Comparison of the wear of aged and non-aged ultrahigh molecular weight polyethylene sterilized by gamma irradiation and by gas plasma

J. FISHER[1]*, E.A. REEVES[1], G.H. ISAAC[2], K.A. SAUM[3], W.M. SANFORD[2]
[1]*Department of Mechanical Engineering, University of Leeds, Leeds, LS2 9JT, UK*
[2]*DePuy International, Leeds, UK*
[3]*DePuy-DuPont Orthopaedics, Newark, Delaware, USA*

The wear of ultrahigh molecular weight polyethylene in artificial joints is a major cause of long-term osteolysis and loosening. The wear rate of aged and non-aged ultrahigh molecular weight polyethylene sterilized by both gamma irradiation in air and gas plasma has been studied in simple configuration wear tests. Fourier transform infrared analysis (FTIR) showed marked oxidative degradation of the irradiated and aged material compared to the gas plasma sterilized and aged material. The wear rate of the irradiated and aged material was significantly (three times) higher than the gas plasma sterilized, gas plasma sterilized and aged, and non-sterilized materials. Alternative sterilization procedures such as gas plasma, when used instead of gamma irradiation in air, are likely to reduce the incidence of long-term osteolysis.

1. Introduction

The generation of ultrahigh molecular weight polyethylene (UHMWPE) wear particles and the resulting osteolysis is now recognized as a major cause of long-term loosening in total artificial joints [1, 2]. The reduction in the volumetric wear rate of UHMWPE in total artificial joints and hence extension of the clinical lifetime of prostheses is a major aim of many researchers in the field. Over the last twenty-five years UHMWPE in joint replacements has been primarily sterilized by gamma irradiation in the presence of oxygen or air. The irradiation (2.5 to 4 MRads) has been shown to generate long-lived free radicals which can cause both chain scission of the polymer and crosslinking [3]. In the presence of air, free radicals preferentially produce chain scission and oxidation of the UHMWPE [2, 4], a reduction in molecular weight, and deterioration of important mechanical properties such as toughness, ductility and fatigue strength [5] over a long period of time. The oxidation and degradation is at a maximum close to the surface of the polyethylene, increases in magnitude and varies spatially with time forming a band up to several millimetres thick, which peaks 0.5 to 2 mm below the surface after a period of 5 to 10 years [3, 5, 6]. It is generally felt that the degradation rate *in vivo* may be lower than that of components left on the shelf, although the rate of *in vivo* oxidation has not been quantified. However, shelf life prior to implantation has historically received little attention or control, within a maximum limit of 5 years.

The average linear wear rate representative of clinical hip prostheses is in the range 60 to 120 μm per year, hence the depth of oxidized material is likely to influence the wear of UHMWPE for between 10 to 20 years in the majority of patients. It has been recently shown [7] that the material from cups that have been aged on the shelf for between 5 and 7 years has a threefold increase in wear rate compared to non-irradiated material, when the material was worn at a depth of approximately 1 mm below the surface. Recently irradiated material of less than 3 months ageing, was found to wear about 50% more than non-irradiated material.

Many alternative approaches to sterilization have been considered in the last two years. Ethylene oxide sterilization (E_tO) has been introduced by two companies as this is considered not to significantly alter the properties of UHMWPE. Other groups have chosen to irradiate and package in a vacuum or inert atmospheres such as nitrogen or argon. This is claimed to provide some benefits of crosslinking without substantially generating oxidative degradation. Recent work has shown that in recently irradiated material [8], gamma irradiation in inert packages produces lower wear than gamma irradiation in air. In addition, it has been claimed that gamma irradiation with vacuum and inert packaging has lower wear than E_tO sterilized material [9, 10]. In a further study, the difference between recently irradiated and non-irradiated material was found to be dependent on the duration of the tests and on the femoral head roughness

*Author to whom all correspondence should be addressed.

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[11]. However, as the degradation of polyethylene increases with time after sterilization comparison of the different sterilization methods are of limited clinical value unless they introduce real time [7] or accelerated ageing [6]. Blunn and Bell compared polyethylene that had been gamma irradiated in air and material that had been gamma irradiated in an inert atmosphere and subsequently stabilized [12], after both materials had undergone accelerated ageing. This showed a marked reduction in wear with the stabilized material. However, the stabilized material did show signs of degradation after ageing.

