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Comparison of Cross-Linked Polyethylene Materials for Orthopaedic Applications

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Cross-linked polyethylenes are being marketed by orthopaedic manufacturers to address the problem of osteolysis caused by polyethylene particulate wear debris. Wear testing of these cross-linked polyethylenes in hip simulators has shown dramatic reduction in wear rate compared with standard ultrahigh molecular weight polyethylene, either gamma irradiated in air or nitrogen - or ethylene oxide-sterilized. However, this reduction in wear rate is not without cost. The cross-linking processes can result in materials with lower mechanical properties than standard ultrahigh molecular weight polyethylene. To evaluate the effect of the various cross-linking processes on physical and mechanical properties of ultrahigh molecular weight polyethylene, commercially available cross-linked polyethylenes from six orthopaedic manufacturers were tested. This study was the culmination of collaboration with these manufacturers, who provided cross-linked polyethylene for this study, wear characteristics of the material they provided, and review of the physical and mechanical properties measure for their polyethylene. Cross-linked materials were evaluated as received and after an accelerated aging protocol. Free radical identity and concentration, oxidation, crystallinity, melt temperature, ultimate tensile strength, elongation at break, tensile stress at yield, and toughness are reported for each material. By comparing these physical and mechanical properties, surgeons can evaluate the trade-off that results from developing materials with substantially lower wear rates.

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Cross-linked polyethylenes are described by their developers as a major advance against wear in total hip replacement, and most of the major orthopaedic manufacturers provide some form of radiation cross-linked polyethylene for clinical use. Although all claim dramatic reduction in wear, other material characteristics may prove important in the overall perfor-

mance of these materials for long-term clinical applications, particularly if the materials are used in total knee replacement. The goal of the current study, in collaboration with orthopaedic implant manufacturers, was to compare and contrast the tradeoffs in mechanical properties that each company has made in developing their specific cross-linked polyethylene.

Gamma-sterilized polyethylenes, implanted as hip and knee bearings since the 1970s, are cross-linked to a certain extent by the sterilization process. However, gamma sterilization in air also begins a process of oxidation in polyethylene. Gamma irradiation sterilization produces free radicals in polyethylene. These free radicals are long lived, and react in the presence of oxygen to cause oxidation.[15] This oxidation reduces cross-linking and degrades mechanical properties to such an extent that cracking and delamination can occur. Sixty-five percent of 600 retrieved gamma-in-air sterilized knee bearings with duration in vivo greater than 4 years had evidence of fatigue damage.[7] The frequency of cracking or delamination in retrieved acetabular bearings after 4 years in vivo is 20%.[19] These data support the importance of high strength and significant ductility in the polyethylene-bearing surfaces to resist fatigue. Materials with reduced properties need to be reviewed carefully to determine their applicability in high-stress applications.

To avoid the problems caused by oxidation resulting from gamma sterilization in air and shelf storage,[10] orthopaedic implant manufacturers are using alternate sterilization techniques: gamma sterilization in vacuum or inert atmosphere, ethylene oxide, or gas plasma. Although nongamma sterilization methods avoid polyethylene oxidation, as seen from analysis of retrieved, long duration ethylene oxide-sterilized bearings,[21] wear testing of bearings sterilized by these various techniques shows that cross-linking secondary to gamma sterilization produces a more wear-resistant material than the same material sterilized by ethylene oxide or gas plasma.[12] Clinical data support these findings: the wear rates of ethylene oxide-sterilized hip components typically are higher than those of the lowest wearing gamma-sterilized devices.[4] These findings led to a search for a bearing material that would have the oxidation resistance and stability of nongamma-sterilized material with the improved wear resistance of cross-linked material.

Two processes have been used for cross-linking ultrahigh molecular weight polyethylene[11]: chemical and irradiation. Chemical cross-linking of ultrahigh molecular weight polyethylene using organic peroxides is the standard in the polymer industry and is used to produce the majority of industrial cross-linked polyethylene. However, polyethylene containing organic peroxide does not have Food and Drug Administration approval and would require extensive testing to establish its safety for implanted devices. Therefore, orthopaedic implant manufacturers have chosen irradiation cross-linking as the technique to produce cross-linked bearings.

Gamma- and electron beam-irradiation cross-linking techniques use controllable doses of radiation. Gamma irradiation cross-linking is a relatively slow process that takes as many as 24 hours for a dose of 5 Mrad. Full penetration of standard bars of polyethylene with gamma irradiation is accomplished easily, and the dose is expected to be uniform through the thickness. Electron beam irradiation requires much less time to provide an equivalent dosage. Irradiation time of seconds or minutes is sufficient, compared with the hours required with gamma irradiation cross-linking. However, the depth of penetration by electron-beam radiation is limited to approximately 4 cm. Manufacturers typically use either sections of rod (cylindrical discs) or preforms of acetabular cups to ensure that the radiation fully penetrates the components. Companies using electron-beam irradiation have developed proprietary techniques to produce uniform dosing of polyethylene thickness greater than 4 cm.

Free radicals remain in polyethylene after irradiation cross-linking. Annealing can be used to increase the mobility of the polymer chains and encourage recombination or addi-

tional cross-linking of these free radicals. Annealing at the melt temperature produces a highly cross-linked polyethylene with no detectable free radicals,[11] permitting the use of higher irradiation doses without concern that the material will become more oxidation-prone in vivo. Gamma irradiation causes little or no heating of the polyethylene; therefore, a separate heating process is needed to anneal the material. The electron beam dose rate is much higher than with gamma irradiation, and it heats the polyethylene measurably. In some electron beam processes, cross-linking and annealing are combined through the addition of heat before, during, or after irradiation.

The variation in resin and fabrication technique, irradiation method, dose, dose rate, annealing time, and temperature may result in different mechanical properties for these cross-linked materials. Cross-linked polyethylene acetabular liners have been tested extensively in hip simulators.[6,13,14,20] All have shown dramatic reductions in wear rates for the new cross-linked materials when compared with standard polyethylene that has been gamma sterilized in air or nitrogen. Most of these researchers have looked at the effect of irradiation dose on wear rate and found that the wear rate is decreased as the irradiation dose and resulting cross-linking are increased. However, increased radiation dosage can have a negative influence on the mechanical properties of polyethylene.[13]

The goal of the current study was to determine the properties of each clinically available cross-linked polyethylene and to relate them to the wear rates advertised by the manufacturers of the bearings to provide insight into the trade-offs that each manufacturer has made. All of the major orthopaedic implant manufacturers that are developing cross-linked polyethylene (Biomet Warsaw, IN; DePuy/Johnson & Johnson Warsaw, IN; Stryker Howmedica Osteonics, Rutherford, NJ; Smith & Nephew Memphis, TN; Sulzer Orthopaedics, Austin, TX; and Zimmer, Warsaw, IN) were contacted and invited to participate in this study of the mechanical properties of cross-linked polyethylene and all agreed to participate. All participants were asked to provide a minimum of three implantable, acetabular bearing inserts and an equal number of standard inserts for comparison purposes. These standard components ideally would be the same starting material as the cross-linked material, but before the cross-linking and annealing process. Because only one company was able to provide this type of standard, this part of the study will not be reported. Instead, the Hospital for Special Surgery, Poly Hi Solidur, Hoechst Celanese reference ultrahigh molecular weight polyethylene[5] was used as the standard material for chemical and mechanical property comparisons.

