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Ultra High Molecular Weight Polyethylene: Mechanics, Morphology, and Clinical Behavior

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Abstract

Ultra high molecular weight polyethylene (UHMWPE) is a semicrystalline polymer that has been used for over four decades as a bearing surface in total joint replacements. The mechanical properties and wear properties of UHMWPE are of interest with respect to the *in vivo* performance of UHMWPE joint replacement components. The mechanical properties of the polymer are dependent on both its crystalline and amorphous phases. Altering either phase (i.e., changing overall crystallinity, crystalline morphology, or crosslinking the amorphous phase) can affect the mechanical behavior of the material. There is also evidence that the morphology of UHMWPE, and, hence, its mechanical properties evolve with loading. UHMWPE has also been shown to be susceptible to oxidative degradation following gamma radiation sterilization with subsequent loss of mechanical properties. Contemporary UHMWPE sterilization methods have been developed to reduce or eliminate oxidative degradation. Also, crosslinking of UHMWPE has been pursued to improve the wear resistance of UHMWPE joint components. The 1st generation of highly crosslinked UHMWPEs have resulted in clinically reduced wear; however, the mechanical properties of these materials, such as ductility and fracture toughness, are reduced when compared to the virgin material. Therefore, a 2nd generation of highly crosslinked UHMWPEs are being introduced to preserve the wear resistance of the 1st generation while also seeking to provide oxidative stability and improved mechanical properties.

Introduction

For over four decades, ultra high molecular weight polyethylene (UHMWPE) has been used as one-half of the metal- or ceramic-on-plastic bearing couple in total joint replacement (TJR) components due to its toughness, durability, and biological inertness (Kurtz 2004). Though there are metal-on-metal and ceramic-on-ceramic bearing couples, the majority of joint replacement designs utilize UHMWPE. In 2004, over 700,000 total hip and total knee replacements were performed (AAOS 2008) and lifetimes of 15-20 years can often be attained (Karuppiiah, Sundararajana *et al.* 2006). Projections show that the overall number of total joint replacements will greatly increase by 2030, reaching 850,000 to 4.3 million hip and knee replacement procedures (Kurtz, Ong *et al.* 2007; AAOS 2008). The most current failure rates from the Canadian Joint Replacement Registry (2007) found that aseptic loosening (48%), followed by osteolysis (27%), UHMWPE wear (26%) and instability

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(14%) were the leading reasons reported for revisions of a primary hip replacements in 2005–2006. The same report stated that the reasons for revisions of primary total knees were aseptic loosening (33%), followed by UHMWPE wear (30%) and instability (17%). Thus failure of UHMWPE is still a leading contributor to failure in total joint replacements. It is not yet known how modern formulations of UHMWPE will affect these revision rates.

However, a larger percentage of these replacements are expected to be put into younger, more active patients which does merit concern (Kurtz, Lau *et al.* 2008). Part of this changing paradigm in the patient population may be related to the obesity epidemic in the USA. One study has shown that the percentage of patients needing TJR that are obese (52% in 2005) is greater than the percentage of the general population that is obese (24% in 2005) (Fehring, Odum *et al.* 2007). Regardless of the cause, the necessity to develop longer lasting more resilient formulations of UHMWPE is clear in light of these increasing demands on TJRs.

UHMWPE Structure and Mechanical Behavior

UHMWPE is a member of the polyethylene family of polymers with the repeat unit $[C_2H_4]_n$, with n denoting the degree of polymerization. The international Standards Organization (ISO 11542) (ISO) defines UHMWPE as having a molecular weight of at least 1 million g/mole, resulting in a minimum degree of polymerization of $n \approx 36,000$ (Edidin and Kurtz 2000), while the American Society for Testing and Materials (ASTM D 4020) (ASTM) specifies that UHMWPE has a molecular weight greater than 3.1 million g/mole ($n \approx 110,000$). The UHMWPEs used in orthopaedic applications typically have a molecular weight between 2–6 million with a degree of polymerization between 71,000–214,000 (Li and Burstein 1994; Kurtz 2004).

UHMWPE is a linear (non-branching) semi-crystalline polymer which can be described as a two phase composite of crystalline and amorphous phases. The crystalline phase contains chains folded into highly oriented lamellae, with the crystals being orthorhombic in structure (Lin and Argon 1994). The lamellae are 10–50 nm thick and 10–50 μ m long (Kurtz 2004). The lamellae are oriented randomly within the amorphous phase with tie molecules linking individual lamellae to one another.

The two resins of UHMWPE that are currently used in orthopaedics are GUR 1020 (3.5 million g/mole) and GUR 1050 (5.5–6 million g/mole) (Kurtz 2004). These resins can either be compression molded into sheets or ram extruded into rods. Both resin and conversion method are significant predictors of tensile mechanical properties (Table 1) and impact strength (Kurtz 2004). It is also important to note that studies have reported subtle differences in the morphology and fatigue crack propagation resistance between the two conversion methods (Kurtz 2004).

