Published in final edited form as:

Biomaterials. 2009 April ; 30(10): 1870–1880. doi:10.1016/j.biomaterials.2008.12.029.

Improved resistance to wear and fatigue fracture in high pressure crystallized vitamin E-containing ultra-high molecular weight polyethylene

Ebru Oral^{a,b}, Christine A. Godleski Beckos^a, Andrew J. Lozynsky^a, Arnaz S. Malhi^a, and Orhun K. Muratoglu^{a,b,*}

^aMassachusetts General Hospital, Department of Orthopaedic Surgery, Boston, MA 02114, USA

^bHarvard Medical School, Boston, MA, USA

Abstract

Higher crystallinity and extended chain morphology are induced in ultra-high molecular weight polyethylene (UHMWPE) in the hexagonal phase at temperatures and pressures above the triple point, resulting in improved mechanical properties. In this study, we report the effects of the presence of a plasticizing agent, namely vitamin E (α -tocopherol), in UHMWPE during high pressure crystallization. We found that this new vitamin E-blended and high pressure crystallized UHMWPE (VEHPE) has improved fatigue strength and wear resistance compared to virgin high pressure crystallized (HP) UHMWPE. This suggested different mechanisms of wear reduction and fatigue crack propagation resistance in UHMWPE.

Keywords

Semi-crystalline; Plasticity; Cross-linking; Oxidation resistance; Fatigue resistance; Biomaterials

1. Introduction

Adhesive/abrasive wear of ultra-high molecular weight polyethylene (UHMWPE) components used in total joint arthroplasty is believed to cause peri-prosthetic osteolysis and limit the longevity of implants. Reduction in wear of UHMWPE components can be achieved by decreasing the large-scale deformation ability of the polymer. Cross-linking by ionizing radiation is generally used for this purpose [1-3] with a concomitant decrease in strength [4]. Cross-linking polyethylene with high dose radiation reduces chain mobility, reducing the extent of large-strain plastic deformation on wear surfaces during articulation [4]. Radiation also creates residual free radicals that are the well-known precursors to long-term oxidation in polyethylene. Currently the method of choice to improve the oxidation resistance of irradiated UHMWPE is melting, which decreases the concentration of residual free radicals to undetectable levels but also decreases the crystallinity of polyethylene. The combination of reduced chain mobility and reduced crystallinity decreases the resistance of irradiated and melted polyethylene to propagation of fatigue cracks [4]. An alternative approach to rendering UHMWPE oxidation resistant is to incorporate an antioxidant, such as vitamin E (α -tocopherol) into irradiated UHMWPE [5]. This vitamin E-stabilized irradiated

UHMWPE showed improved mechanical properties compared to irradiated and melted UHMWPE [5-7] because the decrease in crystallinity caused by post-irradiation melting was avoided. The hypothesis is that additional increase in the crystallinity of UHMWPE will increase the strength and fatigue resistance of the polymer. One approach is to increase the fatigue strength of unirradiated UHMWPE by high pressure crystallization and subsequent radiation cross-linking of this improved UHMWPE [8-11].

Polyethylene is a semi-crystalline material; the molecular weight of medical grade UHMWPE is in the range of $2-6 \times 10^6$ g/mol and it is 55–60% crystalline. High toughness and high fatigue strength of polyethylene are attributed to energy absorbing mechanisms such as cavitation and plastic deformation. The major energy absorbing mechanism in polyethylene is the plastic deformation of the amorphous and crystalline domains (crystal plasticity), which depends on ductility and the crystalline content. The crystalline lamellae of UHMWPE, which are embedded in an amorphous matrix, exhibit the ‘folded chain’ morphology when crystallized from the melt at close to ambient pressures.

Polyethylene exhibits a hexagonal crystalline phase at elevated temperatures and pressures [12]. In this phase, which is only encountered at pressures in excess of 210 MPa (Fig. 1), the individual chain stems are rotated at random phase angles with respect to each other, allowing for chains to slide past each other. The crystalline lamellae formed in this phase are called ‘extended chain’ crystals (ECC) and these crystals can grow to larger extent and also result in higher crystallinity [12,13]. This is believed to be a consequence of less hindered crystallization kinetics in the hexagonal phase compared with the orthorhombic phase [12,13]. High pressure crystallization of unirradiated GUR1050 UHMWPE at above 160 °C and 300 MPa yielded an approximately 70% crystalline UHMWPE, compared to 50–60% for conventional UHMWPE [14]. An increase in crystallinity of UHMWPE by HPC was shown to increase the resistance of UHMWPE to the propagation of fatigue cracks by about 25% [15] while no significant changes in ultimate tensile strength were observed [8].