MATERIALS AND METHODS

Rationale

To evaluate and compare cross-linked materials, the following techniques were used: Fourier transform infrared spectroscopy, mechanical testing, differential scanning calorimetry, electron paramagnetic resonance spectroscopy, and accelerated aging. Accelerated aging in an oxygen-rich, above-body temperature environment was used to determine a material's resistance to oxidation. In this study, the accelerated aging protocol is not claimed to represent any specific period of either shelf-aging or in vivo aging; however, it is a screening method to evaluate the relative potential for oxidation. Fourier transform infrared spectroscopy was used to evaluate the initial oxidation level in the as-received cross-linked polyethylene and to determine whether accelerated aging of the cross-linked polyethylene resulted in increased oxidation. Mechanical testing provided data on the strength and ductility of the cross-linked materials as marketed and after accelerated aging. Differential scanning calorimetry was used to determine the crystallinity of the cross-linked materials, which may provide insight into the variations measured in mechanical properties.[3] Electron paramagnetic resonance was used to measure the free radical concentration in the cross-linked materials, providing another indication of oxidation potential.

Sample Selection, Preparation, and Examination

Never implanted, cross-linked polyethylene acetabular bearings from six manufacturers (Table 1)

TABLE 1. Cross-linked Materials Tested

Manufacturer	Resin	Fabrication	Radiation Source	Dose to Cross-link	Anneal
Biomet ArCom®	1900H	Direct compression molded or machined from molded bar	Gamma	2.5–4 Mrad	None
DePuy/Johnson & Johnson Marathon™	1050	Machined from extruded bar	Gamma	5 Mrad	Above-melt temperature (150°C)
Smith & Nephew Reflection™ XLPE	1050	Machined	Gamma	5 Mrad	At-melt temperature (136°C)
Stryker Howmedica Osteonics Crossfire™	1050	Machined	Gamma	7.5 Mrad*	Below-melt temperature (>120°C)
Sulzer Orthopaedics Durasul™	1050	Machined from compression molded sheet	Electron beam	9.5 Mrad	Above-room temperature preheating before electron beam; melt anneal; controlled heat and cool rates; warm irradiation with adiabatic melting
Zimmer Longevity™	1050	Compression molded and machined	Electron beam	10 Mrad	Above-room temperature preheating before electron beam; process between cold irradiation with subsequent melting and warm irradiation with adiabatic melting

*Subsequently irradiated with a conventional sterilization dose of 3 Mrad

were analyzed in this study. The bearing materials fall into four categories: gamma irradiation cross-linked with subsequent at- or above-melt temperature annealing (Marathon™, DePuy/Johnson & Johnson; Reflection™ XLPE, Smith & Nephew); electron-beam irradiation cross-linked with subsequent above-melt temperature annealing (Durasul™, Sulzer Orthopaedics; Longevity™, Zimmer); gamma irradiation cross-linked with subsequent below-melt temperature annealing (Crossfire™, Stryker Howmedica Osteonics); and traditionally cross-linked by gamma sterilization in argon with barrier packaging (ArCom®, Biomet).

Acetabular bearings with large annular regions (outer diameter minus inner diameter) and flat, planar flange regions were required to obtain adequate test specimens. The minimum size for an acetabular bearing made for a 28-mm head was 64 mm. An acetabular bearing made for a 22-mm head could have an outer diameter as small as 56 mm.

To examine the polyethylene, each bearing was cut with a band saw into thirds, two flange portions and one apex portion (Fig 1). Thin sections (approximately 200-μm thick) were cut parallel to the surface of one of the flange portions of the bearing using a Jung microtome (Jung, Heidelberg, Germany). A sequence of thin sections representing a depth to approximately 4 mm (20 sections) was taken from one flange sample. These thin sections were analyzed to provide the as-received data. The apex portion of each bearing was reserved for additional testing.

Accelerated Aging

The second flange portion of each cross-linked material was subjected to accelerated aging. The ac-

