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Gamma-Irradiated Ultra-high Molecular Weight Polyethylene : Anisotropic Changes in Crystallinity and Crosslinking

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= Abstract =

The effect of gamma-irradiation sterilization on molecular structural changes in orthopaedic surgical-grade polyethylene was studied. The relative crystallinity and percent crosslinking of the substance increased as a result of the gamma irradiation and varied anisotropically as a function of depth. Samples from the articulating surfaces showed 5% greater relative crystallinity than those from the mid-sections, whereas samples from the mid-sections exhibited 15% greater crosslinking than those from the surfaces. These anisotropic variations are discussed in association with oxidation.

Key words : UHMWPE, Gamma-irradiation sterilization, Crystallinity, Crosslinking, oxidation

INTRODUCTION

Because surgical-grade ultra-high molecular weight polyethylene (UHMWPE) has a low friction coefficient, high abrasion resistance, and high impact strength, it has been used for more than two decades as a bearing surface material in total joint implants. However, the generation of wear debris through articulation and the consequent adverse biological reaction in the periprosthetic tissue are important problems[1-3].

Polyethylene components must be sterilized before they are placed in human bodies. The most common method of sterilization is gamma irradiation at a dose of 2.5 to 5.0 Mrad in air. This sterilization procedure causes changes in the chemical molecular structure of polyethylene, which subsequently affect the changes in physical and mechanical properties that definitely influence clinical wear performance. Many sources have documented radiation-induced changes in structural and mechanical properties; increases in carbonyl content, density, crystallinity, watersorption, gel content (representing the percent crosslinking), yield strength, creep resistance, and hardness; and concurrent decreases in molecular weight, elongation at break, ultimate strength, impact strength, and fatigue resistance [4-11]. However, there has been large variation in the effect of irradiation on wear, the most important subject[12-17]. In the present study, typical structural changes, particularly in the degree of crystallinity and crosslinking caused by gamma irradiation, were studied.

Recently, it was reported that creep deformation varies according to the radial location in the cross-section of ram-extruded UHMWPE rod stock from which samples are taken[18]; this phenomenon was postulated to be related to the nonuniform radial distribution of crystallite orientation[19]. Additionally, many studies[20-23] of irradiation-induced oxidation and postirradiation degradation have demonstrated that oxidation profiles vary in depth. Therefore, it is

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necessary to analyze the changes in structural morphology that are induced by gamma irradiation depending on the sample location.

The objectives of the present study were to determine the changes in crystallinity and crosslinking of gamma-irradiation sterilized UHMWPE as a function of radial location and depth.

MATERIALS AND METHODS

1. Experimental Design

A commercially purchased acetabular cup liner (Ring Loc 32mm, Biomet Inc., Warsaw, IN, USA) that had been machined from extruded rod stock, gamma-irradiated (GI) at 2.5-5.0 Mrad in air, and self-stored in an ambient condition for one year was tested. To obtain control data from unirradiated (UI) UHMWPE, a 1-cm-thick wafer cut from extruded rod stock (70 mm Dia., Westlake Plastics, Lenni, PA, USA) that had been manufactured with the same type of resin (GUR 4150HP, Hoechst-Celanese, Houston, TX, USA) as an acetabular cup was also tested.

Two cylindrical cores were obtained by using a 10-mm-diameter punch: one core from the periphery and one from the center of the cup or of the wafer of extruded rod stock. Each punched core was microtomed to slices from the articulating surface for the cup or from a flat surface for the wafer, each slice 200 to 300μm thick. For the irradiated cup, the first slice from the articulating surface was used for crystallinity measurements and the next three slices were used for crosslinking measurements. Crystallinity and crosslinking were also measured on the mid-section slices from a location of 3 to 4 mm deep below articulating surface. For the unirradiated rod, random slices were chosen for both tests because there were no radiation-induced variations in the direction of depth.

2. Crystallinity Measurements

The relative crystallinity of each slice was measured by using the Differential Scanning Calorimetry (DSC) Thermal Analysis System (Perkin Elmer DSC-7 Series, Norwalk, CT, USA). Each thin 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. Samples were heated in a chamber from 30℃ to 180℃ at a rate of 10℃/min, were held at 180℃ for 10 minutes, and were then cooled to 30℃ at a rate of 10℃/min. The heat of fusion was obtained from the plot of heat flow versus temperature. The relative crystallinity was calculated by the heat of fusion for perfectly crystallized polyethylene of 289.74 J/g[24].

