감마선 멸균처리된 초고분자량 폴리에틸렌
Gamma-irradiated ultra-high molecular weight polyethylene

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Abstract

인공관절 라이너에 널리 사용되는 대표적 생체재료인 초고분자량 폴리에틸렌 (Ultra-High Molecular Weight Polyethylene) 은 체내에 삽입되기 전에 멸균처리를 거쳐야 하며, 가장 보편적인 멸균 방법은 감마선을 이용한 멸균처리이다. 그러나, 감마선은 폴리에틸렌의 화학분자 결합구조에 변화를 일으키며, 따라서 물리적, 기계적 물성치에 변화를 야기 시킨다. 이는 인공관절 수명을 좌우하는 변형과 마모현상에도 결정적 영향을 줄 것으로 사려된다. 본 연구에서는 감마선 멸균처리가 UHMWPE의 크리프 변형 및 마모에 미치는 영향이 관찰되었고, 그 결과들은 감마선 멸균처리로 야기된 폴리에틸렌의 화학분자 결합구조의 변화 (Crystallinity, Oxidation, Crosslinking)와 함께 분석되었다. 압출 제작된 초고분자량 폴리에틸렌 봉 (extruded UHMWPE rod)으로부터 원통형의 시편을 제작하여 감마선 멸균처리를 행하고, 압축 크리프 실험과 마모 실험을 실시하여 멸균처리 하지 않은 시편의 결과와 비교하였다. 크리프 변형의 경우, 감마선 멸균처리 된 시편과 멸균처리 하지 않은 시편 사이에는 크리프 복원정도를 제외하고 거의 차이가 없었으나, 반면에 마모의 경우, 감마선 멸균처리 된 시편이 멸균처리 하지 않은 시편보다 훨씬 적은 마모량을 보였다 ($p<0.05$). 이것은 crosslinking 증가에 따른 마모 저항력 향상으로 볼 수 있다.

Keywords: creep, wear, UHMWPE, gamma-irradiation sterilization, crystallinity, oxidation, crosslinking.

1. Introduction

Total joint replacement is considered one of the major surgical advances of the 20th Century since it has restored pain-free mobility to lots of patient. Ultra-high molecular weight polyethylene (UHMWPE) is the viscoelastic polymeric material used for the concave bearing surface of hip and knee prosthetic joint implants. This material creeps and wears with time, which is especially critical for younger, active patients, and produces abundant submicron-sized wear debris. This debris is believed to cause failure of the implant through a process known as aseptic loosening [1].

Many efforts have being made to produce less deformation and wear debris by adapting the modification of polyethylene through an increase of molecular weight and the new processing method of direct compression molding. Though these kinds of engineering approaches are fundamental for the polyethylene quality improvement, there is another crucial factor, that is the sterilization process [2], highly influencing the mechanical performance of polyethylene in the body. All prostheses components should be sterilized before implantation into the body. Gamma irradiation using a Cobalt 60 source has been the industry standard in

conventional polyethylene component sterilization. Gamma irradiation sterilization causes chain scission by breaking chemical bonds and creates reactive free radicals. If oxygen is present in the environment, oxygen diffuses into the polyethylene and reacts with free radicals to cause oxidation, which leads to much shorter molecular chains. Furthermore, several studies [3-6] have recently discussed the oxidation of UHMWPE following radiation and progressive oxidative degradation upon in vivo and shelf-life aging.

The oxidation from gamma sterilization of commercially available UHMWPE component is evidently distinguished by the yellowish color of the final product versus the raw polyethylene before sterilization which is bright white. The resulting oxidized chains can increase density, crystallinity, and fluid absorption [7-9]. And also the oxidative degradation results in reduced elongation and subsequent embrittlement in UHMWPE component [10-12]. These data indicates that long-term degradation can alter the performance of UHMWPE, especially, its resistance to abrasive and fatigue wear which can cause ploughing, pitting, and delamination. However, there are several studies reporting wear resistance improvement after gamma-irradiation [13-15]. This phenomenon was interpreted by the increase of degree of crosslinking in the molecular structure of UHMWPE.