We proposed to use a plasticizing agent (vitamin E) in UHMWPE during HPC. Since the growth of extended chains in the hexagonal phase was attributed to the ability of chain reptation and association resulting in less hindered crystallization kinetics, we postulated that the hindrance on the crystallization kinetics could be further reduced by introducing a compatible plasticizing agent into polyethylene. We hypothesized that the presence of a plasticizing agent during HPC would increase the crystallinity and the fatigue strength of the polymer. Overall, we expected higher crystallinity, higher strength, and higher wear from this material. Surprisingly, we found this material to have low wear despite an increase in its fatigue strength, representing a paradigm shift in our understanding of what governs wear and fatigue in polyethylene.

2. Materials and methods

2.1. Preparation of vitamin E-blended and high pressure crystallized UHMWPE (VEHPE)

Slab compression molded virgin UHMWPE and compression molded blocks of vitamin E/GUR 1050 UHMWPE powder blends (Orthoplastics Ltd, Lancashire, UK) were used. Virgin UHMWPE samples were used without further treatment. VEHPE samples were prepared as follows: 5 wt/wt% vitamin E (D, α -tocopherol, >98%, Fisher Scientific, Houston, TX) was mixed with UHMWPE powder, then the mixture was diluted to contain 0.1, 0.2, 0.3 and 1.0 wt% α -tocopherol by adding UHMWPE powder to the mixture. The mixtures were consolidated into $5.5 \times 10 \times 12$ cm blocks.

The UHMWPEs were machined to approximately 5 cm diameter and 15 cm long cylindrical blocks. One set of blocks from each of the five concentration groups were individually

placed in deionized water in a custom-built high pressure chamber. The sample was heated to 180 °C and kept at that temperature for 5 h, after which the pressure was raised to 310 MPa. The temperature and pressure were kept constant for 5 h. The sample was then cooled down to room temperature under pressure; and subsequently the pressure was released.

In the following studies, we used differential scanning calorimetry (DSC) to determine crystallinity and peak melting point, tensile mechanical testing to determine ultimate tensile strength (UTS), yield strength (YS), elongation to break (EAB) and work-to-failure (WF), fatigue crack propagation testing to determine fatigue strength, pin-on-disc wear testing to determine wear behavior and electron microscopy to investigate fracture surface morphology.

2.2. Determination of percent crystallinity by differential scanning calorimetry (DSC)

Specimens were weighed (approximately 5 mg) with a Sartorius CP 225D balance to a resolution of 0.01 mg and placed in aluminum sample pans. The pan was crimped with an aluminum cover and placed in a Q-1000 Differential Scanning Calorimeter (TA Instruments, Newark, DE). The sample and the reference were then heated at a heating rate of 10 °C/min from -20 °C to 180 °C under nitrogen purge. Heat flow as a function of time and temperature was recorded. Crystallinity of the samples ($n = 3$ each) was determined by integrating the enthalpy peak from 20 °C to 160 °C, and normalizing it with the enthalpy of melting of 100% crystalline polyethylene, 291 J/g. The peak melting point is also reported.

2.3. Tensile mechanical testing

Tensile specimens were stamped out of 3.2 mm-thick sections in accordance with ASTM D-638. These dog bone-shaped specimens ($n = 5$ each) were tested on an MTS machine (Insight, Eden Prairie, MN) at a cross head speed of 10 mm/min. The axial displacement and force were sampled at a rate of 100 Hz. The engineering stress was computed based on the nominal cross sectional area (before any deformation). The yield strength (YS) in MPa, and the ultimate tensile strength (UTS) in MPa were calculated per ASTM D-638 and the work-to-failure (WF), calculated as the area under the engineering stress-strain curve is reported in kJ/m². Elongation to break was measured using a laser extensometer.