Under both ambient laboratory conditions and *in vivo* UHMWPE is well above its glass transition temperature of -150°C , and behaves viscoelastically and viscoplastically, with its mechanical properties being both rate and temperature dependent (Bergstrom, Rimnac *et al.* 2003). In addition, the yield and post-yield deformation of a semicrystalline polymer involves deformation and possible fragmentation and degradation of the crystalline regions in conjunction with chain alignment in the amorphous and crystalline regions (Peterlin 1987; Galeski, Bartczak *et al.* 1992; Lee, Argon *et al.* 1993; Courtney 2000). Thus, the mechanical properties of UHMWPE, as will be described below, have also been found to depend on both the percent crystallinity of the polymer and on the morphology of the crystalline regions.

In ambient laboratory uniaxial tension experiments, the percent crystallinity of UHMWPE was found to be significantly (positively) related to the true polymer yield strength by a quadratic relationship (Kurtz, Villarraga *et al.* 2002). Recent work (Simis, Bistolfi *et al.* 2006) suggests that there is a positive relationship between crystallinity and elastic modulus and microhardness. Other reports suggest that it is not just the bulk crystallinity of UHMWPE that is important, but the thickness of the crystalline lamellae as well. It has also been suggested that smaller, less perfect crystalline lamellae lead to a decrease in modulus (Gomoll, Bellare *et al.* 2002). With respect to yield behavior, several theoretical works of the polyethylene family of polymers have found that yield stress positively correlates to lamellar thickness and crystalline perfection (Young 1974; Young 1988; Sirotkin and Brooks 2001; Seguela 2002). Consistent with these reports, Medel *et al.* (Medel, Pena *et al.* 2007) recently concluded that, for UHMWPE, yield stress increases with increasing lamellar thickness. However, other reports suggest that there is no correlation between lamellar thickness and the tensile properties of UHMWPE (Mishra, Vianob *et al.* 2003; Turell and Bellare 2004). It is possible that there are differences in the degrees of crystalline perfection between the materials examined in these studies; the dependence of tensile properties on lamellar thickness in UHMWPE merits further investigation.

With respect to fatigue crack propagation, work has shown that increasing the crystallinity increases fatigue crack propagation resistance of UHMWPE (Baker, Bellare *et al.* 2003). Recent work has also found lamellar thickness to be positively correlated to an increase in fatigue threshold, ΔK_{th} (Simis, Bistolfi *et al.* 2006). In a study of the S-N fatigue behavior of UHMWPE, it was concluded that an increase in lamellar thickness corresponded to an increase in S-N fatigue lifetime (Medel, Pena *et al.* 2007).

In addition to the crystalline regions, the amorphous regions play a key role in determining physical behavior as well. In examining the behavior of conventional and crosslinked UHMWPE materials, Kurtz *et al.* hypothesized that the thermomechanical behavior of UHMWPE materials can be predicted based on a thermal activation (Arrhenius) model. They found a negative correlation between the activation energies for thermal softening and crystallinity (Kurtz, Villarraga *et al.* 2002). Consequently, they concluded that the reduction in mechanical properties with increase in temperature (e.g., from 20°C-60°C) can be primarily attributed to changes in the amorphous regions of the polymer.

There is evidence that the morphology of UHMWPE evolves as a consequence of mechanical input. For example, it has been observed that wear is preceded by cyclic plastic deformation of the articulating surface at a microscopic scale (Crane, Pruitt *et al.* 1999; Edidin and Kurtz 2000; Kurtz, Rimnac *et al.* 2000). Lamellar alignment within the subsurface damage layers of retrieved UHMWPE joint replacement components has also been documented (Crane, Pruitt *et al.* 1999; Kurtz, Rimnac *et al.* 2000) (Figure 1). Other studies have correlated microstructural evolution with plastic deformation in UHMWPE in that lamellar alignment in cyclic tension testing has been documented, as well as decreased crystallinity in monotonic tension and compression specimens taken past yield (Butler, Donald *et al.* 1998; Meyer and Pruitt 2001; Sobieraj, Kurtz *et al.* 2005). A recent retrieval study of Hylamer™ acetabular cups has shown that the morphology of the wear debris collected had a higher percentage of monoclinic crystalline phase than the original liners (Reggiani, Tinti *et al.* 2006). This same group has also shown that there is an increase in the crystallinity of wear debris from conventional acetabular cups undergoing wear simulator testing as compared to the soak controlled liners (Affatato, Bersaglia *et al.* 2003). Taken together, these studies provide evidence for morphological evolution of UHMWPE in joint replacement components as a consequence of the loading environment. Additionally, a recent retrieval study found that patient gait was correlated to changes in the crystallinity found in the retrieved liners and in the ultimate load that small punch test samples of the

retrieved liners were able to withstand (Davey, Orr *et al.* 2005). Thus, it can be speculated that the mechanical behavior of UHMWPE joint replacement components is also evolving during use due to the modification of its microstructure.