In the present study, the effect of gamma-irradiation sterilization on the creep and wear performance of UHMWPE were characterized and its result was analyzed by evaluating the typical microstructural properties of the level of crystallinity, oxidation, and crosslinking in gamma-irradiated UHMWPE.

2. Materials And Methods

2-1. Specimen

Ram-extruded, un-irradiated, GUR 4150HP UHMWPE rod stock (70 mm diameter, Westlake Plastic, Lenni, PA, USA) was machined to a total of 12 rectangular block specimens (20 mm long x 10 mm wide x 8.8 mm thick) for the creep tests (n=6 per group), and to a total of 8 right angle circular cylinder specimens (10 mm diameter x 8mm long) for the wear tests (n=3 per group) and for the microstructural property measurements. Half of block and cylinder specimens (GI) were sterilized by gamma irradiation with a total dosage of 2.5 Mrad at a rate of 0.9 Mrad per hour in air. Another half of specimens (NI) were tested as they were non-irradiated.

2-2. Creep and Recovery Test

A custom-built creep testing machine [16] was used for conducting the dynamic compressive creep tests. Compressive loads were applied to the specimens by a lever arrangement operated by an electro-pneumatic servo-valve (Proportion Air, McCordsville, IN, USA) and a ractified sine wave function generation program (LabView, National Instruments, Austin TX, USA).

Specimens were compressed under physiologic conditions of double peaks for the hip joint having maximum pressures of 8 MPa and minimum pressures of 0.8 MPa at a frequency of 1 Hz for a total duration of 10, 20, 30, 60, 100, 200, 300, 600, $1x10^3$, $2x10^3$, $3x10^3$, $4x10^3$, $6x10^3$, $8x10^3$, $1x10^4$, $2x10^3$, $3x10^3$, $4x10^3$, $6x10^3$, $8x10^3$, $1x10^4$ minutes (a total of $6x10^5$ loading cycles). All tests were conducted in bovine serum of 37℃ ± 0.3℃ which was diluted with 1% sodium azide solution in a volume ratio of 2:1 (serum:solution) to retard bacterial growth.

The initial thickness and deformed

thickness after each test duration of each specimen was measured with a digital micrometer (± 1 μm repeatability) at five different longitudinal positions. The difference between average of these five thickness and initial thickness are the amount of creep. The creep strain was determined by normalizing all measured creep amounts by the initial thickness of each specimen.

After creep testing, the applied load was completely removed. The creep deformed specimen was allowed to recover in an ambient environment. During recovery period, the thickness of each specimen was measured at the same intervals used for creep testing. The amount of creep strain, rate of creep strain. percentage of creep recovery, and rate of creep stain recovery were compared between two irradiation conditions.

2-3. Wear Test

Pin-on-disc wear tests were conducted with the right angle cylinder polyethylene pins and a rotating orthopaedic grade stainless steel disc (316L, 50.8 mm diameter, R_a = 0.025 μm) in bovine serum diluted with 1% sodium azide solution at a volume ratio of 2:1 (serum : solution) at room temperature. A lever arrangement and a dead weight of 315 N exerts a nominal contact pressure of 4 MPa, which is equivalent to average contact pressure in the hip joint for the normal gait, to each specimen pair. The disc rotating speed of 120 rpm produces a sliding velocity of 125 mm/s at the center of the cylinder specimen.

All tests were interrupted after every 10 km of sliding distance, the specimen was cleaned with deionized water, dried with a tissue, and weighed with a microbalance (Mettler Instrument Corp., Hightstown, NJ, USA, sensitivity of 0.01 mg). Wear testing was continued for one million revolutions that is equivalent to a total sliding distance of 62.5 km. The amount of wear was determined by weight loss of each specimen, which was corrected for the weight gain that was obtained from a soak control test.

2-4. Relative Crystallinity

Relative crystallinity was measured for a non-irradiated and a gamma-irradiated specimen using differential scanning calorimetry (DSC-7 Series Thermal Analysis System, Perkin Elmer, Danbury, CT, USA). 300 μm-thick slices were microtomed from each specimen, and each slice was cut into a small disc sample with an approximate weight of 10.0 mg and was placed into a sample pan for DSC analysis. Sample pan was heated in the DSC chamber from 30℃ to 180℃ at a rate of 10℃/min, held at 180℃ for 10 minutes, and then cooled to 30℃ at a rate of 10℃/min. The heat of fusion was obtained from the plot of heat flow as a function of temperature. The relative crystallinity was calculated by the heat of fusion for perfectly crystallized polyethylene of 289.74 J/g [17].