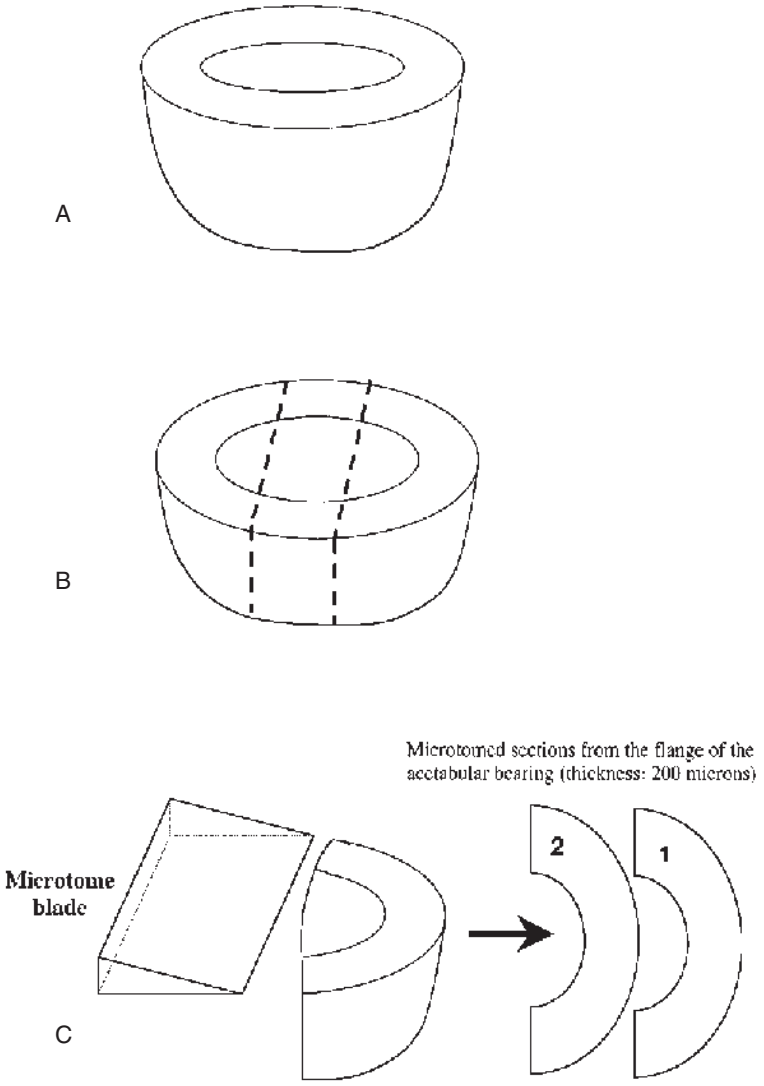

Fig 1A–C. This schematic shows the sampling technique used in this study. (A) As-received acetabular cups were cut into (B) thirds with a band saw. (C) One third was sectioned with a microtome to provide the thin sections (1 and 2) for the as-received analysis. The corresponding third of the cup that remained was accelerated aged and sectioned for the aged-28-days analysis. The center part of the cup was reserved for future additional tests.

celerated aging protocol used in the current study was less severe than some of the protocols reported in the literature.[17,18] Protocols that use higher aging temperatures were found to cause oxidation of virgin polyethylene in studies done by the authors (Fig 2). The temperature and oxygen pressure chosen for use as an accelerated aging protocol in this study did not produce elevated oxidation in virgin polyethylene, but did produce a subsurface oxidation peak in gamma irradiated polyethylene. The aging conditions were 63° C and 3 atm oxygen. The samples were aged for 28 days. After aging, the samples were sectioned by microtome as described above and tested with the following protocols for Fourier transform infrared spectroscopy and mechanical testing to provide the aged 28-days data.

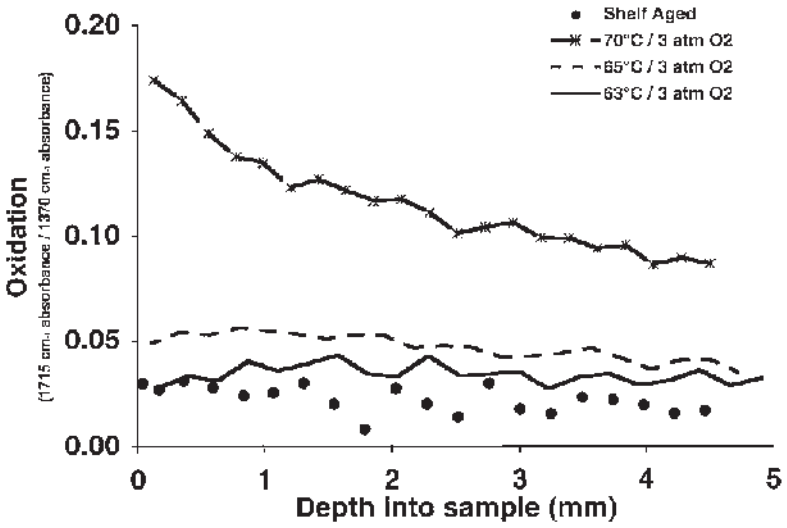

Fig 2. This graph shows the effect of accelerated aging temperature on oxidation of never-irradiated ultrahigh molecular weight polyethylene. Accelerated aging time for these samples was 25 days.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy was used to determine the level of oxidation in each bearing. Fourier transform infrared spectroscopy absorbance spectra were obtained using a Perkin Elmer Spectrum BXII (Norwalk, CT). Oxidation measurements were made on a series of horizontal thin sections, each representing a different depth into the acetabular bearing.

This study evaluated the incorporation of oxygen into the polyethylene by examining the carbonyl region of the Fourier transform infrared spectra, wave numbers between 1800 and 1660 cm^{-1}. The carbonyl region, measuring carbon-oxygen double bonds, indicates the presence of ester, ketone, aldehyde, and carboxylic acid. The oxidation level of the bearing thin section was defined as the measured ketone peak height (1715 cm^{-1}) normalized by the 1368 cm^{-1} peak height.

Mechanical Testing

To measure the mechanical properties of each acetabular bearing, the horizontal thin sections (approximately 200 μm) taken from each bearing flange were stamped, using a metal die, into a dumbbell configuration suitable for mechanical testing (American Society for Testing and Material Standards Type V sample because of bearing geometry limitations).[1] The gauge length was that of an American Society for Testing and Material Standards Type V[1] sample (7.62 mm), but with smaller gripping zones, again because of bearing geometry limitations. Uniaxial tension tests were done using these dumbbell-shaped horizontal thin sections. Ultimate tensile strength, elongation at break, and tensile stress at yield point were measured for each thin section. The tensile stress at yield point is the first point on the stress-strain curve at which an increase in strain occurs without an increase in stress.[1] A calculated toughness value obtained from the integration of the stress-strain curve also is reported.

The apparatus used for the tensile testing consisted of a load frame (Model 8501 Instron Corp, Canton, MA), with a servohydraulic actuator (Model 3398–341), and a 200-lb load cell (Model 2518–806). The thin sections were gripped by Instron Series 2712 pneumatic action grips. Specimen elongation was measured using an Instron noncontacting video extensometer (Model 2663–304) for accurate measurement of specimen strain. Instron Series IX Automated Materials Testing System software (Version 7.26) controlled testing and recorded output. The samples were loaded at a testing speed of 25 mm/minute.

Differential Scanning Calorimetry

Differential scanning calorimetry was used to measure the crystallinity of each of the cross-linked materials. Differential scanning calorimetry scans were obtained using a Mettler-Toledo DSC12E (Mettler-Toledo, Inc, Hightstown, NJ). A heating rate of 10° C per minute was used over a temperature range of 60° C to 180° C. Crystallinity and melt temperature are reported from the first of two temperature scans. Crystallinity is calculated assuming the heat of fusion of crystalline polyethylene to be 290 J/g.[16]

Electron Paramagnetic Resonance Spectroscopy

Electron paramagnetic resonance spectroscopy was done as part of the protocol to identify the species and concentrations of free radicals present in the material, as received and subsequent to accelerated aging.

Cylindrical samples for electron paramagnetic resonance imaging were cut from the acetabular liners using a lathe. The sampling procedure used low rotating speed and a nonoil-based coolant to minimize local heating during the cutting process. The resulting samples were 30-mm diameter cylinders with one convex end (nonarticular surface of the liner) and one concave end (articular surface of the liner). To minimize oxidation before electron paramagnetic resonance testing, the cylindrical samples were vacuum-sealed in foil pouches containing an oxygen scavenger and shipped overnight express to the test facility.