Finite Element Analyses of UHMWPE Components and Constitutive Modeling of UHMWPE

Use of finite element models to simulate *in vivo* loading conditions can provide insight into the complex stress and strain distributions that an UHMWPE implant component experiences during use (Bergstrom, Kurtz *et al.* 2002). However, these simulations, and the knowledge gained from them, are limited by the accuracy of the constitutive model used to define the behavior of the UHMWPE material. Until recently, the material models that have been used to describe UHMWPE have been primarily metals-based models that employed the use of a flow rule (Bergstrom, Kurtz *et al.* 2002). This type of modeling is not adequate for UHMWPE due to the fundamental differences in the deformation mechanisms of polymers and metals. In amorphous polymeric materials, orientation strain hardening due to polymer chain stretching and alignment in the amorphous regions is a primary deformation mechanism (Dowling 1999; Bergstrom, Kurtz *et al.* 2002); thus, physically inspired constitutive models for amorphous polymers have been developed by Boyce and co-workers (Arruda and MC 1993; Hasan and Boyce 1995; Bergstrom and Boyce 1998; Bergstrom and Boyce 2001). These constitutive relations model both viscoelastic and viscoplastic behaviors. Recently, a constitutive model for UHMWPE (the “Hybrid Model”) has been developed based on the models of Boyce and co-workers. The Hybrid Model takes the approach of modeling the semi-crystalline polymer structure as one homogenized composition, whose internal state is found as a function of deformation, which is decomposed into both elastic and plastic components. Although the material is modeled as one that is homogenous, the influence of the crystalline regions is approximated by a term that accounts for the non-linear elastic and plastic processes associated with the crystalline phase (Bergstrom, Kurtz *et al.* 2002; Bergstrom, Rimnac *et al.* 2004). The parameters for the Hybrid Model can be obtained (for any UHMWPE formulation) from monotonic tension tests. The model has been shown to accurately capture the behavior of UHMWPE in monotonic tension and fully reversed loading and unloading (Bergstrom, Kurtz *et al.* 2002; Bergstrom, Rimnac *et al.* 2004), in biaxial punch testing (Bergstrom, Rimnac *et al.* 2003; Bergstrom, Rimnac *et al.* 2005), and in triaxial loading using notched UHMWPE specimens (Kurtz, Bergstrom *et al.* 2007).

Bergstrom and co-workers (Bergstrom, Rimnac *et al.* 2005) further examined the Hybrid Model to determine if it could be used to predict monotonic fracture. They examined 8 failure criteria, including Von Mises stress and strain; maximum principal stress and strain; Coulomb, Tresca, and hydrostatic stress; however, it was found that the best predictor of failure was a strain-based failure criterion, based on the critical chain stretch of amorphous chains in the polymer (Figure 2). The Hybrid Model, or similar physically-inspired constitutive models for UHMWPE, if coupled with dynamic finite element analyses of UHMWPE joint replacement components, could be a powerful pre-clinical screening tool for new geometry/material combinations.

Performance of UHMWPE Total Joint Replacement Components and Clinical Consequences

Osteolysis and related implant loosening has been a significant problem limiting the lifetime of total joint replacements (Wright and Goodman 2001). Osteolysis has been shown to be related to wear of UHMWPE components; the wear debris that is generated during articulation against the mating metallic or ceramic counterface arises from adhesive, abrasive, third-body, and fatigue wear mechanisms (Wright and Goodman 2001). The wear debris can trigger an elaborate immune response which results in osteoclasts resorbing bone

around the implant, which can lead to periprosthetic osteolytic implant loosening (Ingham and Fisher 2005; Abu-Amer, Darwech *et al.* 2007).

Oxidative Degradation of UHMWPE Components—As consideration was being given to the role of UHMWPE debris in osteolysis, the effects of radiation sterilization and subsequent oxidative degradation on the structure and mechanical behavior of UHMWPE also began to be investigated. With early joint replacement components, gamma radiation sterilization in air at a dose level of approximately 25kGy was a major sterilization method (as compared to ethylene oxide gas) due to its economic advantages and ease of use (Kurtz, Muratoglu *et al.* 1999). However, when UHMWPE is exposed to gamma radiation in the presence of air, oxidative degradation can take place. Free radicals are formed by the interaction of the radiation and the UHMWPE; the free radicals can react promptly with oxygen present in the UHMWPE. Hydroperoxides are formed as the first product of oxidation (Costa and Bracco 2004) and upon their decomposition, free radicals are re-generated. Thus, the process is autocatalytic and can lead to the further formation of carbonyl functionalities on the backbone of the polyethylene chains, including ketones, alcohols, esters, and carboxylic acids. Therefore, as long as there is an oxygen source, the cycle can continue and the number of oxidation products will increase without any further irradiation (Costa and Bracco 2004; Bracco, Brunella *et al.* 2006). This process is known as post-irradiation aging and has been shown to occur in implants that were gamma sterilized in air and packaged in air-permeable packaging (Rimnac, Klein *et al.* 1994).

