The Journal of Arthroplasty Vol. 16 No. 8 2001

A Comparison of the Wear and Physical Properties of Silane Cross-Linked Polyethylene and Ultra-High Molecular Weight Polyethylene

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Abstract: Cross-linked polyethylenes are being introduced widely in acetabular cups in hip prostheses as a strategy to reduce the incidence of wear debris–induced osteolysis. It will be many years before substantial clinical data can be collected on the wear of these new materials. Silane cross-linked polyethylene (XLPE) was introduced into clinical practice in a limited series of acetabular cups in 1986 articulating against 22.225-mm alumina ceramic femoral heads and showed reduced wear rates compared with conventionally sterilized (gamma irradiation in air) ultra-high molecular weight polyethylene (UHMWPE). We compared the wear of XLPE manufactured in 1986 with the wear of UHMWPE manufactured in 1986 in nonirradiated and irradiated forms. In the nonirradiated forms, the wear of XLPE was 3 times less than UHWMPE when articulating against smooth counterfaces. The nonirradiated materials did not show signs of oxidation. In the irradiated forms, only UHMWPE showed high levels of oxidation, and this caused a substantial increase in wear. Antioxidants added to XLPE during processing gave resistance to oxidative degradation. When sliding against scratched counterfaces, the wear of UHMWPE increased by a factor of 2 to 3 times. Against the same scratched counterfaces, the wear of XLPE increased dramatically by 30 to 200 times. This difference may be attributed to the reduction in toughness of XLPE. Clinically, XLPE has been articulated against damage-resistant ceramic heads, and this probably has been an important factor in contributing to reduced wear. New cross-linked polyethylenes differ considerably from XLPE. This study indicates that it is prudent to examine the wear of new polyethylenes under a range of conditions that may occur *in vivo*. **Key words:** wear, polyethylene, crosslinking oxidation.

There is currently much interest in the orthopaedic community in cross-linked polyethylene and its potential to reduce the wear of acetabular cups and the resulting wear debris–induced osteolysis [1]. Many of the new irradiation cross-linked polyethylenes have shown reduced wear rates in *in vitro* simulation tests in comparison with conventional polyethylene when articulating against smooth femoral heads. Clinical experience with these new cross-linked materials is limited, however, and it will be many years before clinical wear rates can be determined accurately. There is some limited medium-term clinical experience with irradiated silane cross-linked polyethylene (XLPE) acetabular cups manufactured in 1986 and with 10 years'

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Submitted August 23, 2000; accepted June 5, 2001.

Funds and benefits were received in partial or total support of the research material described in this article from the EPSRC and DePuy International.

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0883-5403/01/1608-0011$35.00/0
doi:10.1054/arth.2001.27234

clinical follow up [2]. In this small series of patients, the XLPE acetabular cups were coupled with a 22.225-mm diameter alumina ceramic femoral head, and these have shown linear penetration rates of 0.037 mm/y substantially lower than conventional Charnley ultra-high molecular weight polyethylene (UHMWPE) acetabular cups on metallic heads (0.08 mm/y) [3]. This superior clinical performance has been cited to support the introduction of new irradiation cross-linked UHMWPEs. The factors contributing to the reduced clinical wear rates with XLPE acetabular cups remain uncertain, however, because the reduction may be attributed to the smoother damage-resistant ceramic femoral head, improved stability, and resistance to oxidative degradation of XLPE as well as the chemical cross-linking itself. Only limited wear testing of XLPE was carried out before its clinical use. This *in vitro* work was carried out in water, and it now is well recognized that this can produce artifactual wear rates, which are of little help in the prediction of clinical wear rates.

In July 1999, 4 XLPE cups, which were manufactured in 1986 (2 of which had been irradiated and 2 of which had not) and which had not been implanted, became available for study. They were matched with UHMWPE (irradiated and nonirradiated of a similar age) and a current UHMWPE, which was used as a control material. The purpose of this study was to compare the wear and physical properties of XLPE with UHMWPE when sliding against smooth and damaged femoral counterfaces in an attempt to gain a better understanding of the factors contributing to the lower clinical wear of XLPE.