Electron paramagnetic resonance spectroscopy was done using a Bruker Elexsys 540 Imaging EPR Spectrometer (Bruker, Coventry, United Kingdom). This specially designed spectrometer was operated at 1-GHz microwave frequency to enhance microwave penetration. The specialized ER 6502BC resonator had an internal sample diameter of 3.4 cm and sensitive length of 3.5 cm. Spectrometer parameters were: incident microwave power 80 mW (the Q of this resonator is much lower than typical X-band cavities); modulation amplitude 0.4 mT; sweep width 12.5 mT; 30 scans averaged. Free radical concentrations were determined by double integration (with baseline corrections) using a stable paramagnetic standard. These free radical concentrations were corrected for sample volume and are presented as moles of radical per cubic decimeter.

Statistical Analysis

The data are presented as the mean ± standard deviation for a minimum of 16 thin sections per material for oxidation and mechanical property measurements. Statistical analysis of the experimental results was done using a two-tailed Student's t test to compare data from cross-linked polyethylene with a control material or data from as-received cross-linked polyethylene to accelerated-aged cross-linked polyethylene. The control material used was Hospital for Special Surgery Poly Hi Solidur, Hoechst Celanese reference ultrahigh molecular weight polyethylene material.[5] Results are presented at a significance level of α less than 0.05.

RESULTS

All of the as-received cross-linked materials showed low to no initial oxidation. Marathon™, Reflection™ XLPE, and Longevity™ had initial oxidation that was at or below the oxidation measured in the reference ultrahigh molecular weight polyethylene material.[5] Durasul™, ArCom®, and Crossfire™ had initial oxidation that was statistically higher than the oxidation measured in the reference ultrahigh molecular weight polyethylene material[5] (Table 2). Accelerated aging had no effect on the oxidation measured in three of the four cross-linked and at- or above-melt temperature-annealed materials (Marathon™, Reflection™ XLPE, and Durasul™). The fourth cross-linked and at- or above-melt temperature-annealed material, Longevity™, had a statistically significant increase in oxidation after aging. However, this material had the lowest oxidation as received, and the magnitude of its oxidation is not sufficient to significantly impact its mechanical properties. The gamma-sterilized, barrier-packaged material (ArCom®) had the highest percentage increase in oxidation, followed by the cross-linked and below-melt temperature-annealed polyethylene (Crossfire™) (Table 3). Both of these materials had a subsurface oxidation maximum after aging (Fig 3).

Electron paramagnetic resonance analyses of the four cross-linked and at- or above-melt temperature-annealed materials (Marathon™, Reflection™ XLPE, Durasul™, and Longevity™) showed no measurable free radical concentration. The gamma-sterilized, barrier-packaged material (ArCom®) and the cross-

TABLE 2. As Received Average Oxidation, Crystallinity, and Melt Temperature

Cross-linked Material	Oxidation	p Value*	Crystallinity (%)	T_m (°C)
Biomet ArCom®	0.042 ± 0.032	$p < 0.01$	64 ± 8.9	142 ± 1.0
DePuy/Johnson & Johnson Marathon™	0.005 ± 0.004	$p < 0.01$	43 ± 1.9	136 ± 1.2
Smith & Nephew Reflection™ XLPE	0.007 ± 0.004	$p < 0.01$	44 ± 3.0	136 ± 1.7
Stryker Howmedica Osteonics Crossfire™	0.036 ± 0.03	$p < 0.01$	58 ± 5.2	141 ± 1.2
Sulzer Orthopaedics Durasul™	0.072 ± 0.027	$p < 0.01$	44 ± 4.1	140 ± 1.3
Zimmer Longevity™	0.004 ± 0.002	$p < 0.01$	44 ± 1.3	140 ± 0.9
HSS Reference UHMWPE[17]	0.022 ± 0.008	–	61 ± 4.6	135 ± 0.6

*Probability values are for the t test between the cross-linked materials and the Hospital for Special Surgery (HSS) reference ultra-high molecular weight polyethylene (UHMWPE)[17]

T_m = melt temperature

linked and below-melt temperature-annealed material (Crossfire™) had measurable free radical concentration (Table 4). The signal-to-noise ratios obtained in these experiments suggested that free radical concentrations in the samples in which no measurable free radicals were detected were at most 1% of those found in materials such as Crossfire™.

Electron paramagnetic resonance imaging (data not shown) did not indicate any local reduction in free radical concentration at the cut faces of the cores used for electron paramagnetic resonance spectroscopy, supporting the assumption that there was no significant quenching induced by heating during machining of the cores. Electron paramagnetic resonance spectra of those samples with detectable free radical concentration were assigned to an allyl-type, carbon-centered radical with hyperfine couplings $A_{H(6)}$ 1.25 mT, $A_{H(1)}$ 0.45 mT. After accelerated aging, none of the materials had measurable free radical concentrations, including materials that had measurable free radical concentration as-received.

Differential scanning calorimetry crystallinity was similar for the four irradiated and at- or above-melt temperature-annealed materials (Marathon™, Reflection™ XLPE, Durasul™, and Longevity™). The gamma barrier-packaged (ArCom®) and the gamma-irradiated and below-melt temperature-annealed (Crossfire™) materials had higher crystallinity than the other four materials (Table 2), and showed increases in crystallinity after aging (Table 3). Melt temperature ranged from 136° C to 142° C for the six materials tested and essentially was unchanged after aging.

The tensile properties measured for the as-received cross-linked polyethylene were: tensile stress at yield point, ranging from 19 to 24 MPa, ultimate tensile strength, ranging from 34 to 60 MPa, and elongation at break, rang-

TABLE 3. Aged 28 Days Average Oxidation, Crystallinity, and Melt Temperature

Cross-linked Material	Oxidation	p Value#	Crystallinity (%)	T_m (°C)
Biomet ArCom®	0.286 ± 0.135	$p < 0.01$	72 ± 5.9	142 ± 1.1
DePuy/Johnson & Johnson Marathon™	0.007 ± 0.003	0.100	46 ± 0.1	136 ± 0.3
Smith & Nephew Reflection™ XLPE	0.007 ± 0.004	0.889	46 ± 2.1	136 ± 1.0
Stryker Howmedica Osteonics Crossfire™	0.302 ± 0.128	$p < 0.01$	65 ± 7.3	141 ± 1.0
Sulzer Orthopaedics Durasul™	0.073 ± 0.016	0.845	44 ± 2.9	140 ± 1.0
Zimmer Longevity™	0.036 ± 0.015	$p < 0.01$	45 ± 2.6	138 ± 0.6

#Probability values are for the t test between the as-received and aged cross-linked material properties