2.4. Fatigue crack propagation testing

Fatigue crack propagation testing was done following ASTM E-647. Compact tension (CT) specimens ($n = 3$) were pre-cracked at the notch using a razor blade. Testing was conducted at a sinusoidal load cycle frequency of 5 Hz and stress ratio of 0.1 in tension. Crack length was monitored optically every 20,000 cycles. The average of the crack length on both sides of the CT specimen was used as the representative crack length for the computation of crack growth rates. Stress intensity factor ranges at crack inception (ΔK_I) were reported in MPa m^{1/2} at a threshold crack growth rate of 10⁻⁶ mm/cycle. All testing was done in an aqueous bath at 40 °C to simulate the physiologic temperature of the joint.

2.5. Freeze fracture and cyclic fracture analysis by scanning electron microscopy (SEM)

The test samples were first cooled down in liquid nitrogen for approximately 30 min. They were then fractured near liquid nitrogen temperatures to prepare freeze-fractured surfaces for SEM analysis. The freeze-fractured surfaces were gold-coated and analyzed with an environmental scanning electron microscope equipped with a field emission gun (SEM) (Phillips/FEI, XL30, Hillsboro, OR) to qualitatively evaluate morphology.

2.6. Determination of wear by pin-on-disc (POD) testing

Cylindrical pin shaped samples ($n = 3$, 9 mm in diameter and 13 mm in length) were used for POD wear testing. These pins were tested on our custom-built bi-directional POD tester [16] at a frequency of 2 Hz for 2 million cycles (MC) with gravimetric assessment of wear at every 0.5 MC. Undiluted bovine serum was used as lubricant with 33 ml penicillin–streptomycin solution per 500 ml as antibacterial agent and 1 mM EDTA as chelating agent. The wear rate was determined by linear regression of the weight change of each pin from 0.5 to 2 MC.

2.7. Determination of crystal structure by wide angle X-ray diffraction (WAXD)

A Rigaku RU-300 diffractometer (185 mm, The Woodlands, TX) was used to determine the crystal structure. The diffractometer was operated at 50 kV and 300 mA. The scatter and divergence slit widths were each $1/2^\circ$. The diffraction pattern was obtained from 5 to 90° at the rate of $4^\circ/\text{min}$. The peaks were fit using JADE (Materials Data Inc., Livermore, CA) with a residual error of $<3\%$.

In the following studies, where $n \geq 3$, statistical analysis was performed using Student's t -test for two-tailed distributions with unequal variance. Data sets with a p -value of 0.05 or lower was considered significantly different.

3. Results

High pressure crystallization (HPC) of virgin UHMWPE significantly increased the crystallinity from 54% to 68% (Fig. 2). Vitamin E presence during HPC increased the crystallinity significantly for the vitamin E concentrations of 0.1, 0.2, and 0.3 wt% in the VEHPE samples. The crystallinity of 1.0 wt% vitamin E-containing VEHPE was slightly higher than that of virgin HP UHMWPE but was significantly lower than that of the VEHPEs containing 0.1, 0.2, and 0.3 wt% vitamin E. The peak melting points were comparable at around 145°C for all VEHPEs regardless of the vitamin E concentration (Table 1). The melting peak contained a shoulder at 137°C that was most prominent in the 1 wt% VEHPE (not shown). Wide angle diffraction patterns showed that the high pressure crystallization did not alter the crystal structure of virgin and vitamin E-containing UHMWPEs (not shown).

The ultimate tensile strength (UTS) increased significantly with high pressure crystallization of virgin and vitamin E-containing UHMWPEs except with 0.1 wt% and 1.0 wt% vitamin E (Fig. 3). The yield strength (YS) of VEHPE increased significantly at all vitamin E concentrations (Fig. 4). The elongation at break (EAB) of virgin HP UHMWPE was significantly decreased while there was no significant difference in the EAB of the VEHPE samples compared to non-HPC vitamin E-blended UHMWPE prepared with the same vitamin E concentration (Fig. 5). Also, the EAB of 0.2, 0.3 and 1.0 wt% VEHPEs was significantly higher than virgin HP UHMWPE and 0.1 wt% VEHPE. The work-to-failure (WF) of virgin HP UHMWPE was comparable to non-HPC UHMWPE, that of 0.1 wt% VEHPE was decreased, and those of 0.2, 0.3 and 1.0 wt% VEHPEs were increased compared to non-HPC vitamin E-blended UHMWPE, but none of these changes were significant (Fig. 6).