2-5. Oxidation Index

100-μm thin films were sliced within the first 500-μm of the flat surface and sequentially at 500-μm intervals into the interior of cylinder specimen. The degree of oxidation of each slice was estimated by comparison of the maximum absorbance of the peak centered near 1715 cm^{-1} in FTIR spectra (Fourier Transform Infrared spectrometer, Perkin-Elmer 1600, He-Ne laser 633 nm wavelength, Norwalk, CT, USA) after normalization to the 720 cm^{-1} peak [18]. The average interior oxidation index is defined as the average of the data points for the interior portion of a sample that is deeper than 500-μm from a surface,

and the average surface oxidation index is defined as the average of the data points for the material that is within the first 500-㎛ of a surface.

2-6. Percent Crosslinking

Degree of crosslinking of specimen was measured on the same 100-㎛ slices of each cylinder specimen as those for the oxidation measurements. The percent crosslinking (insoluble gel content) in each sample was determined by using hot xylene extraction procedure modified from ASTM D2765-90 [19]. This calculation technically provided the percentage of insoluble constituents in the original sample, however, it was assumed that the insoluble fraction of polyethylene is equivalent to the crosslinked fraction.

A group of 10 consecutive surface and interior slices from both flat ends of a cylinder was uniformly cut into 0.8-mm squares with a custom-made stacked razor blade. An amount equal to 0.1 g of these chopped samples was placed between two layer of glass wool in a glass thimble. This assembly was then placed into a soxhlet extractor, and exposed to 140℃ reagent-grade xylene for 6 hours with a reflux time of 15 minutes. The thimble containing the glass wool and the remaining undissolved polyethylene was then dried in a vacuum oven at 100℃ for twelve hours and was cooled to room temperature in a desiccator. The entire assembly was then weighed to an accuracy of 0.01 mg (Mettler Instrument Corp., Hightstown, NJ, USA). The weights before and after extraction were compared to determine the percent crosslinking, ignoring the fraction of filler (which is less than 0.5%).

3. Results

3-1. Creep

The variations of mean dynamic compressive creep strain and creep strain recovery were plotted in Fig. 1 as a function of time for both non-irradiated and gamma-irradiated specimens. Logarithmic time scale fits well (r=0.98) to the creep strain and creep strain recovery. Comparison of non-irradiated specimens with gamma-irradiated specimens shows no significant difference in creep strain, rate of creep strain, or rate of creep strain recovery, but non-irradiated specimens show a significant higher percentage of creep recovery (p=0.023) than gamma-irradiated specimens (Fig. 2).

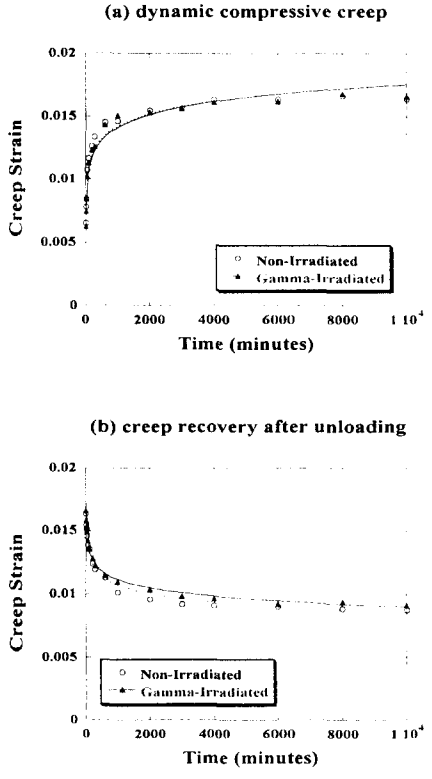

Fig. 1. Variation of creep strain as a function of time for the duration of (a) the dynamic compressive loading and (b) creep recovery.

