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The effects of gamma radiation sterilization and ageing on the structure and morphology of medical grade ultra high molecular weight polyethylene

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Ultra high molecular weight polyethylene (UHMWPE) that had been sterilized with 25 kGy of gamma radiation and non-sterile material processed from the same batch were studied following five years of ageing in air. Differential scanning calorimetry, small angle X-ray scattering, transmission electron microscopy, Fourier transform infra-red spectroscopy and density gradient column measurements were used to characterize the changes in structure and morphology of the UHMWPE as a result of sterilization and shelf ageing. Significant changes were observed. The UHMWPE oxidized and increased in crystallinity as well as density, with chain scission the dominant response to irradiation. The applicability of the results of this study to the evolution of mechanical properties and structural integrity of medical grade UHMWPE for total joint replacement is addressed. Published by Elsevier Science Ltd.

(Keywords: gamma irradiation sterilization; ageing; UHMWPE)

INTRODUCTION

The superior wear, fatigue, and fracture properties of ultra high molecular weight polyethylene (UHMWPE) have made it the material of choice for the last 30 years for the replacement of damaged or diseased articulating cartilage in total joint replacement surgery. The origin of these properties lies in the polymer's molecular weight, which is on the order of 3–6 million (compared to high density polyethylene, which is on the order of 50 000–200 000). However, the orthopaedic material is not without limitations. Over time, the cyclic nature of the contact stresses at the articulating surface of the artificial joint (the UHMWPE articulates against a polished alloy, such as stainless steel or titanium, see *Figure 1*) can lead to loosening of the implant, pitting and delamination of the polymer, and the formation of polyethylene debris particles[1]. It is the generation of polyethylene debris particles that can be most damaging as they can lead to osteolysis and bone resorption[2], which can result in further loosening and degradation of the component.

One of the causes for the degradation of UHMWPE in artificial joints may lie in the sterilization treatment employed before surgery. As with all biomaterials, UHMWPE must be sterilized before it can be implanted in the body and the current standard practice in the medical community is to sterilize the orthopaedic polymer by γ-radiation in an ambient air environment. This is typically accomplished with 25 kGy of ^{60}Co γ-radiation.

It is well known that γ-radiation introduces free radicals into polyolefins[3]. These free radicals can in turn lead to cross-linking and chain scission of the polymer. The dominance of one of these mechanisms over the other is highly dependent upon the sterilization environment. Chain scission is the dominant mechanism when the sterilization is performed in air while cross-linking appears to be the principal mechanism when the material is irradiated in nitrogen[4]. The chain scission mechanism is a time-dependent process and is further complicated by the uptake of oxygen. Oxygen is extremely reactive with the free radicals produced by irradiation. Peroxides form, which in turn can break down and lead to further radical production so that the total number of free radicals generated and total extent of chain scission are greatly increased. Studies have indicated that oxygen uptake in UHMWPE increases upon irradiation and continues to do so as the material ages[4–6].

The scission process is especially important to the structural integrity of the polymer. Over time, as long

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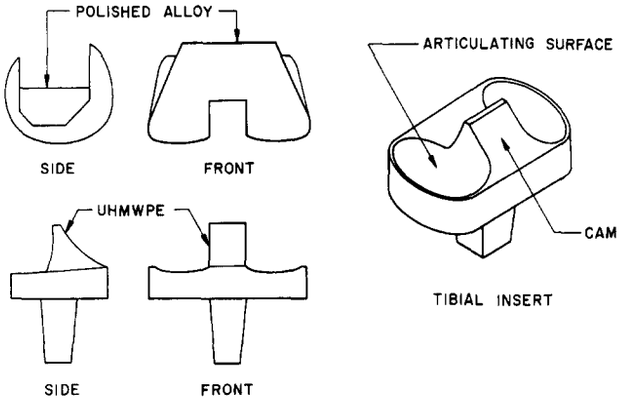

Figure 1 A schematic of a typical total joint replacement and the tibial insert used for this study

chains are broken, the resultant shorter chains are able to pack together more easily, leading to a lower molecular weight material with a higher crystallinity and density. Essentially, the polymer transforms into a high density polyethylene structure. This evolution is further complicated by oxidative degradation, which can stiffen the molecular chains and lead to embrittlement. These structural changes are detrimental to the integrity and performance of the polymer component as the material continually evolves into a structure with reduced fatigue and wear resistance. This structural evolution may be responsible for the limited life of the polymer component, currently 15 years or less.