Materials and Methods

Materials

The 5 polyethylene materials studied are listed in Table 1. The XLPE was manufactured from 100,000 molecular weight polyethylene, which was silane grafted and heavily chemically cross-linked during thermal processing [4]. The UHMWPE was 2 to 4 million molecular weight, compression molded in a sheet known as GUR 1120 in 1999 and previously known as RCH1000 in 1986 and 1992. RCH1000 and GUR1120 contained calcium stearate. XLPE materials A and C did not contain calcium stearate but included antioxidants to prevent degradation during injection molding. The materials A and B were irradiated in air with a dose of 25 KiloGrays.

Six wear test pins were machined from each material with a wear contact face diameter of 8 mm positioned within 1 mm of the articulating surface of the cup (Fig. 1). Additional pins were machined for analysis of gel content and oxidation index.

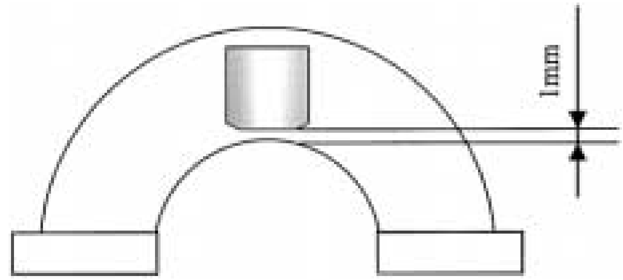


Fig. 1. Diagram shows the position of the wear test pin in the acetabular cup.

Wear Studies

Polished stainless steel counterfaces (n = 6) $R_a = 0.024 \pm 0.008\ \mu m$ were prepared for the wear test. Additionally, scratched polished stainless steel counterfaces $R_p = 1$ to $3\ \mu m$ were prepared using a diamond stylus, with 5 discrete transverse scratches across the wear track to simulate a damaged femoral head [5]. Wear studies were carried out on a multidirectional reciprocating pin on plate wear simulator [6] using 25% bovine serum solution. The conditions of the wear test are given in Table 2, and a line diagram of the wear simulator is shown in Fig. 2.

Wear was determined by weight loss after 15 and 30 km sliding. Wear volume was calculated from the density, and the wear factor (wear volume per

Table 1. Materials Studied

A	XLPE	86	Irradiated in air	XLPE I86
B	UHMWPE	86	Irradiated in air	UHMWPE I86
C	XLPE	86	Not irradiated	XLPE NI86
D	UHMWPE	92	Not irradiated	UHMWPENI92
E	UHMWPE	99	Not irradiated	UHMWPENI99

Table 2. Wear Test Conditions

Load	180N
Contact stress	3.6 MPa
Distance travel/cycle	±20 mm
Rotation/cycle	±40°
Cycle rate	1 Hz
Total sliding distance	30 km

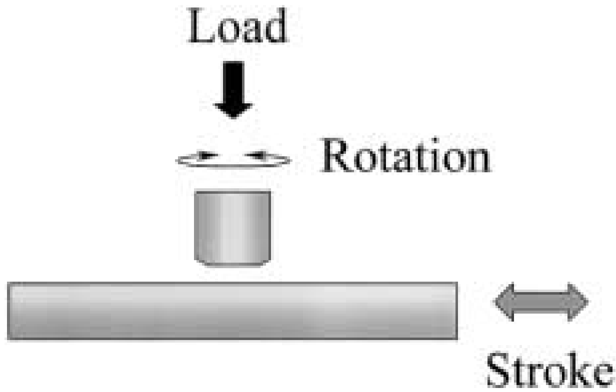


Fig. 2. Diagram of the wear simulator.

unit load and sliding distance) was determined. At the end of the test, the wear surfaces were characterized using a UBM (Messtechnik, Ettlinger, Germany) three-dimensional noncontacting profilometer and scanning electron microscope. All 5 materials (A to E) were tested on the same counterfaces, with 6 specimens of each material being tested. Mean values of wear factors were compared using a one-way analysis of variance (ANOVA) and statistical significance taken at the 95% level.