In this study we compare the wear of UHMWPE using a new sterilization procedure, gas plasma [13], that does not use irradiation, to the conventional method of gamma irradiation in air, for both non-aged and accelerated aged materials, using untreated UHMWPE as a control.

2. Materials and methods

Standard GUR415 ram extruded bar was used for the study (Polyhi Solidur processed the bar with GUR415 powder supplied by Hoescht). All specimens were taken from the same bar of material. The material was tested in five forms: non-sterile (N); sterilized with gamma irradiation in air with 2.5 MRads of irradiation (I); sterilized with gamma irradiation and accelerated aged (IA); sterilized with gas plasma (GP); and sterilized with gas plasma and accelerated aged (GPA). The gas plasma sterilization process [13] has been described previously and is currently being introduced into clinical practice by DePuy International. The accelerated artificial ageing process involves storage at 70 °C for 14 days under pure oxygen [14], which is believed to simulate approximately 4–5 years natural ageing. McKellop *et al.* [6] have recently shown that this ageing produces a similar oxidative level to 4 years *in vivo*.

The wear pins were prepared from the GUR415 bar cut with the axial direction of the pin parallel to the direction of the bar. Six pins were manufactured for each of the five processes to be studied. The wear surfaces of the pins were microtomed to remove residual strain from machining. The pins were then sterilized by either gamma irradiation or gas plasma and, where appropriate, accelerated aged. The pins were then soaked for more than 1 month prior to the test. In all cases the wear test started within 2 months of the sterilization procedure and lasted for no more than a further two months. The effect of the ageing or oxidation process on the material was studied on the wear pins after the test using Fourier transform infrared technique FTIR [15]. The areas under the carbonyl peaks (ketone, acid and ester) were calculated and normalized for the sample thickness, as calculated from the intensity of a reference peak. The carbonyl area per mil, is therefore a measurement of the concentration of the oxidized groups. The FTIR was carried out on wear pins which had been gamma irradiated in air and gas plasma sterilized after accelerated ageing, both on a worn surface and an unworn surface.

Wear studies were carried out in a pin-on-plate reciprocating wear tester using methods described previously [16]. Essentially this consists of a constant load of 240 N producing a stress of approximately 10 to 12 MPa on a 5 mm diameter wear pin face. Bovine serum was used as a lubricant with 0.1% sodium azide as an antibacteriological agent, and wear of the polymer pins was determined by gravimetric measurements. Control pins were used to compensate for moisture uptake. Lapped stainless steel counterfaces were used in all tests with a surface roughness R_a in the range 0.01 to 0.015 μm. The surfaces remained unchanged throughout the test. Tests were carried out for wear distances greater than 200 km with wear measurements being taken at approximately 50 km intervals. The incremental change in wear volume was used to determine an incremental wear factor. Wear factor is defined as wear volume divided by load and sliding distance. Between 17 and 24 wear measurements were made for each of the material types. Two configurations were used for the tests. For the control material, tests were run out up to 400 km with three pins of the material as the wear factor did not alter substantially between pins, or through the test. This generated 24 data points for the incremental wear factor. For the sterilized and accelerated aged material, the wear rates could potentially have changed between pins due to variation in the oxidation or sterilization and also with depth of wear, hence six pins were tested in each material for approximately 200 km sliding distance, hence producing between 17 and 24 measurements of the incremental wear rate for each material.

For each material group of pins, the mean and standard error of the wear factors were calculated and analysis of variance used to establish statistical significance of the differences between the mean incremental wear factors. This method of wear testing has been used extensively in the past and has been successful in identifying some of the key tribological variables that influence clinical wear, such as femoral head counterface roughness, third-body damage to the counterface, contact stress levels and oxidative degradation of the polymer following real-time ageing. While it does not predict absolute clinical wear rates, it can be used effectively in comparative tests to study the effect of important tribological variables. The repeatability of the wear measurement is good, typically one standard error on the mean is about 10% of the mean wear rate, indicating that a difference in the mean wear rate of the materials that are greater than 25%, can easily be differentiated within 95% confidence limits.