3. Crosslinking Measurements

The percent crosslinking (insoluble fraction) in UHMWPE was determined by extracting the soluble fraction[25,26]. This method is based on the decrease in solubility that accompanies the crosslinking of long polymer chains. Three microtomed slices were cut into 0.8-mm squares with a custom-made stacked razor blade cutter to ensure uniform exposure of the samples to the hot solvent. An amount equal to 0.1 g of these chopped samples was weighed and placed into a thimble with glass wool; this assembly was then placed into a soxhlet extractor. The assembly was 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 polyeth-

Table 1. Mean (± standard deviation) values of relative crystallinity and percent crosslinking for unirradiated and gamma-irradiated UHMWPE at various sample locations

Test Sample	Radial Location	Depth Location	Relative Crystallinity(%)	Percent Crosslinking(%)
UI(rod)	center	—	47.50±0.74	71.55±1.12
	periphery	—	47.79±0.78	70.57±1.84
GI(cup)	center	surface	57.17	82.93
	center	mid-section	54.32	95.30
	periphery	surface	56.79	83.32
	periphery	mid-section	54.54	96.31

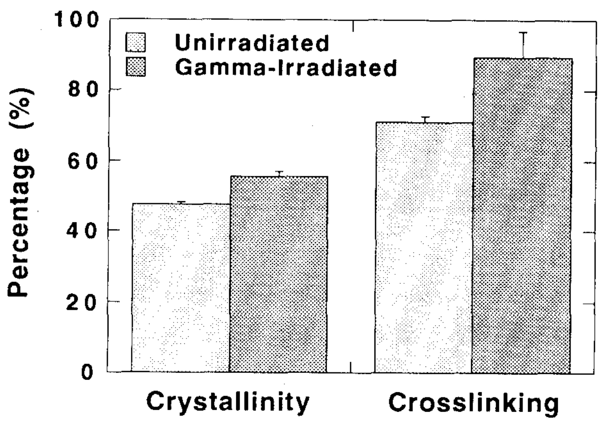

Fig. 1. Effect of gamma irradiation on the variation of relative crystallinity and percent crosslinking.

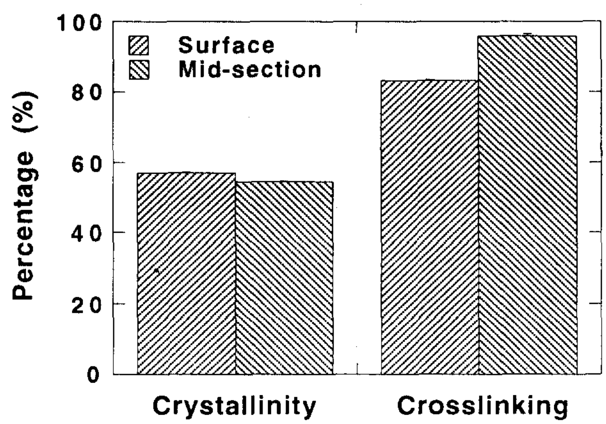

Fig. 2. Variations of relative crystallinity and percent crosslinking in the gamma-irradiated UHMWPE cup as a function of depth.

ylene was then dried in a one-half atmosphere vacuum oven at 100℃ overnight and was cooled to room temperature in a desiccator. The entire assembly was then weighed to an accuracy of ±10㎍ (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%). 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.

RESULTS

The results of relative crystallinity measurements and percent crosslinking measurements at each sample location are listed in Table 1 for both unirradiated (UI) UHMWPE extruded rod stock and gamma-irradiated (GI) acetabular cup.

1. Effect of Gamma Irradiation

When the results obtained from samples of gamma-irradiated cup were compared with those obtained from samples of unirradiated rod stock, it was observed that gamma-irradiation sterilization caused increases in relative crystallinity and in percent crosslinking in UHMWPE. Figure 1 shows the gamma-irradiation-induced increase in the molecular structural properties of UHMWPE. The relative crystallinity was increased by an average of 17%, and the percent crosslinking was increased by an average of 26%.

2. Variation with Depth

Negligible changes in relative crystallinity and percent crosslinking were observed in both a gamma-irradiated acetabular cup and unirradiated extruded rod stock as a function of the radial location (center versus periphery) from which test samples were obtained. However, there were remarkable variations in relative crystallinity and percent crosslinking as a function of the depth (surface versus mid-section) in a gamma-irradiated acetabular cup (Fig. 2).

Samples from the articulating surfaces showed 5% greater crystallinity than did those from the mid-sections, whereas samples from the mid-sections exhibited 15% greater crosslinking than did those from the surfaces.