Post-irradiation oxidative aging embrittles UHMWPE, leading to a decrease in the elongation to failure, an increase elastic modulus, a decrease in ultimate stress, a decrease in toughness (Edidin, Jewett *et al.* 2000), a decrease in fatigue crack propagation resistance (Goldman, Gronsky *et al.* 1996), a decrease in wear resistance (Shaw 1997; Lee and Lee 1999; Young, Keller *et al.* 2000), and decreased S-N fatigue life (Ries, Weaver *et al.* 1996). Clinically, oxidative degradation has been shown to negatively impact the performance of acetabular hip components (Sutula, Collier *et al.* 1995; McKellop, Shen *et al.* 2000; Kurtz, Rimnac *et al.* 2005) and tibial knee components (Collier, Sperling *et al.* 1996; Currier, Currier *et al.* 1997; Williams, Mayor *et al.* 1998; Won, Rohatgi *et al.* 2000) both in terms of wear and fracture resistance. For example, one study demonstrated a link between subsurface oxidative degradation and an increased prevalence of delamination in tibial components of one total knee replacement design (Won, Rohatgi *et al.* 2000).

To mitigate oxidation and its subsequent effects on wear and mechanical properties of UHMWPE, orthopaedic implant manufacturers turned to modified sterilization protocols, including gamma radiation sterilization in vacuum-packaging or inert-gas packaging (to reduce or eliminate oxygen) (Kurtz, Muratoglu *et al.* 1999). These approaches greatly reduce or eliminate the potential for oxidation during shelf storage due to the lack of oxygen; however, the free radicals created still remain and, thus, *in vivo* oxidation is still possible. In fact, several studies have shown that *in vivo* oxidation of components sterilized under reduced-oxygen conditions does occur, and the highest oxidation indexes tend to occur at stress concentrations inherent in the UHMWPE component design (Kurtz, Rimnac *et al.* 2005; Currier, Currier *et al.* 2007; Kurtz, MacDonald *et al.* 2008; Kurtz, MacDonald *et al.* 2008).

Gross fracture and component cracking of conventional UHMWPE total joint replacement components has been reported. A brief review of the literature has found reports of cracks and/or gross fracture along acetabular rims (Collier, Mayor *et al.* 1992; Berry, Barnes *et al.* 1994; Astion, Saluan *et al.* 1996; Birman, Noble *et al.* 2005), the stabilizing posts in noncruciate sparing tibial components (Mariconda, Lotti *et al.* 2000; Mestha, Shenava *et al.* 2000; Hendel, Garti *et al.* 2003; Mauerhan 2003; Chiu, Chen *et al.* 2004) (Figure 3), and

along the rims of total disc replacements (Kurtz, van Ooij *et al.* 2006). All of these design features where the cracks occurred are inherent stress concentrators. Oxidation of these regions may be expected to further increase the susceptibility to fracture. For example, a recent study of retrieved conventional UHMWPE acetabular liners found that the percentage of retrieved liners that showed cracking increased as the level of oxidation present in the liners increased (Birman, Noble *et al.* 2005).

Crosslinking of UHMWPE for Wear Resistance: 1st Generation—While efforts were being directed to improve the wear and mechanical performance of UHMWPE through control of oxidation, efforts were also directed towards improving the wear resistance through material modifications such as crosslinking. As early as the 1970's, Oonishi and co-workers (Oonishi, Takayama *et al.* 1992; Oonishi, Takayama *et al.* 1992; Oonishi, Ishimaru *et al.* 1996) showed that crosslinking UHMWPE leads to decreased wear. In those clinical studies, the components were crosslinked by exposure to 1000 kGy of gamma radiation. It has been shown that UHMWPE becomes highly crosslinked after an absorbed dose of 50 kGy, with the level of crosslinking approaching an asymptotic level at a dose between 100 to 150 kGy (Muratoglu, Bragdon *et al.* 1999). The, so-called 1st generation crosslinked materials, introduced in the 1990's and early 2000's, were exposed to irradiation levels between 50-105 kGy (Kurtz 2004). *In vitro* wear simulator laboratory studies supported that 1st generation crosslinked UHMWPE materials had a significant reduction in wear rate when compared to conventional materials (McKellop, Shen *et al.* 1999; McKellop, Shen *et al.* 1999; Muratoglu, Bragdon *et al.* 1999; McKellop, Shen *et al.* 2000; Muratoglu, Bragdon *et al.* 2001; Abt, Schneider *et al.* 2003; Greer, King *et al.* 2003).