3. Results and discussion

Fig. 1 shows the average oxidation versus depth profile for the wear pins which had been gamma irradiated in air and accelerated aged, and pins that had been gas plasma sterilized and accelerated aged. The carbonyl area per mil was much greater for the pins irradiated in air than the pins sterilized by gas plasma indicating much higher levels of oxidative degradation. The magnitude and profile of oxidation for the

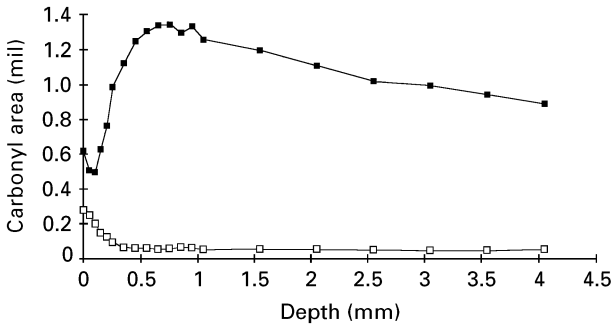

Figure 1 Oxidation profiles determined by FTIR for the irradiated aged (IA, ■) and gas plasma and aged (GPA, □) pins.

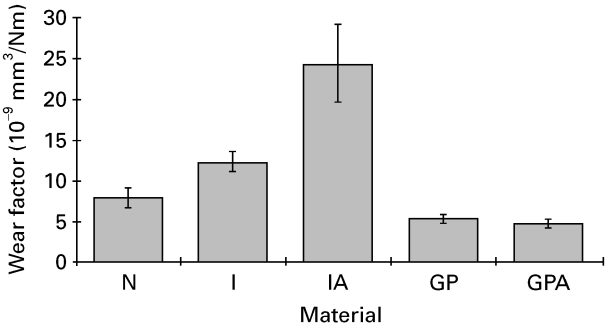

Figure 2 Mean and standard errors of the incremental wear factors for the five different materials.

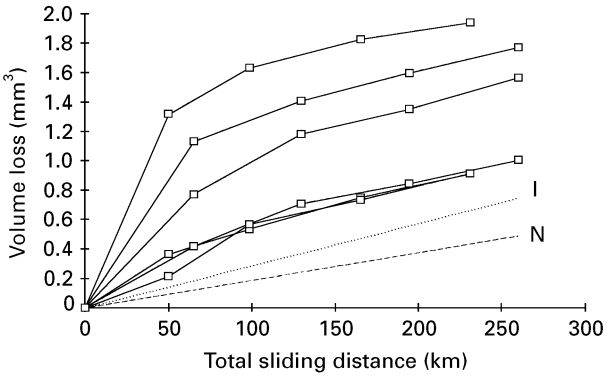

Figure 3 The mean wear volumes for the non-irradiated (N, ----) and irradiated (I, -----) materials compared to the individual wear volumes for the irradiated and aged (IA, –□–) pins.

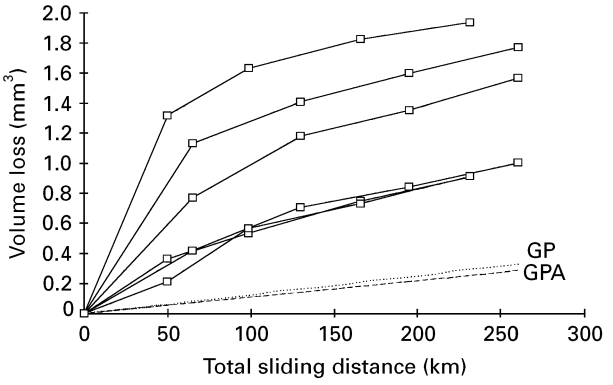

Figure 4 The mean wear volumes for the gas plasma (GP, ...) and gas plasma and aged (GPA, -----) pins compared to the wear volume for the individual irradiated and aged (IA, –□–) pins.

irradiated in air material is similar to that which has been reported previously. The wear test took place at the surface of the pins, removing approximately 100 μm. Although the carbonyl area in the gamma irradiated pin is lower at this depth than further into the material, the level of oxidation at the surface is still substantially higher than for the gas plasma sterilized material.

