plotted in an order of in vivo aging time again in Figure 4. Still there was no direct correlation between wear and in vivo aging time for all tested liners.

Discussions

For all tested liners, linear reciprocal sliding motion induces higher wear than uni-directional repeat pass sliding motion. Under the linear reciprocal sliding motion surface traction changes in an opposite direction every half cycle, while it does in a certain direction (depends on the radius of wear track) from the direction of sliding at any moment under the uni-directional repeat pass motion. This difference in a range of directional variation between two kinematic motions induces a totally different stress state in a UHMWPE pin specimen. For

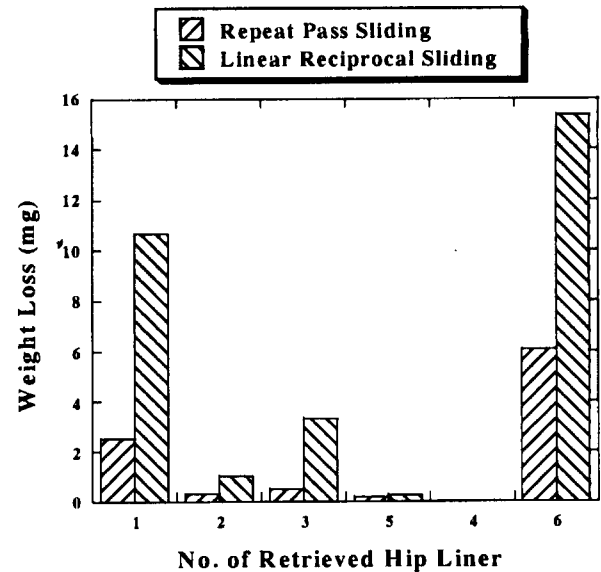


Fig. 4. Wear of retrieved liners under both kinematic motions in the order of in vivo aging time.

the brittle liners having the high degree of oxidation and subsequent low level of crosslinking, the more directional change in contact stress, the more readily crack or fragmentation forms and the wear remarkably increases.

Actually the liners having brittle cracks and highly-oxidized white band region wore 2.5-7.0 times more under the linear reciprocal sliding motion than under the uni-directional repeat pass sliding motion. In the other hand, the liners having no cracks wore 1.2-3.0 times more under the linear reciprocal sliding motion than under the uni-directional repeat pass sliding motion.

Wear of retrieved liners did not have any correlation with total or in vivo aging time. Most of liners having white band region were brittle even though their ranks of aging time among the tested liners were low, while liners having no white band were in relatively higher rank of aging time. It does not mean that the more aging time, the higher oxidation. In the previous study for the shelf-aged liners [21], generally the degree of oxidation increases, crosslinking decreases, and wear increases as the aging time increases. In the present study, however, wear depends on the brittleness of UHMWPE rather than aging time.

There is no evidence that the existence of white band is related to the history of mechanical loading in vivo. The formation of white band may depend on the resin type, processing method, procedure in sterilization, etc. Unfortunately, there is no information about what kind of resin was used, what kind of additive was used, how to manufacture the polyethylene rod or sheet and final product, and what are dose, temperature, environment of gamma-irradiation process. The total aging time for all liners may be inaccurate because there is also no information about the pre-implantation shelf aging time after sterilization for each retrieved liners. No direct relationship of wear of retrieved liners with aging time is consistent with other report [24].

Conclusion

From the pin-on-disk wear tests, wear of retrieved (aged) UHMWPE acetabular liners does not have direct relationship with total or in vivo aging time. In the viewpoint of kinematic motion effect, linear reciprocal sliding motion induces remarkable increase of wear in the aged liners having brittle cracks and white bands. To the extent that the mechanical brittleness predominantly affects wear of polyethylene, the oxidative degradation and white band formation should be prevented or retarded in UHMWPE for the total joint replacement.

Acknowledgment

This work was supported by Taegu University Research Grant 1999.

