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Variation of mechanical properties and oxidation with radiation dose and source in highly crosslinked remelted UHMWPE

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ABSTRACT

Ultra-high molecular weight polyethylene (UHMWPE) is the current gold standard for bearing materials used in total joint arthroplasty. High-dose radiation is commonly used to crosslink UHMWPE, thereby improving its wear resistance. A subsequent remelting step eliminates trapped residual free radicals to promote oxidative stability on the shelf, and to prevent material degradation over the long term. Assessment of clinically retrieved, highly crosslinked UHMWPE devices shows signs of unanticipated oxidation occurring in vivo, despite the absence of free radicals prior to implantation. These findings warrant further investigation into possible factors impacting this phenomenon along with its clinical implications. The overall objective of this work is to quantify the influence of irradiation dose and source on UHMWPE's oxidative stability, along with the effects of oxidation on the ultimate mechanical properties, including strength, ductility, and toughness. The results showed a strong positive correlation between maximum oxidation and initial transvinylene content. Critical oxidation levels in the context of mechanical property loss were determined for e-beam and gamma treatments at various radiation doses. Further, it was shown that critical oxidation was more dependent on radiation dose and less dependent on source. If in vivo oxidation persists in these devices, this can potentially lead to mechanical failure (e.g. fatigue damage) as observed in terminally gamma-sterilized devices.

1. Introduction

Medical grade ultra-high molecular weight polyethylene (UHMWPE) is the current gold standard for joint bearing materials used in total joint arthroplasty (TJA). The use of this semicrystalline polymer in orthopedic applications is attributed to its outstanding physical and mechanical properties. Specifically, this includes chemical inertness, lubricity, abrasion resistance, impact resistance, wear resistance, and toughness.

Although TJA involving UHMWPE as a bearing surface has been one of the most successful procedures of the last century, the issue of wear has been an obstacle to the longevity of joint replacements. Wear debris can trigger a series of biological reactions leading to osteolysis, a condition resulting in long term resorption of the bone around the implant (Cooper et al., 1992; Harris, 1994; Jasty, 1993; Kovacik et al., 2000; Peters et al., 1992). Further, excessive wear can lead to substantial mechanical failure, in the form of fracture and dissociation (Lombardi et al., 1988; Stulberg et al., 1988; Wright et al., 1992), and to implant loosening attributed to biological response to debris (Peters et al., 1992; Santavirta et al., 1991).

Radiation crosslinking of UHMWPE significantly improves its wear resistance, as evidenced by in vivo clinical studies (Digas et al., 2007; Oonishi, 1995) and in vitro hip simulator studies (McKellop et al., 1999; Muratoglu et al., 2003). During irradiation, crosslinks are formed between polymer chains through homolytic cleavage of C-H and C-C bonds. However, ionizing radiation also produces free radicals randomly throughout UHMWPE as part of the crosslinking process. These long-lived species can react with oxygen, triggering a cyclic complex cascade of chemical reactions (Premnath et al., 1996). While free radical oxidation involves a number of possible pathways with different mechanisms and end products (Reinitz et al., 2014), the overall outcome includes polymer chain scissions which reduce the molecular weight, and various oxidative products such as hydroperoxides, ketones, alcohols, and carboxylic acids (Costa et al., 2009, 1998). Overall, this cascading oxidative reaction is responsible for progressive embrittlement of the material (Oral and Muratoglu, 2007). Oxidative degradation manifests in a reduction of wear resistance and mechanical properties (Bohl et al., 1999; Ries et al., 1996; Sutula et al., 1995).

Oxidation of UHMWPE is a serious concern as it limits the overall lifetime and success of the joint replacement. Hence, the elimination of

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free radicals in UHMWPE has been an important focus of orthopedic manufacturers ever since the industry's response to shelf storage oxidation occurring in gamma-in-air sterilized devices (Berry et al., 2012; Currier et al., 1997). In collaboration with materials research laboratories, device manufacturers have developed a variety of post-irradiation thermal treatments with the goal of promoting oxidative stability (Kurtz et al., 2003; McKellop et al., 1999; Muratoglu et al., 2001). Several manufacturers utilize a remelting step to eliminate free radicals from the crosslinking process and provide oxidation resistance (McKellop et al., 1999; Muratoglu et al., 2001; Oral and Muratoglu, 2007).

Retrieval analyses conducted by Currier et al. (2013, 2010) showed that despite the absence of free radicals (prior to implantation), highly crosslinked remelted acetabular liners and tibial inserts showed signs of oxidation occurring in vivo (Currier et al., 2013, 2010). The crosslinking radiation dose significantly impacted the material's oxidation potential. Additionally, the in vivo oxidation rate significantly correlated with transvinylene bond concentration (also referred to as unsaturations) (Currier et al., 2013). These findings warrant further investigation into possible factors impacting this phenomenon along with its clinical implications, such as the impact of oxidation on the material's mechanical properties.

The objective of the current study is to investigate how the starting level of transvinylene unsaturations affects the oxidative behavior of highly crosslinked remelted UHMWPE. We hypothesize that higher levels of initial transvinylene unsaturations facilitate the oxidation process in these materials. Furthermore, we hypothesize that similar to free radical containing materials, a reduction in mechanical properties will be observed once a critical oxidation is reached. To test this hypothesis, the study will map ultimate tensile strength (UTS), ductility, and toughness values to various oxidation levels for different crosslinking doses.