The wear rate of virgin UHMWPE increased significantly after high pressure crystallization, whereas there was no significant change in the wear rate of vitamin E-containing UHMWPEs (VEHPEs) after high pressure crystallization (Fig. 7). High pressure crystallization significantly increased the fatigue strength of all UHMWPEs. The fatigue strengths of VEHPE samples were significantly higher than that of virgin HP UHMWPE except at 1.0 wt% (Fig. 8). The UTS and fatigue strength showed positive weak correlations

with increasing crystallinity (Fig. 9a and b, respectively), whereas the wear rate showed a strong negative correlation with increasing crystallinity in VEHPEs (Fig. 9c).

The SEM analysis of the freeze-fractured surfaces of virgin UHMWPE showed cavities after high pressure crystallization (Fig. 10). The vitamin E-containing UHMWPE samples showed no cavities under SEM (Fig. 11). After high pressure crystallization, the vitamin E-containing UHMWPE samples showed cavities as well with the exception of the 0.1 wt% blend (Figs. 12 and 13). Under high magnification some of the lamellae were also visible (Fig. 13). The cavitation in the 0.2, 0.3, and 1 wt% vitamin E-containing UHMWPE samples was more prevalent than the virgin UHMWPE after high pressure crystallization.

4. Discussion

According to our main hypothesis, vitamin E would act as a plasticizing agent in UHMWPE, increasing chain mobility during high pressure crystallization, thus leading to higher crystallinity than virgin UHMWPE. Our hypothesis tested positive. The increased peak melting point (Table 1) of virgin and vitamin E-containing UHMWPEs after high pressure crystallization indicated the formation of extended chain crystals and the increase in crystallinity in VEHPE in comparison to virgin HP UHMWPE suggested that vitamin E incorporation enhanced crystallization kinetics. We suggest that the pressure–temperature phase diagram of UHMWPE was altered by the presence of vitamin E (Fig. 14) with a lower critical temperature and pressure limit for transition into the hexagonal phase. Turell et al. [14] have shown that the crystallinity of UHMWPE increases with increasing pressure used during the HPC process, indicating that the further away the crystals are from the orthogonal to hexagonal transition, the higher is the resulting crystallinity. Hence, it is possible that vitamin E shifted the orthogonal to hexagonal transition to a lower pressure such that the vitamin E-containing UHMWPE was deeper into the hexagonal phase than virgin UHMWPE at the temperature we carried out our investigations, namely 180 °C.

The ultimate tensile strength (UTS) and yield strength (YS) of all UHMWPEs were improved after high pressure crystallization (Figs. 4 and 5, respectively), perhaps suggesting that the increased crystallinity enhanced these properties. On the other hand, the correlation between UTS and crystallinity was weak (Fig. 9a), suggesting that there may be other material properties affecting the UTS. It was expected that the increased crystallinity would lead to a decrease in the elongation at break (EAB) for HPC UHMWPE due to increased stiffness and decreased amorphous content. However, the decrease in the EAB of VEHPE due to HPC was less than that for the virgin HP UHMWPE even though the former showed higher increase in crystallinity. Furthermore, the EAB of VEHPE containing 0.2 wt% or more vitamin E was substantially higher than that of virgin HP UHMWPE, suggesting a possible increase in the mobility of the chains in the amorphous phase due to the presence of vitamin E despite overall higher crystallinity. These observations point to the possibility of vitamin E induced plasticization of UHMWPE in the high pressure crystallized form.

Our current understanding of wear reduction is based on a decrease in ductility brought about by the cross-linking of chains in the amorphous phase [17]. Because cross-linked UHMWPE is less ductile than unirradiated UHMWPE, it also followed that a decrease in wear was accompanied by a decrease in ductility. In fact, the mechanism of wear fibril break-up can be explained through the large-strain plastic deformation shown by ductile unirradiated UHMWPE. Since this material is able to deform to a large extent, orientation in the principal arc of motion is severe, causing these oriented fibrils to grow weaker in the transverse direction (Fig. 15). When the articulation at an angle to the principal motion causes tensile and shear stresses in the transverse direction exceeding the break stress of these fibrils, break-up of the fibrils occur leading to wear particle generation. While cross-

linked UHMWPE has lower tensile strength than unirradiated UHMWPE, it is less prone to large-strain plastic deformation and orientation, therefore resulting in less drastic changes in mechanical strength in the transverse direction.