This paper seeks to examine the effects of the γ-radiation sterilization treatment on the structure and morphology of UHMWPE after additional ageing 'on the shelf' for 5 years. Emphasis is given to the evolution of crystallinity and density, oxygen uptake, and structural rearrangements within the polymer. To study the effects of irradiation and ageing, both non-sterile and sterile UHMWPE manufactured from the same batch are investigated.

EXPERIMENTAL

Materials

Samples of medical grade UHMWPE were supplied by the Hospital for Special Surgery in NY, NY. All material in this study was Hostalen GUR 415 (Hoechst Celanese, Houston, TX), compression-moulded by Westlake Plastics (Lenni, PA) in 1989. Some of the physical properties for UHMWPE in the unaged and non-sterile condition are given in *Table 1*. UHMWPE was supplied in two forms: non-sterile compression-moulded sheet, and sterile tibial inserts (a schematic of the tibial insert is shown in *Figure 1*) which had been machined from a compression-moulded sheet. The tibial components had been sterilized in air using 25 kGy of ^{60}Co gamma radiation. Radiation sterilization was performed by a commercial vendor (Isomedix Operations, Whippany, NJ) at a dose rate of 0.0015 MGy h^{-1}. All material had shelf-aged in air for 5 years. The tibial components were clinically relevant in that they could have readily been implanted in a patient rather than subjected to this study.

Table 1 Physical properties of GUR 415 medical grade UHMWPE (Westlake Plastics, Lenni, PA)

Property	Value
Molecular weight	>3 million
Density	0.931 g cm^{-3}
Ultimate tensile strength	6130 psi
Yield strength (0.2% offset)	2880 psi
Elongation at break (moulded)	350%
IZOD impact strength	No break
Deformation under load	0.4%
Shore 'D' hardness	67

Differential scanning calorimetry

Differential scanning calorimetry (d.s.c.) was performed on a Perkin Elmer DSC-7 using a heating rate of 5°C min^{-1}. Sample weight ranged from 2.9 mg to 3.1 mg. For the irradiated tibial component, specimens were taken as a function of thickness (representing a profile of radiation dose, with the articulating surface of the component being exposed to the largest amount of radiation). Seven different samples were investigated for each thickness of the irradiated component as well as for the unirradiated material. Sample crystallinity was determined by comparing the heat of fusion for the sample to the heat of fusion for a fully crystalline polyethylene material (288 J g^{-1})[7].

Small angle X-ray scattering

Small angle X-ray scattering (SAXS) was performed at Oak Ridge National Laboratory[8]. Specimens (both irradiated and non-sterile) were discs with a diameter of 1 cm and a thickness of 3 mm. A 40 kV, 100 mA rotating anode Cu Kα X-ray source was used with a sample-to-detector distance of 5.119 m. Data were analysed with particular attention paid to changes in average spacing between crystalline regions as well as changes in electron densities in both the crystalline and amorphous regions (possibly indicative of a change in elemental composition).

Transmission electron microscopy

Specimens were prepared for transmission electron microscopy (TEM) by staining the UHMWPE (in both sterile and non-sterile form) with chlorosulfonic acid (99% conc.) at 60°C for 9 h at which time the material appeared black in colour. The purpose of the chlorosulfonic acid was to cross-link and stabilize the amorphous regions of the polymer[9]. This staining was followed by an acetone rinse (at 0°C) followed by distilled water. The stained polymers were then dried at 60°C for 30 min. Next, the samples were embedded in epoxy resin and cured for 24 h at 60°C. Using a diamond knife, the specimens were ultramicrotomed to a nominal thickness of 65 nm. After being placed on carbon coated substrates, the specimens were post stained in 2% uranyl acetate solution for 3 h in order to enhance contrast in the TEM. Characterization of polymer morphology was performed using a JEOL 100CX operating at 80 kV.

Fourier transform infra-red spectroscopy

Fourier transform infra-red spectroscopy (*FT*i.r.) measurements were performed on a Bruker IFS 66V spectrometer in transmission mode. A globar source was used along with a KBr beam splitter and MCT detector. Samples (one for each of the irradiated and unirradiated

polymers) were discs with a diameter of 1 cm and a thickness of 1 mm. Oxidation was characterized through analysis of the ketone carbonyl peak at 1720 cm^{-1}.

