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Crystallization pathways to alter the nanostructure and tensile properties of non-irradiated and irradiated, vitamin E stabilized UHMWPE

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ABSTRACT

The superior tribological and mechanical properties of ultrahigh molecular weight polyethylene (UHMWPE) have enabled its use as components of total joint replacement prostheses for several decades. UHMWPE has been used in non-crosslinked, lightly crosslinked and highly crosslinked forms. In recent years, there has been considerable attention on the mechanical properties of UHMWPE due to a well-known decrease in mechanical properties in radiation crosslinked UHMWPE compared to non-crosslinked UHMWPE. Radiation crosslinking has been shown to be necessary for high resistance to wear and thus there is a need to increase mechanical properties of crosslinked UHMWPE. In this study, we aimed to establish a correlation between the semicrystalline morphology of both non-crosslinked and highly crosslinked UHMWPE, containing vitamin E as an anti-oxidant stabilizer, and their tensile properties. We subjected the polymer to a variety of thermal treatments, in order to induce modifications to the semicrystalline morphology and thereby to influence macroscopic tensile properties. A combination of differential scanning calorimetry, small angle X-ray scattering and tensile testing demonstrated that isothermal crystallization and isothermal annealing significantly increase the modulus and yield stress of both non-crosslinked and radiation crosslinked UHMWPE but did not affect their large strain properties, whereas melt-quenching resulted in a lower modulus and yield stress, and also increased maximum strain for the non-crosslinked UHMWPE but did not affect the maximum strain for the crosslinked UHMWPE. In summary, this investigation provides crystallization pathways to either increase or decrease small-strain tensile properties of UHMWPE without substantially altering large-strain tensile properties, which can guide in optimizing the lamellar morphology of UHMWPE for the orthopedic implant application.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) was introduced in orthopedics more than fifty years ago and is currently used as a bearing material for acetabular components of total hip replacement prostheses or for tibial and patellar components of total knee replacement prostheses. It is still the subject of extensive research to determine the optimum

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macromolecular and morphological parameters to provide the maximum mechanical properties, wear resistance and oxidation resistance. Each of these factors determines the lifetime of UHMWPE components in these orthopedic implants [1–3].

Contemporary UHMWPEs require mechanical properties that allow them to resist high-contact stresses in these medical devices, which can overcome the yield stress of UHMWPE and create permanent deformation and irreparable damage to the functioning of the prosthesis. The mechanical properties of polyethylene are strongly related to its lamellar morphology, which in turn are influenced by various macromolecular factors such as molecular weight, molecular weight distribution, type and degree of branching of polymer chains, crosslink density as well as processing conditions such as sintering of the reactor powder and crystallization conditions (pressure, temperature, time). These structure–property relationships have prompted research into all areas of processing from the original grade of resin powder of PE used, to the resulting stock material and final machining of implant components [1]. Truss et al. [4] showed that Young's modulus, yield stress, strain hardening rates, work of fracture (WOF) and ultimate tensile properties varied as a function of cooling rate from the melt temperature of 133 °C. In fact, under conditions of rapid cooling (quenching), the nucleating density is much higher than that of slow cooling and lamellar growth and thickening are reduced, providing UHMWPE with a lower crystallinity. In contrast, slow cooling increases the overall degree of crystallinity due to a lower nucleation density and increased lamellar thickening, leading to a smaller number of thick lamellae compared to quenched polyethylene. [5]. The thickness of crystalline lamellae increases with an increase in annealing temperature. The primary consequence of a higher crystallinity is an increase in Yield Stress and Young's modulus [2]. It is also known that higher moduli UHMWPEs have a higher impact strength and resistance to fatigue crack propagation, which are necessary for implant applications [6–11].

UHMWPEs used in implant applications have historically been sterilized using a gamma radiation dose of approximately 25 kGy. In recent years, ionizing radiation has been used to crosslink UHMWPE in order to increase its resistance to wear. The consequence of radiation is not merely crosslinking in the amorphous regions but also the creation and entrapment of free radicals in the lamellar regions, which can over time migrate to the lamellar surface and result in oxidation, which is associated with chain scission [12–17]. Oxidation is thus the second major factor that reduces the performance of total joint replacement prosthesis, especially through the mechanism of delamination wear, caused by chain scission and, thereby decreased molecular weight of PE. In addition, there is an increase in crystallinity in subsurface regions of PE that makes it more brittle and susceptible to fatigue-related damage mechanisms [18–20].

The wear resistance of UHMWPE is the most important factor controlling the lifetime of joint replacement prosthesis utilizing PE components. The major effects of wear are the progressive loosening of implant components and periprosthetic osteolysis (bone loss) as a consequence of wear particles that may enter periprosthetic tissue. In most cases, revision surgery is necessary to replace the implant to avoid an excessive component loosening and the fracture. Radiation cross-linking is a method to reduce wear of UHMWPE [21,22]. In the amorphous regions high-dose of ionizing radiation creates carbon free radicals that have enough mobility to form cross-links between the polyethylene chains. However, free radicals formed in the crystalline phases have a lower mobility and cannot recombine but remain trapped for prolonged periods of time in the lamellae, migrate to the lamellar surface and result in oxidation, chain scission, recrystallization and embrittlement, and reduction in the mechanical properties of UHMWPE. Post-irradiation melting is used effectively to remove the residual free radicals. Unfortunately, both cross-linking irradiation and post-irradiation melting reduce tensile properties, fracture toughness and resistance to fatigue crack propagation [21–27].

An alternative method of processing UHMWPE, to avoid melting to quench free radicals trapped in lamellae, which alters the crystalline morphology and decreases toughness and resistance to fatigue crack propagation, is to incorporate an antioxidant, such as α-tocopherol (synthetic vitamin E) into UHMWPE. Vitamin E is a natural and very effective antioxidant, biocompatible and lipophilic owing to its phenyl tail, and easily blends into UHMWPE. The presence of vitamin E eliminates the need for post-irradiation melting, thus allowing preservation of crystalline morphology [28–31].

In this study, our goal was to establish a correlation between the semi-crystalline morphology of UHMWPE and its tensile properties. Subjecting samples of non-crosslinked UHMWPE with 0.1% by weight of α-tocopherol to three different thermal treatments, it was possible to induce changes both to the crystalline and amorphous regions, in order to influence macroscopic tensile properties. We also subjected radiation crosslinked UHMWPE to identical thermal treatments to determine the constraining effect of crosslinking on the resulting morphology and tensile properties of UHMWPE since it was expected that the lamellar morphology and consequently tensile properties would be affected in a different manner compared to uncrosslinked UHMWPE.

2. Materials and methods

2.1. Starting materials and sample preparation

Commercially available compression molded sheets (Meditech Medical Polymers, Fort Wayne, IN) of 0.1% vitamin-E blended, GUR 1020 PE (Celanese, Bayport, TX) was the starting material. The sheets were sectioned into 1 mm thick slices. Each slice was subjected to one of the following thermal treatments: untreated as the control material (C), annealed at 127 °C for 48 h (CA), melted at 200 °C for 10 min and subsequently immediately quenched in liquid nitrogen (MQ), melted at 200 °C for 10 min and then annealed at 127 °C for 48 h (MA).