T_m = melt temperature

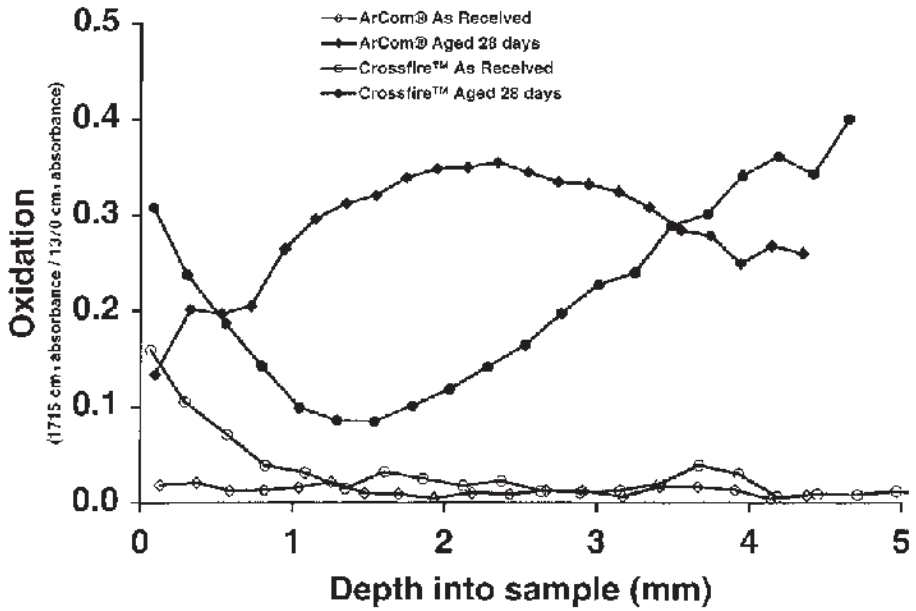

Fig 3. Oxidation profiles versus depth into the bearing before and after accelerated aging for ArCom® and Crossfire™ never-implanted bearings are shown.

ing from 230% to 330%. These properties compare with tensile properties measured for reference ultrahigh molecular weight polyethylene tensile stress at yield point 21.7 MPa, ultimate tensile strength 58 MPa, and elongation at break 380% (Table 5).

Accelerated aging caused a very small, but statistically significant difference in the tensile stress at yield point for four of the cross-linked materials tested (ArCom®, Crossfire™, Durasul™, and Reflection™ XLPE). Aging had no statistically significant effect on the ultimate tensile strength and elongation of Marathon™, Reflection™ XLPE, and Longevity™. The ultimate tensile strength and elongation of Durasul™ showed a statistically significant drop after aging. Crossfire™ and ArCom® had a statistically significant increase in elongation

TABLE 4. Electron Paramagnetic Resonance Spectroscopy Results

Manufacturer	As-Received Free Radical Concentration (mol/dm^{-3})	Aged 28 Days Free Radical Concentration (mol/dm^{-3})
Biomet ArCom®	3.8×10^{-4}	ND
DePuy/Johnson & Johnson Marathon™	ND	ND
Smith & Nephew Reflection™ XLPE	ND	ND
Stryker Howmedica Osteonics Crossfire™	7.3×10^{-4}	ND
Sulzer Orthopaedics Durasul™	ND	ND
Zimmer Longevity™	ND	ND

mol/dm^{-3} = moles/cubic decimeter

ND = none detected, Maximum concentration is less than 1% of free radical concentration measured in Crossfire™

TABLE 5. As-Received Average Mechanical Properties

Cross-linked Material	Yield Point (MPa)	p Value*	Ultimate Tensile Strength (MPa)	p Value*	Elongation (%)	p Value*
Biomet ArCom®	24 ± 0.8	$p < 0.01$	59 ± 4.7	0.3826	240 ± 38	$p < 0.01$
DePuy/Johnson & Johnson Marathon™	21 ± 0.5	$p < 0.01$	56 ± 7.0	0.1892	300 ± 14	$p < 0.01$
Smith & Nephew Reflection™ XLPE	20 ± 1.3	$p < 0.01$	56 ± 7.1	0.1895	300 ± 20	$p < 0.01$
Stryker Howmedica Osteonics Crossfire™	22 ± 1.0	0.8177	53 ± 5.3	$p < 0.01$	230 ± 17	$p < 0.01$
Sulzer Orthopaedics Durasul™	19 ± 1.6	$p < 0.01$	34 ± 3.4	$p < 0.01$	330 ± 19	$p < 0.01$
Zimmer Longevity™	21 ± 1.1	0.0271	43 ± 5.3	$p < 0.01$	250 ± 25	$p < 0.01$
HSS Reference UHMWPE[17]	21.7 ± 1.0	—	58 ± 4.7	—	380 ± 10	—

*Probability values are for the t test between the cross-linked materials and the Hospital for Special Surgery (HSS) reference ultra-high molecular weight polyethylene (UHMWPE)[17]

and decrease in ultimate tensile strength after aging (Table 6).

Mechanical properties versus depth into individual as-received components showed no systematic variation. After aging, the mechanical properties of the gamma-irradiated materials that were not melt-temperature-annealed (ArCom® and Crossfire™) varied with oxidation, while those of the irradiated and at- or above-melt temperature-annealed materials (Marathon™, Reflection™ XLPE, Durasul™, and Longevity™) did not, as seen in the plot of ultimate tensile strength versus oxidation (Fig 4). Calculated toughness is seen to be a function of received irradiation dose, with an increased irradiation dose resulting in lower toughness (Fig 5). A cross-plot of the reduction in wear rate as advertised by the individual manufacturers (Table 7) with received irradiation dose is shown in Figure 6.

DISCUSSION

The cross-linked materials tested represented two irradiation approaches and numerous annealing techniques. Of the six materials tested, four were cross-linked with various doses of gamma radiation (ArCom®, Crossfire™,

TABLE 6. Aged 28 Days Average Mechanical Properties

Cross-linked Material	Yield Point (MPa)	p Value#	Ultimate Tensile Strength (MPa)	p Value#	Elongation (%)	p Value#
Biomet ArCom®	25 ± 1.4	$p < 0.01$	40 ± 8.1	$p < 0.01$	300 ± 60	$p < 0.01$
DePuy/Johnson & Johnson Marathon™	21 ± 1.5	0.3877	56 ± 5.7	0.8699	290 ± 14	$p < 0.01$
Smith & Nephew Reflection™ XLPE	21 ± 1.4	0.0393	58 ± 7.3	0.2643	300 ± 37	0.9858
Stryker Howmedica Osteonics Crossfire™	24 ± 1.3	$p < 0.01$	48 ± 7.2	$p < 0.01$	280 ± 37	$p < 0.01$
Sulzer Orthopaedics Durasul™	20 ± 0.7	0.0279	30 ± 7.1	$p < 0.01$	280 ± 74	$p < 0.01$
Zimmer Longevity™	21 ± 1.0	0.1662	43 ± 9.8	0.8006	240 ± 35	0.0718

