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The effect of accelerated aging on the wear of UHMWPE

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Oxidative degradation of UHMWPE has been found to be a cause of elevated wear rate of the polymer in total joint replacement leading to failure of these devices. In order to evaluate long term stability of polymers, various accelerated aging methods have been developed. In this study, wear rates of shelf aged UHMWPE and ''accelerated aged'' UHMWPE were compared using a multi-directional pin-on-plate wear test machine in order to evaluate the effect of the accelerated aging on wear. Wear factors of the aged materials were found to depend on their density, which is a measure of oxidation level. Finally, accelerated aging was calibrated against shelf aging in terms of wear rate.

Introduction

Total hip replacement is now a common orthopaedic procedure. It is said that around 800 000 joint replacements are implanted every year in the world with the majority being total hip replacements [1]. Many total hip replacements used these days consist of a metal femoral head and a ultra-high molecular weight polyethylene (UHMWPE) acetabular cup. These artificial joints can last over 20 years. However, aseptic loosening caused by adverse cellular reactions against UHMWPE wear debris is a major limitation to the lifetime of total hip replacements. Therefore, reduction of wear is one of the major research aims in this field.

Damage to the metal femoral head and degradation of the polymer cup have been identified as major causes of high wear rate of UHMWPE [2]. Metal femoral heads have been found to be damaged by third body particles such as bone and bone cement [3, 4]. Once the metal femoral head is damaged, asperities of the damaged head have been considered to become a cause of increased wear of UHMWPE [2, 5]. On the other hand, degradation of the polymer has been found to relate to the terminal product sterilization method. Gamma irradiation of the polymer components for sterilization has been carried out in the presence of oxygen for more than two decades. Gamma irradiation in air has been found to generate free radicals within the polymer, causing gradual oxidation of the material and eventually a deterioration in its wear resistance [2].

Alternative sterilization methods and improved materials have now been developed. Many of these materials have been introduced already in clinical use to address this long term aging problem [6]. The aim of this study was to assess the effect of accelerated aging on the wear of UHMWPE, which has been aged and not aged.

Materials and methods

The materials tested in this study are listed in Table I. UHMWPE grade GUR1050 (Perplas Medical Ltd.) was used as a control material. It was studied without any irridiation and following gamma irradiation at 25 kGy in air. Two shelf aged UHMWPE materials with different periods of aging were prepared. UHMWPE grade GUR1050, which had been irradiated at 25 kGy in air was aged on the shelf for three years. UHMWPE grade 412, which had been irradiated at 25 kGy in air was aged on the shelf for five years. The difference of the grade was due to availability of shelf aged materials. Two ''accelerated aged'' materials were prepared to match the shelf aged materials. UHMWPE grade GUR1050, which had been gamma irradiated at 25 kGy in air was ''accelerated aged'' for eight days. UHMWPE grade GUR412, which had been gamma irradiated at 25kGy in air was ''accelerated aged'' for 14 days. Marathon™ material (DePuy International) was also tested as it represents one of recently introduced stabilized cross-linked materials. The Marathon™ material used was produced from UHMWPE grade GUR1050, which had been gamma irradiated at 50 kGy in an inert atmosphere followed by a melt stabilization heat treatment. Marathon™ was tested in the as-received condition and following accelerated aging for 14 days prior to wear testing. The accelerated aging process was carried out

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TABLE I UHMWPE materials tested in this study

Material	Irradiation		Aging
GUR1050	—	—	—
GUR1050	25 kGy	in air	—
GUR1050	25 kGy	in air	3 years shelf aged
GUR1050	25 kGy	in air	8 days accelerated aged
GUR412	25 kGy	in air	5 years shelf aged
GUR412	25 kGy	in air	14 days accelerated aged
GUR1050	50 kGy	in vacuum	—*
GUR1050	50 kGy	in vacuum	14 days accelerated aged*

*Marathon material (Heat treated after gamma irradiation).

TABLE II Multi-directional pin-on-plate test conditions

Load/Contact Stress	180 N/3.58 MPa
Stroke/Rotation	± 20 mm/ ± 40 °
Lubricant	25% bovine serum
Duration/Total distance	1 week/15 km
Smooth counterface	Stainless steel, Ra < 0.025 μm
Scratched counterface	Stainless steel, Rp $= 1$–2 μm

according to ASTM standard method B, in pure oxygen bomb at 5 Atm at temperature of 70 °C for either eight days or 14 days [7, 14].