Density gradient column measurements

Density was measured on a Techne Density Gradient Column (DGC) according to ASTM D1505-85 standard[10] at the Hospital for Special Surgery[11]. Samples were 4.5 mm diameter cores, microtomed into 0.2 mm thick sections. For the sterilized tibial insert, specimens were taken as a function of thickness in the cam section (see *Figure 1*) of the component (representing a profile of sterilization dose). Two samples were each investigated for thickness of the irradiated component as well as for the unirradiated material. Sample density was determined by submerging the specimens in a density gradient column of isopropanol and distilled water containing calibrated density floats.

RESULTS

Differential scanning calorimetry

The value for the average crystallinity obtained by d.s.c. of four different unirradiated samples was 47.5% ± 3.3%. *Figure 2* shows a plot of heat flow *versus* temperature for an unirradiated sample, the heat of fusion is obtained from the area under the curve normalized by a fully crystalline polyethylene heat of fusion to give the percent crystallinity of the sample. An average value (averaged over five samples) of 57.9% ± 1.3% was obtained for the crystallinity at the articulating surface of the irradiated tibial component. Crystallinity therefore increases upon irradiation and subsequent ageing.

Small angle X-ray scattering

The SAXS results are shown in *Figure 3*, which is a plot of relative intensity ($Q^2I(Q)$) *versus* Q, where Q is the invariant. It can be seen that irradiation causes both a decrease in intensity and a shift in peak position to a higher Q. This is indicative of a decrease between the centres of the crystalline regions, d, which was calculated using $Q = 2\pi/d$ to be approximately 620 Å.

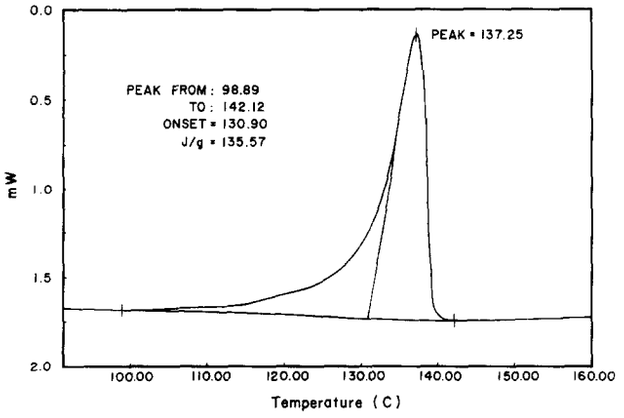

Figure 2 A plot of heat flow *versus* temperature for a non-sterile sample obtained by d.s.c. The crystallinity (47.0%) of this specimen can be obtained by dividing its heat of fusion (135.57 J g^{-1}) by the heat of fusion for a purely crystalline polyethylene material (288 J g^{-1})

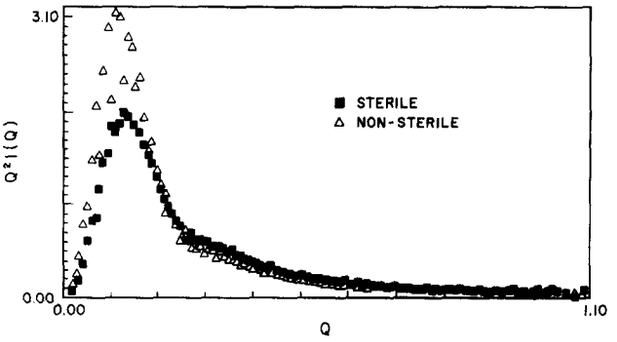

Figure 3 A plot of relative intensity, $Q^2I(Q)$, *versus* the invariant Q (nm^{-1}) obtained by SAXS for both the irradiated and unirradiated specimens. Changes in peak intensity and peak position occur subsequent to irradiation and ageing

Transmission electron microscopy

TEM micrographs are shown of both the unirradiated (*Figure 4a*) and the irradiated (*Figure 4b*) specimens. It can be seen that the lamellae thicken upon irradiation, and form a kinked morphology with a high degree of tortuousity, evident at a higher magnification (*Figure 4c*).

Fourier transform infra-red spectroscopy

Figure 5 shows spectra for both the unirradiated and irradiated samples. A dramatic increase can be seen in the band at 1720 cm^{-1} in the sterilized specimen. This band corresponds to the stretching of the ketonic carbonyl group. In addition, slight increases in the bands at 1898 cm^{-1} and 2002 cm^{-1} appear after irradiation, and these are the crystalline bands for polyethylene[11].