2. Materials & methods

2.1. Crosslinking and remelting

Bar stock of compression molded, medical grade GUR 1020 was irradiated using electron beam (e-beam) or gamma radiation (STERIS Isomedix Services, Whippany, NJ). Three crosslinking doses of 50, 75, and 100 kGy were investigated, using never-irradiated material as a control. A post-irradiation remelting was performed at 150 °C for 24 h followed by an annealing step at 120 °C for 24 h. These thermal treatments were based on previous work demonstrating removal of residual free radicals (via remelting) and recrystallization (via annealing) (McKellop et al., 1999; Muratoglu et al., 2001; Oral and Muratoglu, 2007).

2.2. Sample sectioning, accelerated aging, and sectioning

Rectangular prisms (5 × 5 × 8 cm) were machined from the stock material after irradiation and remelting. These were placed in a pressure vessel for evaluation after 4, 6, and 10 weeks of accelerated aging at 63 °C and 5 atm oxygen. This aging protocol was selected over ASTM F2003 (ASTM, 2000) based on previous work demonstrating broader application: emulation of a subsurface oxidation peak and clinical relevance when compared to highly crosslinked, gamma-barrier, and annealed UHMWPE devices (Collier et al., 2003; Currier et al., 2011; Kennedy et al., 2003).

After each aging duration, a 7 mm thick test coupon was cut from the end of each sample using a band saw. Thin sections (250 μm thickness) were microtomed from the test coupon (transverse side) and the longitudinal side of the prism for oxidation analysis. At the completion of aging, mechanical testing was performed using thin sections from the longitudinal side of the prism (Fig. 1).

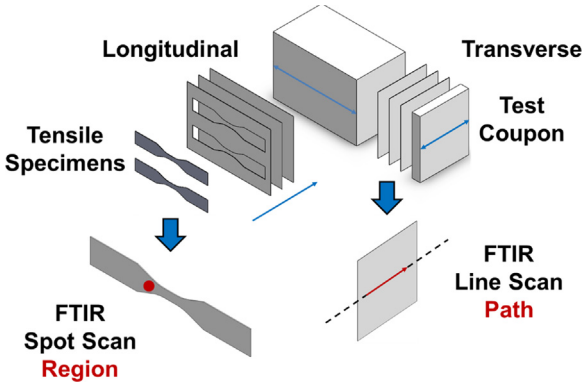

Fig. 1. Sectioned 5 × 5 × 8 cm rectangular prism sample. Tensile specimens stamped from microtomed thin sections (longitudinal side) along with FTIR spot scan region; FTIR line scan path on thin section from test coupon (transverse side).

2.3. Oxidation & transvinylene analysis

Fourier Transform Infrared (FTIR) spectroscopy was performed using either a Perkin-Elmer AutoIMAGE FTIR microscope with a Perkin Elmer Spectrum 100 spectrometer (Perkin Elmer Inc., Shelton, CT) or a Thermo-Scientific iN10 FTIR microscope (Thermo Fisher Scientific, Inc., Madison, WI). The former was used to perform spot scans (16 scans per point) and obtain a representative ketone oxidation index from the region adjacent to the gage section of tensile specimens (prior to mechanical testing). The latter was used to perform line scans (32 scans per point) in 100 μm steps through the center of thin sections (Fig. 1) obtained from test coupons. Using this approach, a cross-sectional (i.e. transverse direction) oxidation-depth profile was determined. For both microscopes, absorption was measured from 4000 cm^{-1} to 800 cm^{-1} at a wave number resolution of 2 cm^{-1}. Examples of FTIR absorbance spectra for UHMWPE along with highlighted peaks of interest are shown in Fig. 2.

Oxidation was reported using ketone oxidation indices (ketone peak height ratios) which were calculated using the height of 1715 cm^{-1} peak normalized to the height of 1368 cm^{-1} peak (Currier et al., 2007). Others have used this non-ASTM oxidation index (Currier et al., 2013, 2010, 2007, 2000, 1997; Reinitz et al., 2014) as it allows separate evaluation of oxidation products (e.g. ketone) from absorbed carbonyl species (e.g. ester) (Currier et al., 2007). For validation of this experimental approach, a cross-plot of ASTM oxidation index (calculated in accordance with ASTM F2102) (ASTM, 2000) and ketone oxidation index ($r^2 \sim 1$) was included for reference (Fig. 3). Transvinylene indices (TVI) were calculated using the area under 965 cm^{-1} peak normalized to the area under 1370 cm^{-1} peak per ASTM F2381 (ASTM, 2000; Currier et al., 2013).

2.4. Mechanical testing

Thin sections from the longitudinal sides of the prism were stamped into ASTM Type V tensile specimens (Fig. 1) per ASTM D638 (ASTM, 2000). After FTIR spot scans were collected from each specimen, uniaxial tension testing was performed using an Instron 5544 load frame, including pneumatic grips, ± 2 kN static load cell, and video extensometer (Instron, Norwood, MA). Specimens were marked at the gage section boundaries (10 mm apart) using a white oil-based paint marker to establish initial gage length (Edding, Ahrensburg, Schleswig-Holstein). Testing was performed at a constant extension rate of 25.4 mm/min until fracture. This corresponds to a nominal strain rate of 100%/min in the gage region as recommended by Note C in the ASTM standard. Data was collected and recorded by BlueHill software to determine mechanical properties including ultimate tensile strength (UTS), elongation at break (EAB), and toughness, defined as the area under the stress versus strain curve. This defined toughness has been