Interestingly, the wear rate of VEHPEs was slightly less than their non-HPC counterparts (Fig. 7) while their ductility was comparable or higher. Also, the wear rate of virgin HP UHMWPE was higher than that of non-HPC UHMWPE, also supported by other's findings [11]. There was also a 50% difference between the wear rate of the virgin high pressure crystallized UHMWPE at 14 mg/MC and those of the high pressure crystallized vitamin E-containing UHMWPEs at about 7.5 mg/MC, even though the latter had on average higher elongation at break. These results suggest that the wear fibril break-up theory that explains the decrease in the wear resistance of virgin UHMWPE with cross-linking may not necessarily apply to high pressure crystallized UHMWPEs, especially in the presence of vitamin E. According to the wear fibril break-up theory described above, there are two ways in which wear can be reduced: One is by decreasing plastic deformation and strain hardening to reduce the formation of the fibrils (cross-linking does this), and the other is by increasing the strength of the oriented fibrils in the transverse direction. The former cannot explain the wear reduction in the presence of vitamin E in HPC UHMWPE. The latter may be more applicable because of the increase in the crystallinity in HPC UHMWPE with vitamin E; however this increase in crystallinity did not translate to any measurable increase in the tensile strength of the polymer (Fig. 3). On the other hand, the increase in the fatigue strength with the vitamin E addition in HPC UHMWPE may have played a role in improving the wear rate of the polymer. We propose to investigate this mechanism further and also augment the increase in wear resistance with cross-linking of the vitamin E-containing UHMWPE either before or after high pressure crystallization.

Our goal in increasing the crystallinity of UHMWPE by adding vitamin E prior to high pressure crystallization was to increase the fatigue strength of the polymer. The fatigue strength of 0.1, 0.2 and 0.3 wt% VEHPEs was enhanced compared to virgin HP UHMWPE (Fig. 8), but as with the UTS, fatigue strength was only a weak function of crystallinity (Fig. 9c). This suggests that there are additional mechanisms by which fatigue strength is increased or more specifically, by which crack growth is arrested. The increased number of cavities may have played a role in the crack growth arrest and increase in the fatigue strength. The cavities may have formed during high pressure crystallization through phase separation of vitamin E from the UHMWPE matrix. Upon cooling down and release of pressure the vitamin E occupying the cavities likely diffused back into the matrix. Cavities typically act as crack arrestors and may have increased the fatigue crack propagation of UHMWPE. At 1 wt% vitamin E there was a precipitous drop in the fatigue strength, which may be related to the concentration and size of the cavities. Beyond a critical size the cavities could act as initiation sites for secondary cracks and result in premature failure. Crystals in the hexagonal phase are less dense than those in the orthorhombic phase, which allows for more mobility and diffusion of chains along the *c*-axis of the crystal, resulting in extended chain growth [18]. Therefore the cavities observed in HPC UHMWPE could also have been caused by the shrinking of the crystals when UHMWPE underwent the phase transformation from hexagonal back to the orthorhombic phase upon cooling and depressurizing.

The wear and fatigue behavior of high pressure crystallized vitamin E-containing UHMWPE represent a paradigm shift in that our current understanding of wear reduction with cross-linking is also accompanied by a reduction in fatigue strength. It appears that we unveiled a new wear reduction mechanism in UHMWPE by plasticization and/or phase separation during high pressure crystallization. Therefore, it may be possible that when this material is cross-linked, it will need fewer cross-links to achieve the wear resistance of radiation cross-

linked UHMWPEs that are currently in clinical use and thus result in much higher fatigue strength. This material would also be expected to be oxidatively stable because of the antioxidant capability of vitamin E.