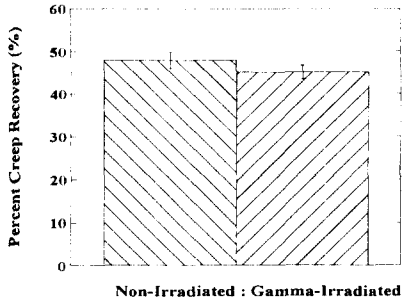

Fig. 2. Comparison of the percent creep recovery between gamma-irradiated and non-irradiated specimens.

3-2. Wear

The variations of mean weight loss of the non-irradiated and gamma-irradiated specimens during the entire test duration are shown in Fig. 3. After a total sliding distance of 62.5 km the mean wear of gamma-irradiated specimens was significantly less (36%, $p<0.05$) than that of non-irradiated specimens.

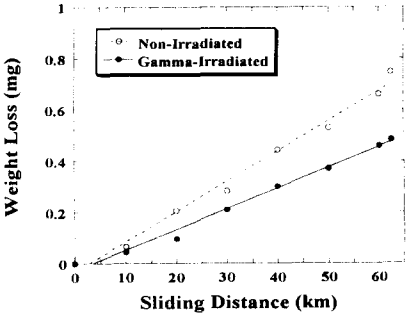

Fig. 3. Variation of weight loss as a function of sliding distance for the gamma-irradiated and non-irradiated specimens.

3-3. Microstructural Properties

The results of microstructural property changes, the relative crystallinity, oxidation index, and percent crosslinking, in the non-irradiated and gamma-irradiated specimens are given in Table 1. For the gamma-irradiated specimen the microstructural properties were measured at both surface and interior of specimen. There was a slight increase in the relative crystallinity, but oxidation index and percent crosslinking were significantly increased ($p<0.05$) by gamma-irradiation. Relative crystallinity and oxidation index from the surface of specimen were higher than those from the interior of specimen, while percent crosslinking from the surface of specimen was lower than that from interior of specimen.

Table 1. Microstructural properties at surface and interior of both gamma-irradiated and non-irradiated specimens.

Test Spec.	Crystallinity (%)		Oxidation Index		Crossliking (%)	
	surf.	inter.	surf.	inter.	surf.	inter.
GI	51.93	51.73	0.06	0.04	91.05	93.11
NI	47.79		0.02		70.57	

4. Discussion

From the results of present creep tests no significantly different creep and recovery behaviors except the percentage of creep recovery were observed between the gamma-irradiated and non-irradiated UHMWPE. This finding agrees with other reports on no statistically significant difference in hardness [8] and in the shape of stress-strain curves including elastic modulus [20]. However, there were several reports showing the increase in surface hardness and creep resistance of UHMWPE after gamma-irradiation [2, 9]. The increase in crystallinity and crosslinking would be

responsible for this increase in deformation resistance.

The large variation among the wear data reporting the effect of gamma-irradiation on the wear performance attribute to the difference in the wear test scheme such as the lubricant, sliding motion, counter-piece material and surface roughness. It is clear that the elongation at break and fracture toughness of UHMWPE remarkably decrease with gamma-irradiation [4, 5, 10, 21]. This is associated with the oxidation-induced reduction of ductility.

In the present study, gamma-irradiation induced the oxidation in the specimens. Therefore, it seems that the ductility will be decrease and eventually this may decrease the wear resistance. Oxidation process will continue as free radicals trapped inside of UHMWPE react with oxygen. Oxidative degradation involving embrittlement progressively will deteriorate the wear property in UHMWPE.

However, the result was opposite. Gamma-irradiation induced the increase in the level of crosslinking as well as oxidation. There are many reports that the higher the level of crosslinking, the higher wear resistance [22-24]. Thus, in the short period after gamma-irradiation the effect of increase in crosslinking overcomes the adverse effect of oxidation on the wear. After a certain period after gamma-irradiation oxidative degradation will overwhelm the benign crosslinking effect on wear. According to the observation for the variation of crosslinking as a function of aging period, transition of abrupt reduction of level of crosslinking at the gamma-irradiation sterilized UHMWPE products occurred after about 5 years [6, 25]. Therefore, more tests on the aged sample are necessary to study the relationship between the wear and crosslinking and oxidation.

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