DISCUSSION

The most important findings of the present study are that gamma irradiation causes increases in relative crystallinity and percent crosslinking in the molecular structure of UHMWPE, and that these variations are anisotropic as a function of the depth (surface versus mid-section) from which test samples were obtained.

The findings of increases in relative crystallinity and percent crosslinking in the gamma-irradiated UHMWPE agree with those of other studies. These phenomena have been analyzed as follows. Two important processes involved in the exposure of highenergy photons (gamma rays) are the crosslinking and the molecular chain scission accompanying the formation of free radicals[27-29]. The scission of tie molecules at the intercrystalline region permits polymer chains to have high mobility and to reorganize in the direction of further crystallization. Chain scission also allows increasing perfection of existing folded-chain crystallites[30]. At the same time, gamma irradiation induces crosslinking preferentially at the fold surfaces of folded-chain lamellae, forming an insoluble network in polyethylene[31].

To interpret the anisotropic variations of structural properties as a function of depth, these variations must be combined with oxidation in UHMWPE. The free radicals formed from molecular chain scission react with the oxygen that exists at the surface and that is diffused into the subsurface from the environment; this reaction results in the carbonyl bond in polyethylene molecules. Carbonyl content increases as a function of the dose of gamma irradiation[9,10]. Radiation-induced oxidation and postirradiation aging accompany the increase in crystallinity[11,29].

The degree of oxidation varies according to depth because of the limitation of oxygen diffusion. The maximum oxidation occurs at the surface or at 1 to 2 mm below the surface, after which the oxidation profile decreases in depth[22,23]. Rimnac et al.[22] reported the decrease in density as a function of depth and analyzed its relationship to the decrease of the oxidation profile as depth increases. Roe et al.[5] converted the density value to the degree of crystallinity, compared this crystallinity with that calculated from the heat of fusion as determined by differential scanning calorimetry, and showed a reliable trend of increase in crystallinity as a function of the dose of gamma irradiation[7,30]. On the basis of these reports, the finding of a greater degree of crystallinity at the surface (high degree of oxidation) than at the mid-section (low degree of oxidation) of gamma-irradiated acetabular cup can be explained by the effect of oxidation.

The finding of greater crosslinking at the mid-section than at the surface of the same sample can also be explained by understanding the effect of oxidation on the variation of crosslinking in UHMWPE. The gel content of UHMWPE increases immediately after gamma irradiation, and the irradiation environments (air, vacuum, or inert gases) determine the increased level of gel content and the level of oxidation. However, the gel content of irradiated UHMWPE varies as a function of aging time. Patel et al.[32] reported a decrease in gel content in shelf-aged UHMWPE acetabular cups; this finding agreed with the results of tests of in-vivo aged UHMWPE acetabular cups[20]. These findings suggest that the more oxidation, the less gel content. They also support the present result of less crosslinking at the surface, where more oxidation is present. The anisotropic variation of crosslinking demonstrated in the present study shows that oxidation and crosslinking compete with each other in a time-dependent manner.

These two competing effects can induce opposite results in wear performance. Recently it has been accepted that the increase of crosslinking after gamma irradiation improves wear resistance[17,33] and that severe oxidation during the postaging period is adverse to wear performance[34,35]. Consequently, for the best wear performance, it can be suggested to sterilize the polyethylene components with a method which can increase the level of crosslinking and can retard the oxidative degradation after sterilization.

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=국문초록=

대퇴부 인공관절의 베어링 요소로 사용되는 생체폴리머인 울트라하이 몰레큘라 웨이트 폴리에틸렌(UHMWPE)은 멸균처리용 감마선을 쪼이게 되면 화학 분자구조에 변화가 생기게 된다. 이 변화에 따라서 물리적, 기계적 물성치에 변화가 생기게 되며, 또한 임상 측면에서의 인공관절 수명에도 영향을 주게 된다. 본 연구에서는 감마선 멸균처리가 UHMWPE의 대표적인 물성치인 Crystallinity와 Crosslinking에 끼치는 영향을 고찰하였다. 감마선 멸균처리된 시편은 안된 시편에 비해서 17%의 Crystallinity증가와 26%의 Crosslinking증가를 보였으며, 이들 변화는 시편의 깊이 방향으로 서로 상반되는 변화추세를 보였다. 즉, 감마선 멸균처리된 시편 표면에서의 Crystallinity는 내부보다 5% 더 높은 것으로 측정된 반면에, Crosslinking은 시편 내부가 표면보다 15% 더 높은 것으로 나타났다. 이러한 깊이에 따른 상반된 물성치 변화추세가 멸균처리시 동시에 발생하는 산화작용에 의한 변화와 연관되어 있는 것으로 분석되었다.