Wear testing was conducted using a multi-directional pin-on-plate wear test machine. The applied load was 180 N, which corresponded to a nominal contact stress of 3.58 MPa with 8 mm diameter of the contact surface of the wear test pins. Multi-directional motion was introduced by means of a simple rack and pinion gear mechanism [8], as this has been reported to replicate the kinematic conditions and wear mechanism found *in vivo* [9]. The stroke length was ± 20 mm while rotation was ± 40°. Six wear pins per material were tested and tests were carried out for over one million cycles. Bovine serum diluted to 25% with 0.01% sodium azide was used as a lubricant. Two kinds of counterface were used. One was a smooth stainless steel counterface polished to surface roughness of less than 0.025 μm, reproducing an undamaged metal femoral head. The other was a scratched stainless steel counterface representing a damaged metal femoral head. Scratched counterface was prepared by creating scratches perpendicular to the wear track at intervals of 5 mm on smooth stainless plate using a diamond stylus. Heights of the asperities (Rp) were controlled between 1–2 μm [10]. Wear test conditions and surface characteristics of the counterfaces are summarized in Table II.

Wear pin specimens were soaked in deionized water for more than 250 h prior to testing in order to stabilize water content. Control pins were prepared in the same manner as wear test pins and soaked in the lubricant during the wear testing. Wear pins and control pins were weighed before and after wear testing to the accuracy of 1 μg. The weight loss was then converted into volume loss. Wear results were compared using wear factor *K*, which was calculated by following equation,

$$K = \frac{W}{L\,x}$$

where K, W, L and x are wear factor (mm^3/Nm), volume loss (mm^3), load (N) and sliding distance (m) respectively. The Student's *t* test was carried out to determine the statistical significance of the difference between wear factors.

Measurement of density was carried out using an ethanol-water density gradient column. Specimens were cut into slices and the density at various depths from the wear surface was measured. The density at the wear surface was compared to the wear rates in this study.

Results

Fig. 1 shows the wear factors for the polyethylene pins on the smooth counterfaces. Fig. 2 shows the wear factors on the scratched counterfaces. These graphs showed very similar trends, but the scratched counterfaces produced 1.7–4.4 times higher wear factors for each material than

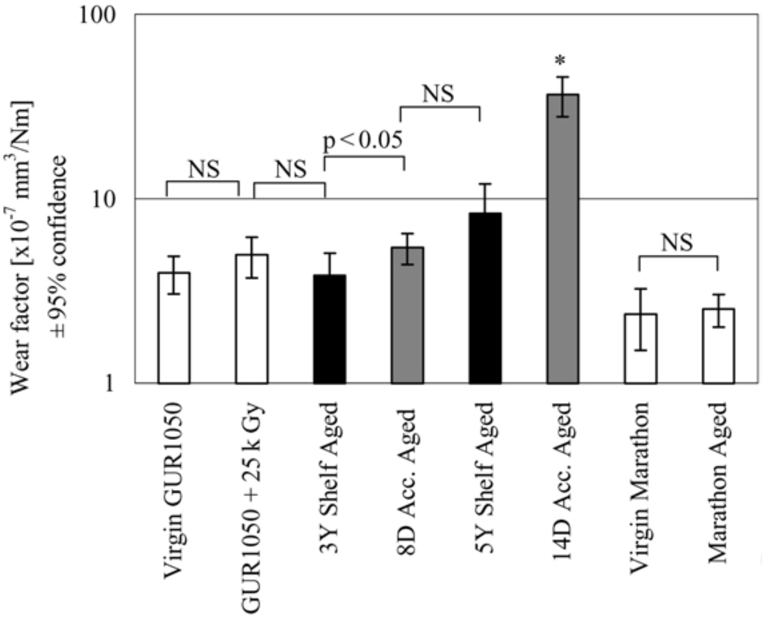

Figure 1 Wear factors of tested materials on smooth counterfaces.