To minimize *in vivo* oxidative degradation, 1st generation crosslinking methods utilized a post-crosslinking thermal treatment to extinguish or reduce unreacted free radicals: annealing, which is accomplished below the melt transition (T_m); and, remelting, which is accomplished above T_m . Both post-processes are conducted at ambient pressure (Kurtz, Villarraga *et al.* 2002). With respect to annealing, because this occurs below T_m , the crystalline regions do not undergo dissolution. Therefore, any residual free radicals present within the crystalline lamellae, are unlikely to be extinguished during the annealing process. Consequently, crosslinked UHMWPE's that are post processed via annealing may still be susceptible to *in vivo* oxidative degradation (McKellop, Shen *et al.* 2000; Shen and McKellop 2002). Annealing of UHMWPE and other forms of polyethylene has been shown to lead to the formation of small thin crystals and to thicken existing crystals (Fischer 1972; Hearle 1982), resulting in a slight increase in crystallinity following annealing (Kurtz, Villarraga *et al.* 2002; Sobieraj, Kurtz *et al.* 2005; Medel, Pena *et al.* 2007). Remelting, on the other hand, involves the dissolution and reformation of crystalline regions, therefore minimizing the possibility of residual free radicals. However, remelting causes an irreversible decrease in the overall crystallinity of the material (McKellop, Shen *et al.* 1999).

Though the 1st generation crosslinked materials have been successful in reducing wear, there is a tradeoff with respect to other mechanical properties. Ultimate stress and strain are reduced for the 1st generation highly crosslinked UHMWPEs (Lewis 2001; Muratoglu, Bragdon *et al.* 2001; Gomoll, Bellare *et al.* 2002; Kurtz, Villarraga *et al.* 2002; Abt, Schneider *et al.* 2003; Greer, King *et al.* 2003; Wang, Manley *et al.* 2003; Pruitt 2005; Sobieraj, Kurtz *et al.* 2005) (Figure 4), with materials irradiated using an e-beam showing a smaller decrease in these properties than those irradiated with gamma irradiation (Greer, King *et al.* 2003). Also, the 1st generation crosslinked materials that used GUR 1020 as the base resin have higher elongation at a given dose of gamma radiation than comparably prepared materials that used GUR 1050 as the base resin (Greer, King *et al.* 2003). Remelted materials additionally show a decreased yield stress (Sobieraj, Kurtz *et al.* 2005; Medel, Pena *et al.* 2007), which is likely due to the decreased crystallinity of the materials.

Several authors have shown that crosslinking decreases fatigue crack propagation resistance (Baker, Bellare *et al.* 2003; Gencur, Rimnac *et al.* 2006; Varadarajan and Rimnac 2006; Medel, Pena *et al.* 2007) compared to conventional materials, with increasing dose being correlated with increasing reduction of fatigue crack propagation resistance. Furthermore, remelted materials have reduced fatigue crack propagation resistance compared with annealed materials (Gencur, Rimnac *et al.* 2006; Varadarajan and Rimnac 2006; Medel, Pena *et al.* 2007) (Figure 5). Because the annealed materials may be subject to oxidative degradation, however, their long-term fatigue crack propagation resistance may be further reduced by oxidation.

Crosslinking also reduces fracture toughness as determined by an estimate of K_{IC} (Gencur, Rimnac *et al.* 2003), by J-integral fracture toughness tests (Gomoll, Bellare *et al.* 2002; Medel, Pena *et al.* 2007), Izod impact toughness (Greer, King *et al.* 2003; Medel, Pena *et al.* 2007), and Charpy impact toughness (Abt, Schneider *et al.* 2003), with higher doses of irradiation causing larger reduction in the different toughness measures. Again, it has been shown that e-beam radiation better preserves impact toughness as compared to gamma radiation, and that crosslinked UHMWPE made from GUR 1020 resin better preserves impact toughness than crosslinked UHMWPE made from GUR 1050 resin (Greer, King *et al.* 2003). Remelting was found to have a more detrimental effect on both J-integral fracture toughness and Izod impact strength than annealing (Medel, Pena *et al.* 2007) and on $\Delta K_{inception}$ (Gencur, Rimnac *et al.* 2006; Varadarajan and Rimnac 2006; Medel, Pena *et al.* 2007).

Interestingly, Medel *et al.* showed that crosslinked and non-heat-treated UHMWPEs survive longer in S-N testing (smooth specimens, strain based failure criterion) than virgin material, with increased irradiation dose imparting greater survival (e-beam irradiation, highest dose of 150kGy) (Medel, Pena *et al.* 2007) (Figure 6). This work further showed that both annealing and remelting reduced this apparent gain, with the higher dose annealed materials behaving similarly to the virgin material, and with the remelted materials all having significantly reduced survival compared with the virgin material (Medel, Pena *et al.* 2007). Baker *et al.* (Baker, Bellare *et al.* 2003) also conducted smooth specimen S-N tests of non-crosslinked and highly crosslinked UHMWPE materials in which a strain based failure criterion was utilized. In contrast to the study by Medel *et al.*, Baker and coworkers found that at the highest level of crosslinking (gamma irradiation, 200kGy) that the remelted materials survived as long as the untreated virgin material (Baker, Bellare *et al.* 2003). The reason for the improved fatigue life of the crosslinked UHMWPE materials in these tests is not fully understood, however, Baker *et al.* hypothesized that it may be related to strengthening of the amorphous regions, suppressing void formation and thus increasing the number of cycles for crack initiation.