Density gradient column measurements

The density of the non-irradiated UHMWPE was constant into the bulk of the solid with a density of 0.933 g ml^{-1} ± 0.0002 g ml^{-1}. For the sterilized tibial insert, an increase in density was observed up to 3.5 mm depth from the articulating surface. Samples taken from the articulating surface had a density of 0.96 g ml^{-1} ± 0.0002 g ml^{-1}. Hence, density increases 3.0% due to irradiation and subsequent ageing. These findings are consistent with recent studies by Rimnac *et al.*[12].

DISCUSSION

Together these results clearly indicate that crystallinity and density increase in UHMWPE after irradiation in air and subsequent shelf-ageing for 5 years. Evidence appears in each of the characterization techniques used in this study. SAXS data show a shift in peak position to higher Q, indicative of a decreasing distance between the centres of the crystalline regions of the polymer. This finding is consistent with a widening of crystalline regions and a concomitant shrinking of amorphous regions, also corroborated by the TEM morphology studies, which showed an increase in lamellae thickness upon irradiation. *FT*i.r. data confirm a slight increase in the two crystalline bands in the irradiated specimen relative to the non-sterile sample. Finally, d.s.c. and DGC not only echoed these findings but also provided a

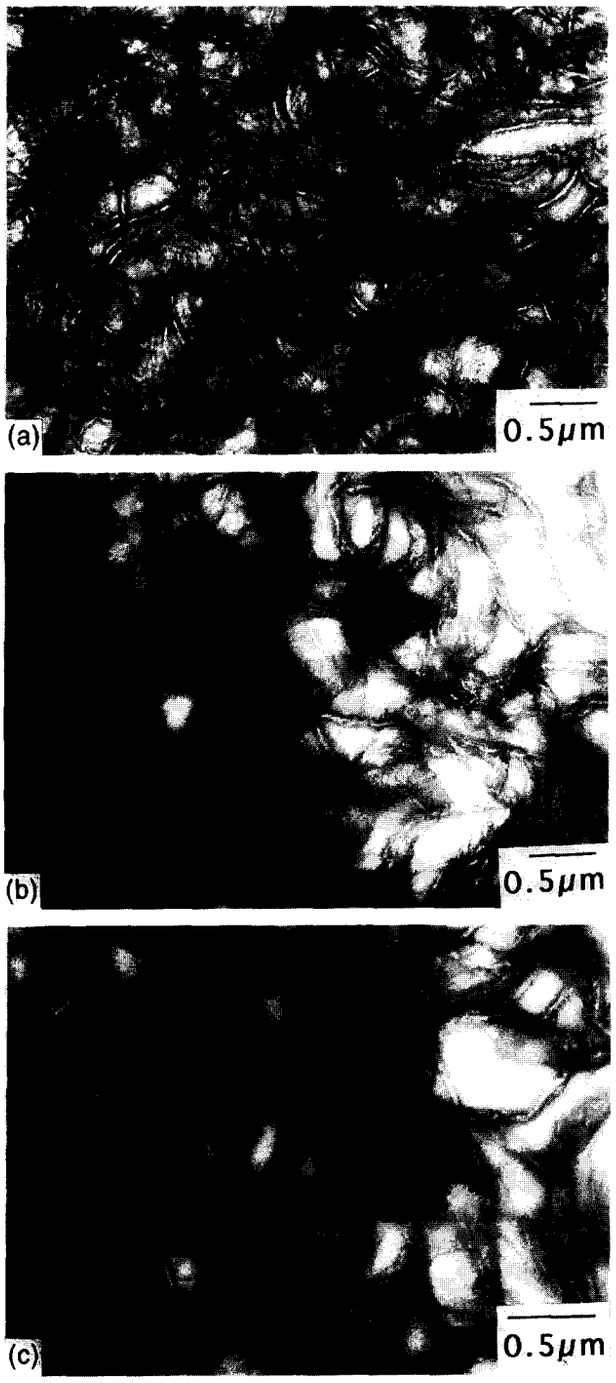

Figure 4 TEM micrographs of (a) unirradiated specimen, (b) irradiated specimen and (c) the tortuosity of the lamellae upon sterilization and ageing. Note that the lamellae appear to thicken and kink upon irradiation and ageing

quantitative measurement of the change in crystallinity and density, respectively.