#Probability values are for the t test between the as-received and aged cross-linked material properties

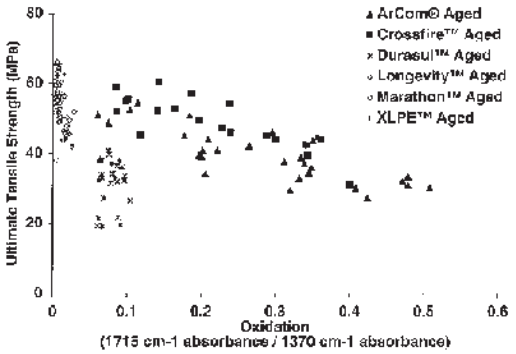

Fig 4. Change in ultimate tensile strength as a function of oxidation after accelerated aging is shown. Although all materials had a range of ultimate tensile strength, only ArCom® and Crossfire™ showed a decreasing trend with increasing oxidation.

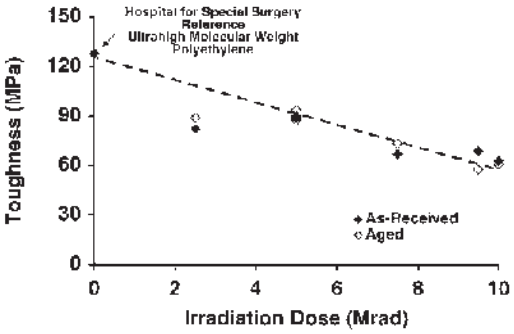

Fig 5. The average toughness is shown for cross-linked and reference ultrahigh molecular weight polyethylene as a function of received irradiation dose.

Marathon™, Reflection™ XLPE) and two were cross-linked with electron beam radiation (Durasul™, Longevity™). With the limited depth of penetration of the electron beam irradiation, there was potential to produce a heterogeneous material with varying degrees of cross-linking and mechanical properties at different depths. However, although all the materials tested (gamma- and electron beam-irradiated materials) had some degree of variation in mechanical properties, there were no systematic variations that might be expected as a function of radiation penetration distance.

The range of ultimate tensile strength values (34–60 MPa) represented the largest variation of any of the mechanical properties investigated. The as-received ultimate tensile strength values were lowest for the electron beam-irradiated materials (Durasul™ and Longevity™) compared with the gamma-irradiated materials (Marathon™, Reflection™ XLPE, Crossfire™, and ArCom®). However, when compared with the reference ultrahigh molecular weight polyethylene, the cross-linked materials separated by irradiation dose rather than irradiation method. The average ultimate tensile strength for ArCom®, Marathon™, and Reflection™ XLPE (all with irradiation doses of 5 Mrad or less) showed no statistical

TABLE 7. Advertised Wear Rate Reduction by Manufacturer

Manufacturer	Material	Advertised Wear Rate Reduction (%)**	Benchmark for Wear Rate Reduction
Biomet	ArCom®	42	Gamma-air
DePuy/Johnson & Johnson	Marathon™	85	Gas plasma
Smith & Nephew	Reflection™ XLPE	86	1050 resin, ethylene oxide
Stryker Howmedica Osteonics	Crossfire™	90	
Sulzer Orthopaedics	Durasul™	100	1050 resin, gamma N_2
Zimmer	Longevity™	90	1050 resin, gamma N_2

**These are advertised wear rate reduction percentages. The wear rates were not measured by a consistent, standardized method. The material used as a benchmark by the individual companies differed in resin type, fabrication method, sterilization method, sterilization dose, aging time after sterilization, and method of aging. Therefore, the wear reductions reported are not necessarily comparable.

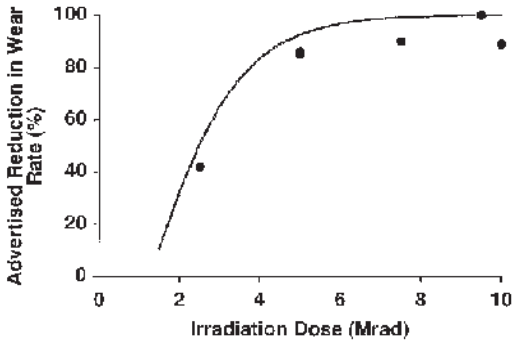

Fig 6. Percent wear rate reduction as advertised by individual manufacturers as a function of received irradiation dose is shown. Advertised wear rate reductions are in relation to various benchmarks, as shown in Table 7.

difference from the reference ultrahigh molecular weight polyethylene ultimate tensile strength. The average ultimate tensile strength values for Durasul™, Longevity™, and Crossfire™ (all with irradiation doses of 7.5 Mrad or higher) were statistically lower than the reference ultrahigh molecular weight polyethylene ultimate tensile strength. All the cross-linked materials tested had ultimate tensile strength values greater than the minimum American Society for Testing and Material Standards specification of 27 MPa[2] for noncross-linked ultrahigh molecular weight polyethylene. The electron beam-irradiated materials retained their initial ultimate tensile strength values after aging, as did Marathon™ and Reflection™ XLPE, but Crossfire™ and ArCom® showed decreased ultimate tensile strength after aging.

All the cross-linked materials tested had average elongation values that were statistically lower than the reference ultrahigh molecular weight polyethylene elongation. The range of elongation measured for the cross-linked materials (230%–330%) was smaller than the range of ultimate tensile strength, but the average elongation for half of the materials was at or below the minimum American Society for Testing and Material Standards specification of 250%[2] for noncross-linked ultrahigh molecular weight polyethylene. The electron beam-irradiated materials retained their initial elongation values after aging, as did Marathon™ and Reflection™ XLPE, but Crossfire™ and ArCom® had statistically higher elongation after aging. This increase in elongation may be related to the oxidation seen in these two materials after aging. Elongation has been found to increase with increasing oxidation initially, but then decreases precipitously as oxidation continues to increase.[22]

Tensile stress at yield point varied approximately 20% among the materials. Aging had little or no impact on the tensile stress at yield point. All of the materials investigated would be expected to yield at similar loading conditions. How the ultrahigh molecular weight polyethylene was annealed (if it was) had a much greater impact on its properties than the cross-linking method. The four materials that were at- or above-melt temperature annealed after irradiation cross-linking (Marathon™, Durasul™, Longevity™, and Reflection™ XLPE) had tensile stress at yield that was statistically lower than the reference ultrahigh molecular weight polyethylene. However, they all met or exceeded the American Society for Testing and Material Standards minimum specification of 19 MPa[2] for noncross-linked ultrahigh molecular weight polyethylene. These materials had no measurable free radical concentration. As would be expected from a material with no measurable free radicals, these materials showed minimal changes in oxidation and mechanical properties after accelerated aging. Because these materials did not contain free radicals, they could be expected to have oxidative and mechanical property stability similar to ethylene oxide-sterilized standard polyethylene over their in vivo duration, but with much lower wear rates than seen in ethylene oxide-sterilized standard polyethylene.[8]