Wang and co-workers (Wang, Manley *et al.* 2003) utilized structural fatigue tests, using an acetabular liner modeled after a design re-called due to a high incidence of fracture, to evaluate the effects of post-irradiation heat treatment on structural integrity (defined by occurrence of fracture in the test). They found that crosslinked and annealed liners had equivalent structural integrity to conventional liners upon testing, while crosslinked and remelted liners showed a decrease in structural integrity (increased incidence of fracture). Therefore, it was concluded that it was post-irradiation heat treatment that most affected the structural integrity of the highly crosslinked UHMWPEs, not the irradiation dose. Further development and standardization of such structural fatigue tests could also be a useful tool for the pre-clinical screening of materials.

Several studies of the *in vivo* performance of acetabular components have shown that the wear rate for highly crosslinked UHMWPE is greatly reduced when compared with

conventional polyethylenes (Digas, Karrholm *et al.* 2004; D'Antonio, Manley *et al.* 2005; Dorr, Wan *et al.* 2005; Krushell, Fingerhuth *et al.* 2005; Manning, Chiang *et al.* 2005; Rohrl, Nivbrant *et al.* 2005; Engh Jr, Ginn *et al.* 2006; Geller, Malchau *et al.* 2006). However, as previously mentioned, several researchers have shown that irradiation sterilized conventional UHMWPE oxidizes *in vivo*, leading to concern that highly crosslinked annealed UHMWPE formulations may be also be subject to oxidation. It has been reported in retrieval studies that remelted acetabular liners show little or no *in vivo* oxidation (Wannomae, Bhattacharyya *et al.* 2006; Kurtz, MacDonald *et al.* 2008), while annealed acetabular liners do in fact undergo oxidation *in vivo* (Kurtz, Hozack *et al.* 2005; Wannomae, Bhattacharyya *et al.* 2006; Kurtz, MacDonald *et al.* 2008), and that the oxidative degradation is greatest near the rims (Wannomae, Bhattacharyya *et al.* 2006; Kurtz, MacDonald *et al.* 2008). In addition, there have been reports in the literature of rim fracture of highly crosslinked remelted UHMWPE components after short term implantation (6 months-3.8 years) (Beaule, Schmalzried *et al.* 2002; Halley, Glassman *et al.* 2004; Tower, Currier *et al.* 2007) and of surface cracking and damage in retrieved highly crosslinked and annealed liners (Kurtz, Hozack *et al.* 2005). Overall, the findings support the need to eliminate the potential for oxidation of crosslinked UHMWPE components so as to avoid the possibly confounding effects of crosslinking and oxidation on the potential for fracture.

Crosslinking of UHMWPE for Wear Resistance: 2nd Generation—In light of the concern for improved fracture resistance, 2nd generation highly crosslinked UHMWPE's have been under investigation. These materials attempt to retain the superior wear resistance of the 1st generation highly crosslinked materials while also retaining the superior mechanical properties of the conventional UHMWPEs. Several methods have been developed: sequential annealing (Dumbleton, D'Antonio *et al.* 2006; Wang, Zeng *et al.* 2006); mechanical deformation (Kurtz, Mazzucco *et al.* 2006); incorporation of vitamin-E (Oral, Wannomae *et al.* 2004; Oral, Christensen *et al.* 2006; Oral, Rowell *et al.* 2006); and, high pressure crystallization after melting highly crosslinked UHMWPE (Simis, Bistolfi *et al.* 2006).

Sequential irradiation and annealing has been introduced as a means by which to more effectively reduce free radicals without remelting the material and without adverse changes in crystallinity (Dumbleton, D'Antonio *et al.* 2006; Wang, Zeng *et al.* 2006). The material is first irradiated at a low dose (e.g., 30kGy), and then annealed for a given period of time. This process is then repeated several times. X3TM (Stryker Orthopaedics, Mahwah, NJ) is currently the only sequentially irradiated annealed UHMWPE on the market. In that process, the crosslinking/heat treatment cycle is repeated three times (at 30kGy) for a total radiation dose of 90kGy. The motivation for the process is that the lower irradiation per crosslinking cycle will leave fewer residual free radicals, and that the annealing steps will, therefore, be more effective at quenching the residual free radicals. By using this process, the manufacturer asserts that a highly crosslinked oxidatively stable UHMWPE is formed (Dumbleton, D'Antonio *et al.* 2006; Wang, Zeng *et al.* 2006). Sequential irradiation and annealing has shown promising results in a rapid aging oxidation study, hip and knee simulator wear studies, and a contact fatigue strength study (Dumbleton, D'Antonio *et al.* 2006; Wang, Zeng *et al.* 2006).