Another effect of irradiation and subsequent ageing of UHMWPE is an increase in the oxygen uptake by the material[5–6,13]. As noted previously, there is a decrease in peak intensity for SAXS upon irradiation. In analysing SAXS data, intensity is given by the equation:

$$I = \varphi_c \varphi_a (\rho_a - \rho_c)^2 \quad (1)$$

where φ_c and φ_a are the volume fractions of the crystalline and amorphous regions, respectively, and ρ_a and ρ_c are the electron densities[14]. From the crystallinity

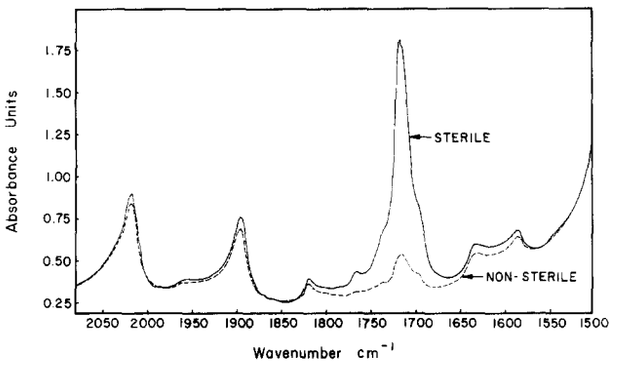

Figure 5 Spectra obtained by *FT*i.r. for both sterile and non-sterile UHMWPE. The ketone carbonyl band at 1720 cm^{-1} which is an indication of oxygen uptake increases dramatically as a result of irradiation and ageing

values obtained by d.s.c., it can be determined that although the individual values of φ_a and φ_c are changing significantly, their product ($\varphi_a \varphi_c$) remains relatively constant. Therefore, a change in electron density difference accounts for the decrease in peak intensity. One way in which this can be explained is by oxygen entering the amorphous region.

*FT*i.r. data confirm that oxygen is in fact entering the material. The peak at 1720 cm^{-1} corresponds to the ketone carbonyl band and is a measure of the amount of oxygen in the specimen. It can clearly be seen that oxygen content in the polymer increases as a result of irradiation and subsequent ageing.

The increases in crystallinity, density and oxygen content suggest that chain scission dominates the structural changes that result from irradiation and ageing. Previous studies have found similar increases in crystallinity after irradiation in air and have attributed them to a result of tie molecules being cut[4], allowing chains to arrange themselves more easily and pack together such that the crystallinity as well as the density rises. In addition, radiation in an ambient oxygen environment (as was done for this material) is known to enhance the occurrence of chain scission[4]. Oxygen is very reactive with free radicals produced by the irradiation process and this leads to reactions which then result in further chain scission[15]:

$$RO_2H,\ RO_2\cdot, R\cdot \rightarrow \text{scission} \quad (2)$$

It therefore appears that the structure and morphology of the UHMWPE evolves to a structure of higher crystallinity and density as a consequence of radiation sterilization and ageing. This in turn can be correlated with a decrease in the mechanical properties of the material. In fact, it has been shown in another study on these same materials[16], that the compression fatigue resistance and tensile fatigue resistance are degraded substantially by sterilization and subsequent ageing. In compression fatigue studies[16,17] it was found that crack saturation distance doubled in length for the sterilized UHMWPE in comparison to the non-sterile material. For tension fatigue studies[16], the rates of crack propagation were found to increase by two orders of magnitude for the same crack driving force for the irradiated UHMWPE as compared to the non-sterile polymer. Additionally, the effect of increasing density has been linked to higher elastic modulus of the polymer

and concomitant increased contact stresses at the articulating surface of total joint replacements, leading to enhanced wear rates[18]. Such degradation of fatigue and wear properties increases the likelihood for polymer damage and debris generation, and currently limits the life of the orthopedic components.

CONCLUSIONS

A significant change in the structure and morphology of UHMWPE occurs as a result of sterilization with 25 kGy ^{60}Co gamma radiation in air and subsequent shelf-ageing for 5 years. The UHMWPE evolves to a more crystalline and dense structure. Oxidation of the polymer subsequent to sterilization is evident from *FT*i.r. analyses. Together these results indicate that chain scission is the dominant mechanism in the polymer's response to irradiation. It is concluded that, though γ-irradiation is successfully employed in the sterilization of medical grade UHMWPE, its effects coupled with post irradiation ageing, cause structural changes that degrade the necessary mechanical properties and limit the useful life of the material for total joint replacements. Ongoing work is aimed at distinguishing degradation mechanisms associated with the sterilization process itself and post-sterilization ageing environments.

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