Fig. 2 summarizes the mean ± SE of the incremental wear factors for all five materials. The control, non-sterile (N), gas plasma (GP) and gas plasma aged (GPA) all showed similar low wear rates, indicating that neither the gas plasma treatment, nor the gas plasma treatment followed by ageing had a significant effect on the wear properties of the material. Irradiation in air produced a 50% increase in wear rate compared to the non-irradiated material and this difference was statistically significant at the 95% confidence level. This difference between non-treated (N) and irradiated in air and tested less than three months after irradiation (I), agreed well with our previous data for similar materials in a pin on disc test [7]. There was a highly significant threefold increase in the wear rate of the gamma irradiated aged material (IA) compared to the non-sterile (N), gas plasma sterilized (GP) and gas plasma and aged (GPA) material, indicating a very clear increase in wear associated with the oxidative degradation following irradiation and accelerated ageing in air, shown in Fig. 1. This result agrees well with our previously reported results of a threefold increase in wear associated with ageing for five years on the shelf following gamma irradiation in air [7].

Fig. 3 shows in more detail the wear volume as a function of sliding distance for the non-sterile N, I and IA materials. As there was little difference between the pins and little change to the wear rate throughout the test, only the average wear rates are shown for the N and I materials. In contrast, there was a variation in the wear rate of the aged gamma irradiated material, both between the six pins and throughout the test. Hence the individual wear rates for the six pins are presented for the IA material. In addition to the mean wear rate of the IA material being greater than the N and I materials, each of the individual pins also had a greater wear rate. The wear rate of the IA material was found to be greater in the initial part of the test and slightly lower after the first measurement. Analysis of the wear for the sliding distance 50 to 250 km gave a wear factor of $14.9 \pm 1.6 \times 10^{-9}$ mm^3/Nm which was two-fold higher than the control N material.

Fig. 4 also shows the wear of the irradiated and aged IA pins as a function of sliding distance compared to the mean wear rates for the gas plasma (GP) and gas plasma aged (GPA) material. There was no difference between the GP and GPA material with both having a constant low linear wear rate throughout the test; again for clarity, only the mean wear rates are shown. All the irradiated and aged pins had higher wear rates than the GP and GPA material, and the

wear rate of the IA material in the second part of the test was two times greater than the GP and GPA rates.

There is considerable interest and debate about relative wear rates of materials that have been processed by different sterilization routes. As we are clearly interested in long-term wear rates and effects of long-term degradation, studies that include either real-time ageing [7] or accelerated ageing [12] will prove to be the most revealing and useful. This study, using accelerated ageing, our previous study of real-time ageing [7] and the work of Blunn and Bell using accelerated ageing [12], all show marked adverse effects (between three and seven times, increased wear rates) with aged polyethylene after it has been irradiated in air. In contrast, neither of the FTIR results or the wear data show any degradation or increase in wear for the polyethylene following gas plasma sterilization and ageing. Previous studies of mechanical properties and fatigue resistance also show that there is no degradation of the material properties of polyethylene following gas plasma sterilization [14].

There remains considerable debate regarding the most appropriate method of sterilization of polyethylenes. In particular, future discussions will compare systems that retain the basic properties of non-sterilized polyethylene and avoid degradation, such as gas plasma or ethylene oxide sterilization, and systems that continue to use irradiation and alternative processing and storage routes to produce crosslinking and reduce, but do not entirely eliminate, oxidative degradation. Future studies using accelerated aged or real-time ageing specimens may shed further light on the relevant benefits of these two systems, and the results may well prove contradictory when tested in different configurations or conditions.

However, it is important not to lose sight of the benefits that have now been demonstrated by moving to alternative sterilization methods such as gas plasma instead of gamma irradiation in air, where studies with aged specimens show a threefold reduction in wear rates and predict a marked reduction in clinical wear rate. This may well have a considerable benefit in reducing the incidence or delaying the onset of wear debris induced osteolysis *in vivo*.

4. Conclusions

- Irradiation in air followed by a short period of real-time ageing produced a 50% increase in wear.
- Accelerated ageing of material irradiated in air produced a marked oxidative degradation and a threefold increase in wear. This was consistent with material which had been aged for 5 years on the shelf following gamma irradiation in air.
- Gas plasma sterilized material did not degrade following sterilization, nor did it degrade following accelerated ageing, and the wear of the sterilized gas plasma (GP) and the gas plasma and aged material (GPA) were the same as the non-sterile material (N).

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