Fourier Transfer Infrared Spectroscopy

Fourier transfer infrared (FTIR) spectroscopy was used as an indicator of oxidative degradation. Wear pins were set in acrylic and held tightly in place with a pin to allow rigid clamping in a microtome. The microtome chamber was cooled to −18°C, and thin slices (approximately 165 μm) were taken from the wear surface to a depth of about 5 mm. The thickness was measured with a CADAR digital micrometer (Sheffield, UK).

Each thin microtomed slice was mounted on a backing card and mounted in a Perkin Elmer FTIR spectrometer (Beckonsfield, Bucks, UK). Spectra were acquired as an average of 16 scans with a resolution of 4 cm^{-1} and fitted with Spectra-Calc software (Galactic Industries, Salem, NH). The region between 1,250 cm^{-1} and 1,400 cm^{-1} was fitted with 3 peaks at 1,305 cm^{-1}, 1,352 cm^{-1}, and 1,370 cm^{-1}, and the region between 1,650 cm^{-1} and 1,850 cm^{-1} was fitted with 1 peak at 1,717 cm^{-1}. A combination of gaussian and lorentzian line shapes was allowed for each peak. The oxidation index was obtained from the ratio of the area of the peak at 1,717 cm^{-1} to the combined area of the peaks at 1,352 cm^{-1} and 1,370 cm^{-1}. The peak at 1,717 cm^{-1} was present in the polyethylene spectrum only when oxidized, and the peaks at 1,352 cm^{-1} and 1,370 cm^{-1} were used as a reference because they were invariant with oxidation.

Gel Fraction

Gel fraction was used as an indicator of the level of cross-linking in the polyethylene. It was analyzed as a function of depth from the surface of the material. Several consecutive microtomed slices were placed in a weighed steel gauze (120G) container. The gauze plus sample were reweighed before and after solvent extraction (190°C) in decalin (decahydronaphthalene) containing antioxidant (2,6-ditertiary-butyl-4-methylphenol, 1% w/v). The gauze container plus sample was cleansed of dekalin by refluxing in acetone (60°C, 10 minutes) and subsequently dried in an oven (110°C, 24 hours). The gauze container weight was subtracted from the weight of the sample plus gauze container before and after solvent extraction, and the postsolvent extracted sample weight was corrected for container weight loss. The gel fraction was taken as the corrected weight of sample after extraction divided by the weight of sample before extraction.

Results

The oxidation index and gel fraction for materials A to D are shown in Table 3. Elevated levels of oxidation were found only in material B, 86 irradiated (I86) UHMWPE. As expected, there was no oxidation in the nonirradiated material, but surpris-

Table 3. Oxidation Index and Gel Fraction

Material	Oxidation Index	Gel Fraction
A XLPE I86	0	0.72
B UHMWPE I86	Peaked at 1 mm depth (see below)	Peaked at 4 mm depth (see below)
C XLPE NI86	0	0.73
D UHMWPE NI92	0	0.57
	Material B Data	
Sample Code	**Average Depth (μm)**	**Gel Fraction**
BB1	487	0.09
BB2	1,240	0.25
BB3	1,761	0.42
BB4	2,265	0.51
BB5	2,766	0.57
BB6	3,264	0.61
BB7	3,759	0.61
BB8	4,253	0.63
BB9	4,750	0.58
BB10	5,086	0.48