Currently, there is one second generation highly crosslinked UHMWPE that uses mechanical deformation in its processing to enhance mechanical properties, ArCom XL (Biomet, Warsaw, IN) (Kurtz, Mazzucco *et al.* 2006). The material is prepared in a four step process: 1) isostatically molded rods are irradiated to a given dose using gamma-irradiation; 2) the crosslinked rods are preheated to a temperature below T_m to help facilitate the deformation processing step; 3) the heated rod is ram extruded through a circular die with a compression ratio of 1.5; and 4) the rod is once again annealed below the T_m for the purpose

or relief of residual stresses. This material, due to the deformation processing, is anisotropic. However, the degree of this anisotropy is somewhat mitigated by the stress-relief annealing. Acetabular components are machined from the treated rod and subsequently sterilized without ionizing radiation. The manufacturer reports that ArCom XL material has better wear resistance than conventional UHMWPEs (Biomet). It has also been reported to have better ΔK_{insep} than first generation highly crosslinked UHMWPEs as well as excellent oxidative stability in an accelerated aging oxidation study (Kurtz, Mazzucco *et al.* 2006).

Vitamin E incorporation with highly crosslinked UHMWPE is another method that is being used and investigated. Two methods of incorporation are currently reported in the literature: one is to mix vitamin E with UHMWPE powder prior to consolidation, and the other is to allow diffusion of vitamin E into bulk UHMWPE (Shibata, Kurtz *et al.* 2006). E-Poly HXLPE by Biomet (Warsaw, IN) is currently the only commercially available highly crosslinked Vitamin-E UHMWPE material in the US. Vitamin E is an antioxidant which is capable of consuming free radicals. Therefore, by impregnating UHMWPE with vitamin E, any free radicals that do not form crosslinks after irradiation should be removed by the vitamin E. Highly crosslinked UHMWPEs that contain vitamin E have shown wear resistance comparable to that of first generation highly crosslinked UHMWPEs, with increased elongation to break, better toughness, better ΔK_{insep} , and superior oxidative stability (Table 2) (Oral, Wannomae *et al.* 2004; Oral, Rowell *et al.* 2006; Shibata, Kurtz *et al.* 2006).

Lastly, high pressure high temperature processing of highly crosslinked UHMWPE is being explored. At elevated temperature and pressure, large crystalline regions having a hexagonal lattice structure are formed; upon cooling and return to ambient pressure, the crystals revert to an orthorhombic structure (Simis, Bistolfi *et al.* 2006). Overall, the process results in an increase in crystallinity and an increase in the size of the crystalline lamellae. As previously noted, an increase in crystallinity has generally been related to an improvement in fatigue crack propagation resistance [25]. Consistent with this observation, this material was shown to have increased crystallinity, increased lamellar thickness, increased modulus, microhardness, and ΔK_{thresh} (Simis, Bistolfi *et al.* 2006).

With these new materials there is little information available to-date on clinical performance. A recent retrieval study (Kurtz, MacDonald *et al.* 2008) included 10 retrieved sequentially annealed liners that had been implanted for 0.6 ± 0.3 years (with an average shelf-life of 0.3 ± 0.3 years). This study found that although the sequentially annealed liners had zero-to-low levels of oxidation following their brief implantation period, they still exhibited measurable oxidation potential, comparable to that of the first generation remelted liners (41 liners, implanted for 0.6 ± 0.8 years, shelf-life of 1.7 ± 0.3 years) in the study. The authors are unaware of any other reports in the literature showing the clinical performance of 2nd Generation highly crosslinked UHMWPEs.

Conclusions

UHMWPE is a complex material and its material, morphological, and mechanical properties are potentially temporal and dependent on functional loading and environmental conditions. It is desirable to understand the material and mechanical properties for individual formulations of UHMWPE and also how the temporal evolution of morphology affects the mechanical properties of these materials. Further elucidation of these basic relationships should allow for development of even more effective formulations of UHMWPE.

UHMWPE has been a clinically successful material in total joint replacements. However, with rising patient demands it is of paramount importance that the UHMWPE materials available continue to be improved. The orthopaedic community has a strong history of

altering techniques related to the manufacture of UHMWPE components to improve performance. Advances in sterilization methods have somewhat assuaged the oxidative degradation that UHMWPE experienced during shelf aging. First generation highly crosslinked materials significantly lowered the *in vivo* wear rates of total joint replacements, which should lead to a decrease in aseptic loosening due to wear particle induced osteolysis. Second generation highly crosslinked materials have been developed that not only preserve these advances in wear resistance, but have improved on the maintenance of other mechanical properties and have also improved on the oxidative stability of highly crosslinked UHMWPE. It is of great interest to the orthopaedic community to see how these materials will perform clinically.

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Figure 1. Adapted from (Wright and Goodman 2001) and (Kurtz, Rimnac *et al.* 2000). Schematic of the plastic damage layer in a component and an SEM showing the aligned lamellae in the damage layer.

Figure 2.

Bar chart showing the r^2 values for several failure criteria for the four formulations of UHMWPE tested in (Bergstrom, Rimnac *et al.* 2005). The chain stretch criterion is concluded to be the best for UHMWPE. Courtesy of (Bergstrom, Rimnac *et al.* 2005).