Electron paramagnetic resonance measurements of the gamma-sterilized, barrier-packaged polyethylene material (ArCom®) and the gamma-irradiated, cross-linked material that was below-melt temperature annealed (Crossfire™) showed that these materials contained

free radicals. Accelerated aging of these materials (63° C, 3 atm oxygen, 28 days) produced a subsurface oxidation maximum, a measurable increase in crystallinity, and a reduction of the free radical concentration in these materials to below detection levels. One previous study suggested that a measurable free radical concentration would be expected after as many as 7 or more years of shelf aging in air.[15] Because this accelerated aging protocol resulted in no detectable free radicals for these materials, the elevated temperature may increase the mobility of the free radicals that are not oxidized by the aging process, allowing them to recombine or cross-link. Therefore, it may understate the material changes that could be seen over duration in vivo. However, it is a moderate screening method to evaluate the oxidative stability of materials. Oxidation resulting from accelerated aging caused changes in the mechanical properties of both materials. Neither of the materials reached an oxidation level during accelerated aging that negatively impacted mechanical properties.[9] However, their mechanical properties and crystallinity did change as the material oxidized, suggesting that the crystallinity and mechanical properties of these two materials could change because of oxidation over their in vivo duration. The ultimate effect of oxidation on their fatigue resistance is unknown.

Cross-plots of toughness with irradiation dose and advertised wear-rate reduction with irradiation dose showed the tradeoff of mechanical properties with wear resistance. Toughness showed a decreasing trend with increasing irradiation dose ($R^2 = 0.788$), even as advertised wear rate decreased. None of the materials tested had toughness values that would be expected to be inadequate in terms of fatigue resistance. However, all the cross-linked materials had toughness values that were statistically lower than the reference ultrahigh molecular weight polyethylene, and long-term differences in performance are possible.

Irradiating polyethylene with either electron beam or gamma irradiation generates free radicals in the materials which are long-lived and which can result in oxidation of the material when exposed to oxygen. By raising the temperature of the irradiated polyethylene to the melting point and holding it at that temperature, these free radicals will either cross-link or recombine. All of the cross-linked materials that were at- or above-melt temperature annealed (Marathon™, Reflection™ XLPE, Durasul™, and Longevity™) have obtained a desired benefit of highly cross-linked polyethylene, the minimization of free radicals. They showed oxidation resistance equal to that of never-irradiated polyethylene as measured by Fourier transform infrared spectroscopy before and after accelerated aging, differential scanning calorimetry crystallinity before and after aging, and electron paramagnetic resonance measurements of free radical concentrations before and after aging. These materials have the potential to remain relatively unaffected by oxidation throughout their duration in vivo.

Each of the manufacturers has taken its own approach to developing a cross-linked polyethylene material for bearing applications. A discussion by each manufacturer of the rationale for its approach to cross-linking is included in the Appendix. According to the manufacturers' data, all of these materials are more wear resistant than polyethylene that has not been cross-linked or that has been gamma irradiated in air. The yield strengths of all of the materials are similar. However, toughness and free radical concentrations in them vary significantly. Toughness seems to be a function of the irradiation dose used to cross-link the polyethylene, with doses greater than 5 Mrad resulting in lower measured toughness. Measurable free radical concentration results from irradiation of the polyethylene without subsequent melt-temperature annealing. The tradeoff of reduction in mechanical properties with increased irradiation dosage and therefore decreased wear rate seems unavoidable.

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APPENDIX: DISCUSSION BY MANUFACTURERS

This paper is the culmination of collaboration with six orthopaedic manufacturers who provided the cross-linked materials for this study and the wear characteristics of the material they provided. The process of developing this paper included independent measurement of the properties of the six cross-linked materials, followed by review of the results by the orthopaedic manufacturers. The manufacturers provided a second review of the completed text and the following sections in which they discuss their specific cross-linked material.

ArCom® (D. Schroeder, Biomet, Warsaw, IN)

ArCom® is compression-molded 1900H polyethylene that is barrier packaged and gamma irradiated. The goal of the ArCom® process is a material that balances mechanical properties and cross-linking to produce more wear resistant polyethylene. The development of ArCom® intentionally avoided making radical changes to the material that could have unexpected consequences—fracture caused by changes in the mechanical, physical, and fatigue properties; biologic consequences of changes in the wear debris—and focused on optimizing proven technology—1900H resin, full consolidation, gamma irradiation, and barrier film technology. Laboratory testing of ArCom® has shown a 42% reduction in volumetric wear compared with gamma-in-air sterilized polyethylene.

Marathon™ (H. McKellop/R. Tarr; DePuy/Johnson & Johnson, Warsaw, IN)

In the Marathon™ process, polyethylene is cross-linked with 5 Mrads of gamma radiation while still in bulk form. It is heated above the melt temperature for an extended period to eliminate the residual free radicals. It then is machined into the final implant, packaged, and sterilized with gas plasma to avoid reintroducing free radicals. The goal of the Marathon™ process was to maintain the mechanical properties of Marathon™ cross-linked polyethylene at a level similar to those of unoxidized polyethylene components that had been gamma sterilized in air at a typical dose of 3.3 Mrads. Laboratory data indicate that the wear rate of Marathon™ is approximately 85% lower than noncross-linked polyethylene.

Reflection™ XLPE (S. Miller, Smith & Nephew, Inc, Memphis, TN)

The XLPE provided for this study was cross-linked with 5 Mrads of gamma irradiation. The goal of this cross-linking process was to reduce wear but to keep the material properties as close to unsterilized polyethylene as possible. This process provided an 86% reduction in volumetric wear in laboratory testing compared with EtO-sterilized polyethylene. However, this cross-linked polyethylene is not commercially available; Smith & Nephew has increased the cross-linking radiation dose it uses to 10 Mrad. Company laboratory data indicate that this higher level of cross-linking reduces the volumetric wear to below the detection limit.