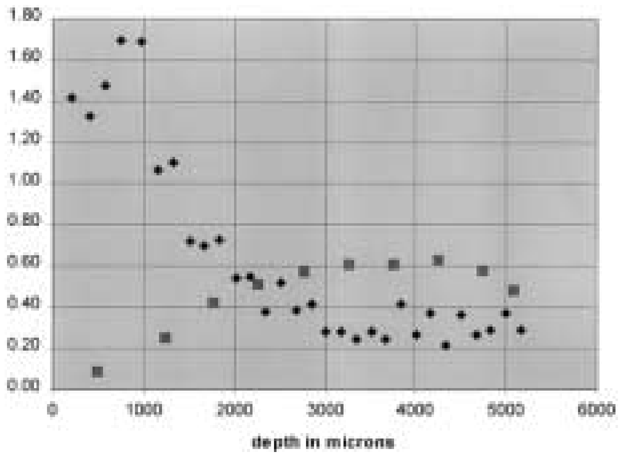


Fig. 3. Oxidation index and gel fraction with depth for material B UHMWPE I86. Oxidation index ◆, gel fraction ■.

ingly owing to the antioxidants used during injection molding, there was no oxidation of the I86 XLPE. The oxidation of the I86 UHMWPE peaked 1 mm below the surface, whereas the gel fraction peaked at a depth of 4 mm (Fig. 3).

The mean wear factor ± 95% confidence limits for the nonirradiated materials (C, D, E) are shown in Fig. 4 for the smooth counterface conditions. The benefit of the chemical cross-linking in the nonirradiated condition was shown clearly with a threefold reduction in wear factor for XLPE 86 nonirradiated (NI86) compared with the UHMWPE NI92.

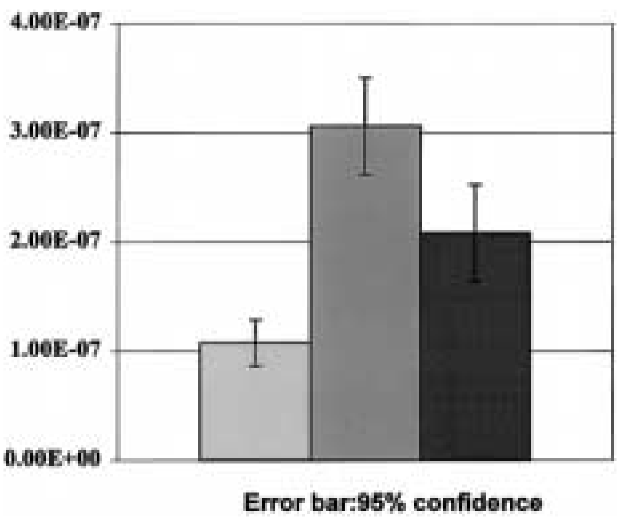


Fig. 4. Wear factors of nonirradiated materials and control UHMWPE on a smooth counterface mm^3/Nm. C:XPLE NI86 ■, D:UHMWPE NI92 ■, Control:UHMWPE NI99 ■.