5. Conclusions

We have found that by using vitamin E during HPC, crystallinity could be enhanced. Concomitantly, fatigue strength was increased and wear rate was decreased. Although these changes could partly be explained by the increases in crystallinity, there appeared to be additional active mechanisms. By combining plasticization during HPC and radiation cross-linking, it may be possible to improve the fatigue strength of cross-linked UHMWPEs thereby obtaining a wear resistant and oxidation resistant joint bearing surface with improved fatigue strength. This is promising because fatigue damage and fatigue behavior under adverse loading conditions remain major concerns for the use of alternate bearing surfaces made of UHMWPE in total hip and especially total knee arthroplasty.

Acknowledgments

This work was funded by NIH R01 AR051142 and departmental funds.

References

- [1]. Muratoglu OK, Bragdon CR, O'Connor DO, Jasty M, Harris WH. HAP Paul Award. A novel method of crosslinking UHMWPE to improve wear, reduce oxidation and retain mechanical properties. *J Arthroplasty*. 1999; 16(2):149–60. [PubMed: 11222887]
- [2]. Muratoglu OK, Bragdon CR, O'Connor DO, Jasty M, Harris WH, Gul R, et al. Unified wear model for highly crosslinked ultra-high molecular weight polyethylenes (UHMWPE). *Biomaterials*. 1999; 20(16):1463–70. [PubMed: 10458559]
- [3]. McKellop H, Shen F-W, Lu B, Campbell P, Salovey R. Development of an extremely wear resistant ultra-high molecular weight polyethylene for total hip replacements. *J Orthop Res*. 1999; 17(2):157–67. [PubMed: 10221831]
- [4]. Oral E, Malhi A, Muratoglu O. Mechanisms of decrease in fatigue crack propagation resistance in irradiated and melted UHMWPE. *Biomaterials*. 2006; 27:917–25. [PubMed: 16105682]
- [5]. Oral E, Wannomae KK, Hawkins NE, Harris WH, Muratoglu OK. α -Tocopherol doped irradiated UHMWPE for high fatigue resistance and low wear. *Biomaterials*. 2004; 25(24):5515–22. [PubMed: 15142733]
- [6]. Oral E, Rowell S, Wannomae K, Muratoglu O. Migration stability of alphas-tocopherol in irradiated UHMWPE. *Biomaterials*. 2006; 27(11):2434–9. [PubMed: 16325903]
- [7]. Oral E, Christensen S, Malhi A, Wannomae K, Muratoglu O. Wear resistance and mechanical properties of highly crosslinked UHMWPE doped with vitamin E. *J Arthroplasty*. 2006; 21(4): 580–91. [PubMed: 16781413]
- [8]. Bistolfi, A.; Me, T.; Lee, Y-L.; Bellare, A. Morphological, wear and tensile properties of high crystallinity crosslinked UHMWPE; Transactions of the 51st annual meeting of the Orthopaedic Research Society; 2005; p. 240
- [9]. Oral, E.; Godleski, C.; Malhi, A.; Muratoglu, O. Cross-linking is not necessary to decrease wear of UHMWPE: a super-tough and low-wear UHMWPE; Transactions of the 52nd annual meeting of the Orthopaedic Research Society; Chicago, IL. 2006; p. 659
- [10]. Oral, E.; Godleski, C.; Muratoglu, O. Highly cross-linked, highly crystalline UHMWPE; Transactions of the 53rd annual meeting of the Orthopaedic Research Society; San Diego, CA. 2007; p. 19
- [11]. Simis KS, Bistolfi A, Bellare A, Pruitt LA. The combined effects of crosslinking and high crystallinity on the microstructural and mechanical properties of ultra high molecular weight polyethylene. *Biomaterials*. 2006; 27(9):1688–94. [PubMed: 16253325]