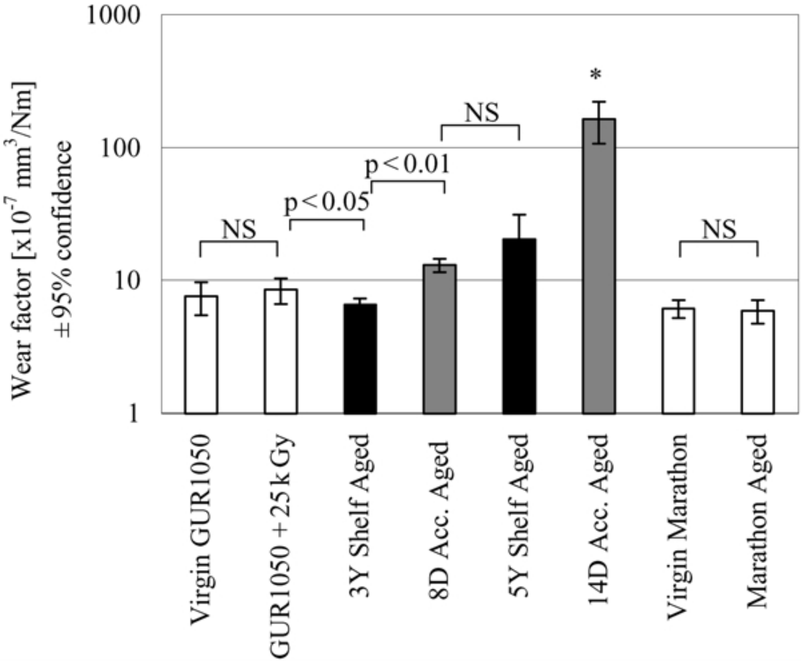

Figure 2 Wear factors of tested materials on scratched counterfaces.

smooth counterfaces. This elevation of wear factor on scratched counterfaces compared to smooth counterfaces was consistent with previous studies [10].

The non-irradiated UHMWPE had wear factors of $3.96 \pm 0.92 \times 10^{-7}$ (mm^3/Nm) (mean ± 95% confidence limit) on smooth counterfaces and $7.55 \pm 2.10 \times 10^{-7}$ (mm^3/Nm) on scratched counterfaces. Gamma irradiated UHMWPE had wear factors of $4.96 \pm 1.24 \times 10^{-7}$ (mm^3/Nm) on smooth counterfaces and $8.50 \pm 1.87 \times 10^{-7}$ (mm^3/Nm) on scratched counterfaces. No difference in wear factor was found between non-irradiated UHMWPE and gamma irradiated UHMWPE on both counterfaces.

Eight days ‘‘accelerated aged’’ material had significantly higher wear factors of $5.43 \pm 1.05 \times 10^{-7}$ (mm^3/Nm) and $1.30 \pm 0.15 \times 10^{-6}$ (mm^3/Nm) on each counterface than three years’ shelf-aged material, which had wear factors of $3.84 \pm 1.21 \times 10^{-7}$ (mm^3/Nm) and $6.56 \pm 0.71 \times 10^{-6}$ (mm^3/Nm) on smooth counterfaces and scratched counterfaces respectively. Five years’ shelf aged material had wear factors of $8.30 \pm 3.70 \times 10^{-7}$ (mm^3/Nm) and $2.04 \pm 1.07 \times 10^{-6}$ (mm^3/Nm) on smooth counterfaces and scratched counterfaces respectively. These values were higher than for the eight days ‘‘accelerated aged’’ material on both smooth and scratched counterfaces. They were, however, not statistically significant. Fourteen days ‘‘accelerated aged’’ materials showed the highest wear factors of $3.68 \pm 0.91 \times 10^{-6}$ (mm^3/Nm) and $1.64 \pm 0.57 \times 10^{-5}$ (mm^3/Nm) on smooth and scratched counterfaces respectively. The differences between 14 days ‘‘accelerated aged’’ materials and other materials were statistically significant in all cases on both counterfaces ($p < 0.01$). Non aged Marathon™ material had wear factors of $2.37 \pm 0.86 \times 10^{-7}$ (mm^3/Nm) and $6.13 \pm 0.97 \times 10^{-7}$ (mm^3/Nm) on smooth and scratched counterfaces respectively. Fourteen days ‘‘accelerated aged’’ Marathon™ had wear factors of $2.52 \pm 0.50 \times 10^{-7}$ (mm^3/Nm) and $5.87 \pm 1.18 \times 10^{-7}$ (mm^3/Nm) on smooth and scratched counterfaces respectively. There was no significant difference in wear factors between non-aged Marathon™ and ‘‘accelerated aged’’ Marathon™.

The relationship between wear factors of gamma irradiated UHMWPE materials and their density at the surface is shown in Fig. 3 for smooth counterfaces and in Fig. 4 for scratched counterfaces. A very high correlation coefficient of 0.90 and 0.92 was found between the wear rate and density on both the smooth counterfaces and the scratched counterfaces respectively. These results strongly support the differences in wear factors found in wear testing. In some cases, differences in wear factors between materials were not statistically significant. However, from the strong correlation with density, it was considered that these materials had been oxidized at different levels, and therefore, they had different wear factors.

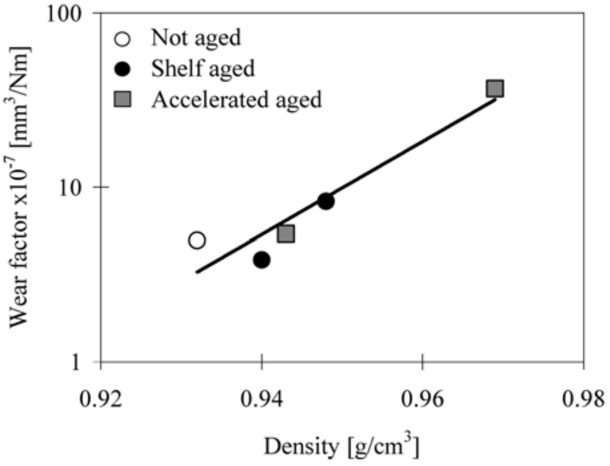

Figure 3 Correlation between surface density and wear factors for UHMWPE against smooth counterfaces.