Figure 3.
Retrieved tibial component with a fractured stabilizing post. Courtesy of (Mauerhan 2003).

Figure 4. Engineering stress-strain curves for a conventional (25kGy irradiation sterilized in N₂) and several first generation highly crosslinked materials. Annealing was performed at 130°C and remelting was performed at 150°C (Murphy, Sobieraj *et al.* 2008).

Figure 5. Fatigue crack propagation results (in ambient temperature and pressure) for a conventional UHMWPE and for first generation highly crosslinked remelted and annealed formulations. Courtesy of (Gencur, Rimnac *et al.* 2006).

Figure 6.

S-N fatigue results for non-irradiated (Virgin), as-irradiated ($\beta 50$ and $\beta 150$), irradiated and remelted ($\beta 50R$ and $\beta 150R$), and irradiated and annealed ($\beta 50A$ and $\beta 150A$) formulations of UHMWPE. Adapted from (Medel, Pena *et al.* 2007).

Adapted from Greer et al. (Greer, King et al. 2003). Yield strength, ultimate tensile stress, elongation at break, and Izod impact toughness for UHMWPEs made of either GUR 1020 or 1050, consolidated into either a compression molded sheet (sheet) or ram extruded bar (bar), and then either γ - or β -irradiation crosslinked at different irradiation levels.

Table 1

Dose	Irradiation	GUR Resin	Sheet or Bar	Yield Strength (MPa)	Ultimate Tensile Stress (MPa)	Elongation at Break (%)	Izod Impact (kJ/m ²)
0	None	1020	Sheet	23.6 ± 0.1	42.1 ± 2.7	396 ± 20	161.3 ± 1.9
			Bar	23.6 ± 0.1	37.2 ± 6.4	376 ± 52	139.5 ± 1.4
		1050	Sheet	22.5 ± 0.1	43.8 ± 3.5	358 ± 20	93.7 ± 3.4
			Bar	22.3 ± 0.4	40.0 ± 5.0	353 ± 33	97.9 ± 2.9
30	β	1050	Sheet	20.4 ± 0.1	36.7 ± 5.8	284 ± 49	90.1 ± 1.2
			Bar	21.0 ± 0.1	43.6 ± 6.8	340 ± 32	86.8 ± 1.0
		1020	Sheet	21.3 ± 0.0	41.6 ± 3.7	315 ± 18	87.4 ± 3.6
			Bar	23.5 ± 0.2	45.3 ± 5.0	335 ± 24	88.1 ± 3.2
60	γ	1020	Sheet	23.1 ± 0.1	36.7 ± 0.7	270 ± 5	74.6 ± 2.0
			Bar	23.1 ± 0.2	35.4 ± 0.8	278 ± 8	74.3 ± 1.0
	β	1050	Sheet	20.4 ± 0.1	36.9 ± 3.8	264 ± 15	73.3 ± 1.2
			Bar	21.2 ± 0.2	39.5 ± 3.1	275 ± 21	70.6 ± 1.5
	γ	1050	Sheet	20.1 ± 0.1	33.2 ± 1.2	247 ± 5	73.0 ± 1.6
			Bar	20.6 ± 0.1	31.6 ± 1.0	243 ± 8	72.0 ± 0.4
	γ	1020	Sheet	21.4 ± 0.1	33.3 ± 1.7	212 ± 7	56.7 ± 0.2
			Bar	21.3 ± 0.3	31.1 ± 2.1	215 ± 9	59.6 ± 1.2
120	β	1050	Sheet	20.6 ± 0.2	34.1 ± 4.0	209 ± 15	60.9 ± 2.0
			Bar	21.2 ± 0.2	36.6 ± 3.2	227 ± 14	57.5 ± 2.1
	γ	1050	Sheet	20.0 ± 0.1	30.2 ± 1.6	188 ± 7	49.9 ± 1.7
			Bar	21.0 ± 0.1	29.2 ± 1.0	185 ± 5	51.4 ± 0.6

Table 2

Adapted from Oral et al. (Oral, Wannomae et al. 2004). Stress intensity factor range at fatigue crack inception (ΔK_i) for different UHMWPE formulations. For the vitamin E doped materials there was a difference in ΔK_i for the border region (vitamin E rich) and the bulk (no vitamin E).

Material	ΔK_i MPa·m ^{1/2}	Samples Tested, n=
Unirradiated	1.37 ± 0.06	3
Conventional (25kGy in air)	1.29 ± 0.04	3
100kGy as-irradiated	0.74 ± 0.01	3
100kGy remelted	0.56 ± 0.02	3
Aged Conventional	0.18 ± 0.06	3
92kGy Vitamin E (border)	0.94	2
92kGy Vitamin E (bulk)	0.76	2
127kGy Vitamin E (border)	0.83 ± 0.02	4
127kGy Vitamin E (bulk)	0.7	1