Crossfire™ (A.A. Edidin, Stryker Howmedica Osteonics, Rutherford, NJ)

Crossfire™ polyethylene was designed to provide the benefit of substantial wear reduction with minimal change in processing from standard nitrogen sterilized and packaged bearings. The total irradiation dose was increased to an average of 10.5 Mrad via a two-step process. The first step delivers approximately 7.5 Mrad gamma-irradiation and is followed by a high temperature anneal. The decision to use a high temperature anneal rather than a melt quenching step was driven by a desire to leave the internal morphologic features and thermal processing history of the ultrahigh molecular weight polyethylene in line with the original material. After machining and nitrogen packaging, the bearings are sterilized by a conven-

tional dose of approximately 3 Mrad. The advertised wear rate reduction for Crossfire is 90%.

Durasul™ (M. C. Shen, Sulzer Orthopaedics, Inc, Austin, TX)

Durasul™ was developed for improved wear resistance of polyethylene. This material is cross-linked by 10 Mrad electron beam irradiation at an elevated temperature, followed by melt annealing. Elevated temperature during irradiation is thought to maximize cross-linking between molecular chains attributable to increased chain mobility. The melt annealing reduces free radicals, the precursor to polyethylene oxidation. This process significantly reduces polyethylene wear (nonmeasurable wear through 27 million cycles in a hip simulator) while maintaining the mechanical properties within the requirements of American Society for Testing and Material Standards and ISO standards.

Longevity™, (C. R. Blanchard, Zimmer, Warsaw, IN)

The goal in developing Longevity™ polyethylene was to produce a material with substantially enhanced wear performance and the mechanical properties required of polyethylene acetabular components. A radiation exposure of 100 kGy provides a balance between wear reduction and retention of mechanical properties that are desirable for the acetabular cup application. Preheating the material before e-beam irradiation impacts the toughness and strength of the material while post irradiation annealing facilitates free-radical reduction, increased cross-linking and the reduced potential for oxidation. Optimizing the crystallinity of the cross-linked polyethylene is done through the annealing heating rate, heating temperature, time at temperature, and the cooling rate. This process provides a 90% decrease in wear rate compared with gamma-sterilized-in-nitrogen polyethylene in laboratory testing.

Orthopaedic implant design and material properties are related to the function and performance of an implant. No single cross-linked formulation should be used for every application. Device testing is ultimately the best proof of the appropriate choice of material properties. The testing of wear, locking mechanism, polyethylene to shell mechanics, impingement, and fatigue are critical to the development of safe and effective cross-linked acetabular devices.

References

1. American Society for Testing and Material Standards D638–99: Standard Test Method for Tensile Properties of Plastics. West Conshohocken, PA, American Society for Testing and Materials 8.01, 1999.
2. American Society for Testing and Material Standards F648–00: Standard Specification for Ultrahigh Molecular Weight Polyethylene Powder and Fabricated Form for Surgical Implants. West Conshohocken, PA, American Society for Testing and Materials 13.01,2000.
3. Baker DA, Hasting RS, Pruitt L: Compression and tension fatigue resistance of medical grade ultrahigh molecular weight polyethylene: The effect of morphology, sterilization, aging and temperature. Polymer 41:795–808, 2000.
4. Bargmann LS, Bargmann BC, Collier JP, Currier BH, Mayor MB: Current sterilization and packaging methods for polyethylene. Clin Orthop 369:49–58, 1999.
5. Bennet AP, Wright TM, Li S: Global reference ultrahigh molecular weight polyethylene: Characterization and comparison to commercial ultrahigh molecular weight polyethylene. Trans Orthop Res Soc 21:472, 1996.
6. Bragdon CR, O'Connor DO, Muratoglu OK, et al: A new polyethylene with undetectable wear at 12 million cycles. Trans Soc Biomater 21:2,1998.
7. Collier JP, Sperling DK, Currier JH, et al: Impact of gamma sterilization on clinical performance of polyethylene in the knee. J Arthoplasty 11:377–389, 1996.
8. Costa L, Luda MP, Trossarelli L, et al: In vivo ultrahigh molecular weight polyethylene biodegradation of retrieved prosthesis. Biomaterials 19:1371–1385, 1998.
9. Currier BH, Currier JH, Collier JP, Mayor MB: Effect of fabrication method and resin type on performance of tibial bearings. J Biomed Mater Res (Appl Biomater) 53:143–151, 2000.
10. Currier BH, Currier JH, Collier JP, Mayor MB, Scott RD: Shelf life and in vivo duration. Clin Orthop 342:111–122, 1997.
11. Lewis G: Properties of cross-linked UHMWPE. Biomaterials 22:371–401, 2001.
12. McKellop HA, Shen FW, Campbell P, Ota T: Effect of molecular weight, calcium stearate, and sterilization method on the wear of UHMWPE acetabular cups in hip joint simulator. J Orthop Res 17:329–339, 1999.
13. McKellop H, Shen FW, Lu B, Campbell P, Salovey R: Development of an extremely wear-resistant ultrahigh molecular weight polyethylene for total hip replacements. J Orthop Res 17:157–167, 1999.

14. Muratoglu OK, Bragdon CR, O'Connor DO, Jasty M, Harris WH: A novel method of cross-linking ultrahigh molecular weight polyethylene to improve wear, reduce oxidation, and retain mechanical properties. J Arthoplasty 16:149–160, 2001.
15. O'Neill P, Birkinshaw C, Leahy JJ, Barklie R: The role of long lived free radicals in the ageing of irradiated ultrahigh molecular weight polyethylene. Poly Degrad Stabil 63:31–39, 1999.
16. Pascaud RS, Evans WT, McCullagh PJJ, FitzPatrick D: Effects of batch to batch variations and test methodology on degree of crystallinity and melting temperature of ultrahigh molecular weight polyethylene as measured by differential scanning calorimetry. J Biomed Mater Res 32:619–626, 1996.
17. Sanford WM, Saum KA: Accelerated oxidative aging testing of UHMWPE. Trans Orthop Res Soc 20:119, 1995.
18. Sun DC, Stark C, Dumbleton JH: Development of an accelerated aging method for evaluation of long-term irradiation effects on UHMWPE implants. Polym Reprints 35:969–970, 1994.
19. Sutula LC, Collier JP, Saum KA, et al: Impact of sterilization on clinical performance of polyethylene in the hip. Clin Orthop 319:28–40, 1995.
20. Taylor S, Serekian P, Bruchalski P, Manley M: The performance of irradiation-crosslinked UHMWPE cups under abrasive conditions throughout hip simulation testing. Trans Orthop Res Soc 24:252, 1999.
21. Williams IR, Mayor MB, Collier JP: The impact of sterilization method on wear in knee arthroplasty. Clin Orthop 356:170–180, 1998.
22. Winslow FH, Hellman MY, Matreyek W, Stills SM: Autoxidation of semicrystalline polyethylene. Poly Engr Sci 6:273–278, 1966.