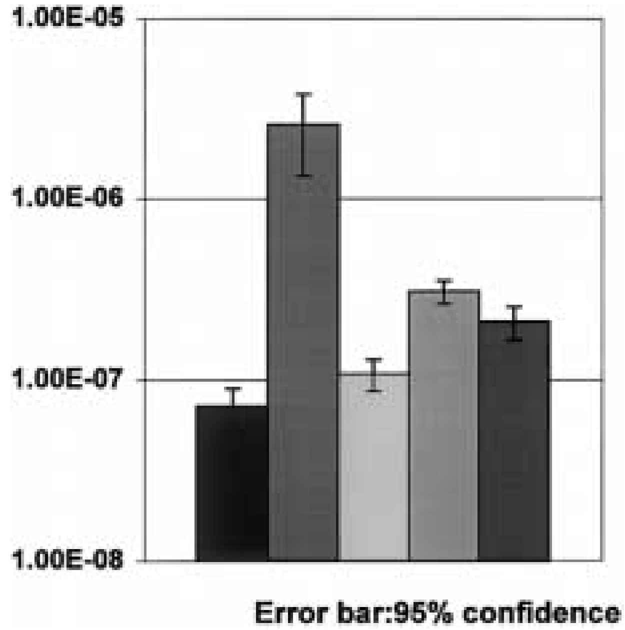
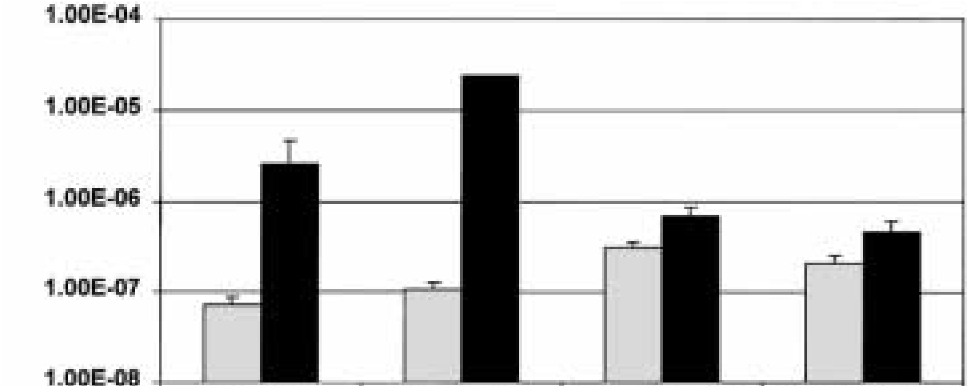


Fig. 5. Wear factors of all tested materials on a smooth counterface mm^3/Nm. A:XPLE I186 ■, B:UHMWPE I86 ■, C:XPLE NI86 ■, D:UHMWPE NI92 ■, Control:UHMWPE NI99 ■.

The difference between the UHMWPE NI92 and UHMWPE NI99 also was statistically significant and may reflect improved manufacturing methods.

The comparative wear factors including the irradiated material on smooth counterfaces are shown in Fig. 5, which is plotted on a logarithmic scale. The large increase in wear in the UHMWPE I86 was consistent with the oxidative degradation shown in the FTIR spectrometry analysis. The significantly reduced wear factor of XLPE I86 could be associated with the additional cross-linking achieved with irradiation, but this was not reflected in the gel content measurement. The results of Fig. 5 were consistent with the clinical finding of this particular XLPE of reduced wear rates on smooth ceramic femoral heads compared with UHMWPE. XLPE had the advantages of cross-linking to give lower wear rates when sliding on a smooth counterface and an improved resistance to oxidative degradation.

The wear results when sliding on the scratched counterfaces were considerably different (Fig. 6). Material availability did not allow us to test material B UHMWPE I86 on the scratched counterfaces. This testing was not considered crucial, however, because the material B had a high wear rate on smooth counterfaces. Because of the limited materials and specimens of XLPE NI86 and XLPE I86 materials, only 3 and 2 specimens were tested. The



	A:XLPE I86	C:XLPE NI86	D:UHMWPE NI92	UHMWPE NI99 GUR1120
□ SMOOTH	7.14E-08	1.08E-07	3.06E-07	2.08E-07
■ SCRATCH	2.60E-06	2.42E-05	6.80E-07	4.59E-07

Fig. 6. Wear factors on smooth and scratched counterfaces mm^3/Nm.

results in Fig. 6 showed that under the scratched counterface conditions, the wear of UHMWPE NI92 and UHMWPE NI99 increased a relatively small amount compared with the wear on the smooth counterface. The wear of XLPE I86 and XLPE NI86 increased 30-fold and 200-fold on scratched counterfaces compared with smooth counterfaces. These differences were highly significant ($P<.01$, Students' t-test).