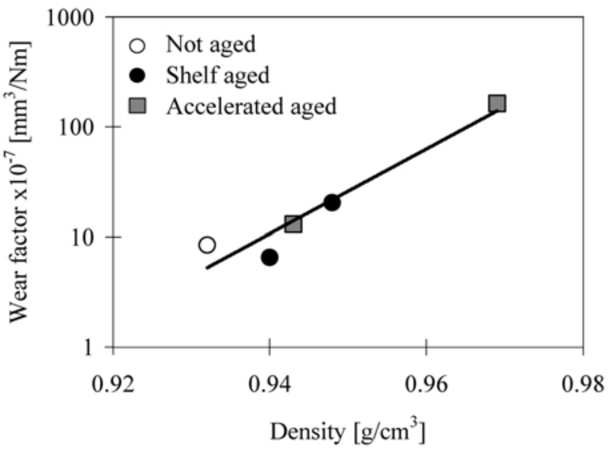

Figure 4 Correlation between surface density and wear factors for UHMWPE against scratched counterfaces.

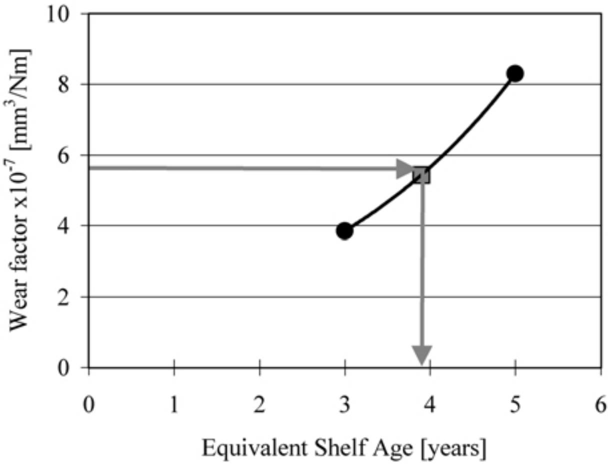

Figure 5 Estimation of equivalent shelf age for eight days accelerated aging.

Discussion

Both accelerated and real time shelf aging produced increases in wear rate on both smooth and rough counterfaces. The exception to this was the three years' shelf aging where additional recombination of free radicals may have increased wear resistance. A strong correlation was found both on smooth counterface and on scratched counterface between wear factor and density. On the smooth counterface, it is considered that most of the deformation within the polymer is elastic and therefore surface asperity fatigue wear is dominant [11]. Conversely, on scratched counterfaces, polymers deform plastically [12, 13], therefore, abrasive wear is considered to be dominant. Hence, different wear mechanisms are likely to be dominant on smooth and scratched counterfaces, and hence different wear properties are considered to determine the wear factor. Fatigue resistance is considered to be important on smooth counterfaces while some mechanical properties such as hardness, fracture stress and elongation are considered to be important on scratched counterfaces [13]. Thus, shelf aging and oxidation reduced both the fatigue wear resistance and the abrasive wear resistance.

One aim of this study was to compare accelerated and real time aging in terms of wear factor of gamma irradiation in air materials. An equivalent aging time in years for eight days accelerated aging was interpolated from the data for the three and five year shelf aged materials, as shown in Fig. 5. The eight day accelerated aging was estimated to be equivalent to 3.9 years of shelf-aging in this study. It should be noted, however, that significant inter-institutional variability in accelerated aging has been reported previously [14] so care should be taken in extending this to accelerated aging in other institutions.

No difference was found between non aged Marathon™ and ''accelerated aged'' Marathon™ both on smooth and on scratched counterfaces. Marathon™ did not show any degradation due to accelerated aging in terms of wear. This result proved the Marathon™ UHMWPE is resistant to oxidative degradation.

Conclusion

1. Gamma irradiation in air showed no immediate effect on wear.
2. Marathon™, a new stabilized polyethylene, showed no deterioration by accelerated aging.
3. Wear rate was dependent on oxidative state and density for UHMWPE gamma irradiated in air.
4. The accelerated aging has been calibrated against shelf aging in terms of wear rate. Eight days accelerated aging was found to be equivalent to 3.9 years' shelf aging for materials gamma irradiated in air.

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