- [12]. Bassett DC, Block S, Piermarini G. A high-pressure phase of polyethylene and chain-extended growth. *J Appl Phys.* 1974; 45:4145.
- [13]. Wunderlich B, Davidson T. Extended-chain crystals. I. General crystallization conditions and review of pressure crystallization of polyethylene. *J Polym Sci B Polym Phys.* 1969; 7(12):2043–50.
- [14]. Turell, M.; Scherrer, P.; Thornhill, TS.; Bellare, A. Effect of high pressure processing on the crystallinity of UHMWPE; Transactions of the 29th annual meeting of the Society for Biomaterials; 2003; p. 376
- [15]. Baker DA, Hastings RS, Pruitt L. Compression and tension fatigue resistance of medical grade ultra high molecular weight polyethylene: the effect of morphology, sterilization, aging and temperature. *Polymer.* 2000; 41(2):795–808.
- [16]. Bragdon CR, O'Connor DO, Lowenstein JD, Jasty M, Biggs SA, Harris WH. A new pin-on-disk wear testing method for simulating wear of polyethylene on cobalt-chrome alloy in total hip arthroplasty. *J Arthroplasty.* 2001; 16(5):658–65. [PubMed: 11503127]
- [17]. Edidin AA, Pruitt L, Jewett CW, Crane DJ, Roberts D, Kurtz SM. Plasticity-induced damage layer is a precursor to wear in radiation-cross-linked UHMWPE acetabular components for total hip replacement. Ultra-high-molecular-weight polyethylene. *J Arthroplasty.* 1999; 14(5):616–27. [PubMed: 10475563]
- [18]. de Langen M, Prins K. NMR investigation of phase transitions in polyethylene in the vicinity of hexagonal high pressure phase. *Polymer.* 2000; 41:1175–82.

Fig. 1. Schematic phase diagram of ultra-high molecular weight polyethylene (UHMWPE). Approximate phase transition temperature and pressure from melt and orthorhombic phases to the hexagonal phase are marked.

Fig. 2.
Crystallinity of HPC UHMWPE as a function of vitamin E concentration.

Fig. 3.
Ultimate tensile strength (UTS) of HPC UHMWPE as a function of vitamin E concentration.

Fig. 4. Yield strength (YS) of HPC UHMWPE as a function of vitamin E concentration.

Fig. 5. Elongation at break (EAB) of HPC UHMWPE as a function of vitamin E concentration.

Fig. 6. Work-to-failure of HPC UHMWPE as a function of vitamin E concentration.

Fig. 7.
Wear rate of HPC UHMWPE as a function of vitamin E concentration.

Fig. 8. Fatigue crack propagation resistance of HPC UHMWPE as a function of vitamin E concentration.

Fig. 9.

(a). Ultimate tensile strength of HPC UHMWPE as a function of crystallinity. (b). Fatigue crack propagation resistance of VEHPE as a function of crystallinity. (c). Wear rate of VEHPE as a function of crystallinity.

Fig. 10.
SEM micrographs of freeze-fractured surfaces of (a and b) virgin non-HPC UHMWPE and (c and d) HPC UHMWPE. Note the arrows showing cavitation in the HPC samples.

Fig. 11.
SEM micrographs of freeze-fractured vitamin E-containing UHMWPE before HPC: (a) 0.1 wt% vitamin E, (b) 0.2 wt% vitamin E, (c) 0.3 wt% vitamin E, and (d) 1 wt% vitamin E.

Fig. 12.

SEM micrographs of freeze-fractured vitamin E-containing UHMWPE after HPC: (a) 0.1 wt % vitamin E, (b) 0.2 wt% vitamin E, (c) 0.3 wt% vitamin E, and (d) 1 wt% vitamin E. Note the arrows showing cavitation.

Fig. 13. SEM micrographs of freeze-fractured vitamin E-containing UHMWPE after HPC: (a) 0.2 wt % vitamin E, (b) 0.3 wt% vitamin E, and (c) 1.0 wt% vitamin E. Note that the arrows are showing cavities and some of the lamellae are marked by circles.

Fig. 14. Schematic phase diagram of vitamin E-blended ultra-high molecular weight polyethylene (UHMWPE).

Fig. 15.
Schematic depiction of a wear fibril in UHMWPE.

Table 1

Peak melting point temperatures of high pressure crystallized UHMWPE as a function of vitamin E concentration. High pressure crystallization was performed at 180 °C and 310 MPa.

Vitamin E concentration (wt/wt %)	Peak melting temperature before HPC (°C)	Peak melting temperature after HPC (°C)
0 (virgin)	135.1 ± 0.0	145.1 ± 0.2
0.1	136.2 ± 0.3	145.8 ± 0.4
0.2	136.4 ± 0.1	145.1 ± 1.2
0.3	136.1 ± 0.1	144.8 ± 0.7
1.0	136.4 ± 0.0	146.2 ± 0.6