References

- Harris, W. H., The problem is osteolysis. *Clin. Orthop.*, 311 (1995) 46-53.
- Amstutz, H. C., Campbell, P., Kossovsky, N. and Clarke, I. C., Mechanism and clinical significance of wear debris-induced osteolysis. *Clin. Orthop.*, 276 (1992) 7-18.
- Goldring, S. R., Clark, C. R. and Wright, T. M., The problem in total-joint arthroplasty: Aseptic loosening [Editorial]. *J. Bone Joint Surg.*, 75A (1993) 799-801.
- Lewis, G., Wear in total hip and knee arthroplasties. *J. Biomed Mater Res (Appl Biomater)*, 38 (1997) 55-75.
- Wang A., Stark, C. and Dumbleton, J. H., Mechanistic and morphologic origins of ultra-high molecular weight polyethylene wear debris in total joint replacement prostheses. *Proc Instn Mech Engrs*, 210 (1996) 141-155.
- Brummitt, K., Hardaker, C. S., McCullagh, P. J. J., Drabu, K. J. and Smith, R. A., Effect of counterface material on the characteristics of retrieved uncemented cobalt-chromium and titanium alloy total hip replacements. *Proc Instn Mech Engrs*, 210 (1996) 191-195.
- Livermore, J., Ilstrup, D. and Morrey, B., Effect of femoral head size on wear of the polyethylene acetabular component. *J. Bone Joint Surg.*, 72A (1990) 518-528.
- Besong, A. A., Hailey, J. L., Ingham, E., Stone, M., Wroblewski, B. M. and Fisher, J., A study of the combined effects of shelf ageing following irradiation in air and counterface roughness on the wear of UHMWPE. *Bio-Medical Materials and Engineering*, 7 (1997) 59-65.
- Premnath, V., Harris, W. H., Jasty, M. and Merrill, E. W., Gamma sterilization of UHMWPE articular implants: an analysis of the oxidation problem. *Biomaterials*, 17 (1996) 1741-1753.
- Birkinshaw, C., Buggy, M. and Daly, S. The effect of gamma radiation on the physical structure and mechanical properties of ultrahigh molecular weight polyethylene. *J. Appl. Polym. Sci.*, 38 (1989) 1967-1973.
- Rimnac, C. M., Klein, R. W., Betts, F. and Wright, T. M., Post-irradiation aging of ultra-high molecular weight polyethylene. *J. Bone Joint Surg.*, 76A (1994) 1052-1056.
- Nusbaum, H. J. and Rose, R. M., The effects of radiation sterilization on the properties of ultrahigh molecular weight polyethylene. *J. Biomed. Mater. Res.*, 18 (1979) 557-576.
- Eyerer, P. and Ke, Y. C. Property changes of UHMW polyethylene hip cup endoprostheses during implantation. *J. Biomed Mater Res*, 18 (1984) 1137-1151.
- Grobbelaar, C. J., Du Plessis, T. A. and Marais, F., The radiation improvement of polyethylene prostheses: a preliminary study. *J. Bone Joint Surg.*, 60B (1978) 370-374.
- Oonishi, H., Takayama, Y. and Tsuji, E., Improvement of polyethylene by irradiation in artificial joints. *Radiat. Phys. Chem.*, 39 (1992) 495-504.
- Wroblewski, B. M., Siney, P. D., Dowson, D. and Collins, S. N., Prospective Clinical and Joint Simulator Studies of a New Total Hip Arthroplasty Using Alumina Ceramic Heads and Cross-Linked Polyethylene Cups. *J. Bone Joint Surg.*, 78-B (1996) 280-295.
- Birkinshaw, A., Buggy, M., Daly, S. and O'Neill, M., Mechanism of ageing in irradiated polymers. *Polymer Degradation and Stability*, 22 (1988) 285-294.
- Pienkowski, D., Patel, A., Lee, K.-Y., Hamilton, D. M., Jacob, R. J., Higgins, J. and Schroeder, D. W., Solubility changes in shelf-aged ultra-high molecular weight polyethylene acetabular liners. *J. Long-Term Effects of Medical Implants*, 9 (1999) 273-288.
- Sutula, L. C., Collier, J. P., Saum, K. A., Currier, B. H., Currier, J. H., Sanford, W. M., Mayor, M. B., Wooding, R. E., Sperling, D. K., William, I. R., Kasprzak, D. J. and Surprenant, V. A., The Otto Aufranc Award, Impact of gamma sterilization on clinical performance of polyethylene in the hip, *Clin. Orthop.*, 319, (1995) 28-40.
- Fisher, J., Chan, K. L., Hailey, J. L., Shaw, D. and Stone, M., Preliminary study of the effect of aging following irradiation on the wear of ultrahigh-molecular-weight polyethylene. *J. Arthroplasty*, 10 (1995) 689-692.
- Lee, K.-Y. and Lee, K. H., Wear of shelf-aged UHMWPE acetabular liners. *Wear*, 225-229 (1999) 728-733.
- McKellop, H., Shen, F.-W., Lu, B., Campbell, P. and Salovey, R., Development of an extremely wear-resistant ultra high molecular weight polyethylene for total hip replacement. *J. Orthop Res*, 17 (1999) 157-167.
- Kurtz, S.M., Muratoglu, O.K., Evans, M., Edidin, A.A.: Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty. *Biomaterials*, 20 (1999) 1659-1688.
- Weightman, A., Swanson, S.A.V., Issac, G.H., Wroblewski, B.M.: Polyethylene wear from retrieved acetabular cups. *J. Bone Joint Surg.*, 73B (1991) 806-810.