Discussion

The current interest and widespread introduction into clinical practice of new cross-linked polyethylenes [1] makes this study of a silane cross-linked polyethylene XLPE introduced into clinical practice in 1986 timely. Material A XLPE I86 was identical to (taken from the same manufacturing batch and sterilized in the same way) the cups used in a clinical study reported by Wroblewski et al [2]. Although preclinical wear and simulation testing of bearing surfaces has increased considerably, validation of test results with clinical studies remains important. These smooth counterface wear test results of XLPE I86 fit well with the clinical experience of this material on size 22.225-mm alumina ceramic femoral heads, showing a similar reduction in wear compared with irradiated in air UHMWPE. The oxidation level of UHMWPE I86 stored in air in its packaging (Fig. 3) is likely to be substantially higher than UHMWPE I86 cups implanted in the body, shortly after sterilization. Nevertheless, the superior stability of XLPE is clearly a contributing factor to its reported lower clinical wear rate.

This improved stability may be contributed to by lack of calcium stearate, the antioxidant used during the processing of XLPE and by the silane cross-links formed in the material. The gel fraction was used as an indicator of cross-linking but cannot be used to quantify directly the number of cross-links. In the absence of oxidative degradation, XLPE produced a 3 times lower wear factor than UHMWPE nonirradiated, showing the benefits of cross-linking for multidirectional motion on smooth counterfaces as found in the hip [1,7,8]. The XLPE I86 showed superior resistance to oxidation in its aged irradiated form compared with aged irradiated UHMWPE I86, and this was reflected in the high wear rate found with the oxidized UHMWPE I86. Current UHMWPE materials that either are irradiated in inert atmospheres or are sterilized without irradiation provide better resistance to oxidative degradation compared with the traditional gamma irradiated in air material, and these are likely to lead to improvements in clinical performance.

The study of the wear resistance of scratched counterfaces is becoming routine for the screening of new materials, following the work of Marrs et al [6], which showed that the preferential reduction in wear of acetylene-enhanced cross-linked material was lost when sliding on rougher counterfaces under multidirectional conditions. The extremely high wear rate of XLPE sliding on the scratched counterface in this study was unexpected. The current small clinical series of XLPE cups [2] are articulating against damage-resistant ceramic femoral heads, and this could be a contributing factor to their improved clinical performance. Lancaster [9] indicated that the wear of polymers under abrasive conditions was inversely proportional to the product of the strength and the ductility of the material. The reduction in ductility of the XLPE [4], which is caused by the formation of the cross-links between the polyethylene molecules that constrain the relative movement of the molecular chains, may be the cause of the acceleration of wear under abrasive conditions.

This study has contributed to understanding the factors that contribute to the lower clinical wear of XLPE. It has shown that the inherent cross-linking of XLPE coupled with its oxidation resistance resulted in the lower wear rates found in the clinical XLPE series with smooth ceramic femoral heads. This study has raised a further important question in relation to the performance of XLPE when articulating against damaged femoral heads. The *discrete scratch* femoral head damage model used in this study has been validated in a hip joint simulator and has been shown to accelerate the wear of conventionally sterilized UHMWPE by 2 to 3 times [5], which is consistent with the increase in clinical wear rates with damaged heads [10]. The heights of the scratch lips in this model were controlled with an R_p in the range of 1 to 3 μm, and this has been shown to be a crucial determinant of polyethylene wear. The XLPE used in this study is substantially different from the cross-linked polyethylenes currently being introduced clinically. This study indicates, however, the need to examine new materials under a range of clinical conditions, and in particular it indicates that there is a clear need to examine the performance of new partially or highly cross-linked polyethylenes against smooth and scratched metallic femoral counterfaces because this condition of a scratched metallic femoral head commonly is found on retrieved prostheses [5,10]. The Wroblewski study [2] using cross-linked XLPE cups also used damage-resistant alumina ceramic femoral heads, and this may have been an important factor leading to the reduced clinical wear rate of cross-linked polyethylene in that study.

Conclusion

This study through comparison of *in vitro* and *in vivo* wear of XLPE shows the benefits of reduced wear of cross-linked polyethylenes with smooth femoral heads, but it raises some potential concerns over the performance of XLPE with damaged counterfaces.

Acknowledgment

Mr. M. C. Vale carried out the FTIR spectrometry and gel content measurement.

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