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Free radical elimination in irradiated UHMWPE through crystal mobility in phase transition to the hexagonal phase

Ebru Oral [a,b], Christine Godleski Beckos [a], Orhun K. Muratoglu [a,b,*]

[a] *Orthopaedic Biomechanics and Biomaterials Laboratory, Department of Orthopaedic Surgery, Massachusetts General Hospital, 55 Fruit Street, GRJ 1206, Boston, MA 02114, USA*
[b] *Harvard Medical School, Boston, MA, USA*

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Ultra-high molecular weight polyethylene (UHMWPE) is radiation cross-linked to decrease wear in total joint applications. Irradiation decreases the strength of UHMWPE and introduces residual free radicals, which can cause oxidation in the long-term. We advanced a method eliminating the free radicals without a reduction in strength. UHMWPE exhibits a hexagonal phase at high pressure and temperature, where chain mobility in the crystalline phase is increased, leading to the formation of extended chain crystals. We hypothesized that the increased chain mobility during transformation from the orthorhombic to hexagonal phase could be used to eliminate the residual free radicals in irradiated UHMWPE. We eliminated the free radicals in 25-, 65- and 100-kGy irradiated UHMWPEs and these materials did not show oxidation after accelerated aging. The ultimate tensile strength and work-to-failure of 25 and 65-kGy irradiated UHMWPEs were improved significantly while that of 100-kGy irradiated UHMWPE was lower compared to irradiated UHMWPE melted at ambient pressure.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is the material of choice for total joint arthroplasty bearings. Radiation cross-linking has recently been used to reduce the wear of UHMWPE bearing surfaces, which has been associated with periprosthetic osteolysis in the long-term. Radiation cross-linking is achieved by the recombination of free radicals induced on the polyethylene chains in the amorphous phase by irradiation. However, free radicals formed in the crystalline phase cannot recombine and are trapped [1,2]. In the long-term, these free radicals presumably migrate to the crystalline/amorphous interface and cause embrittlement by reacting with diffused oxygen. Radiation cross-linked UHMWPEs are thermally treated after irradiation to improve oxidative stability. One approach is to thermally anneal irradiated UHMWPE below the melting point. While this method prevents complete melting and preserves the crystallinity of irradiated UHMWPE [3], it does not eliminate all free radicals, resulting in long-term oxidation [3–5]. Another approach is to melt the crystalline regions completely. This method reduces the residual free radicals to undetectable levels [6], while crystallization in the presence of the crosslinks leads to a lower crystallinity leading to a reduction in the mechanical properties [7,8].

UHMWPE exhibits a hexagonal phase at high temperature and high pressure [9,10], where crystal stems are randomly rotated and their mobility is increased [11,12]. In this more mobile hexagonal phase, 'extended chain crystals' are allowed to grow [13,14], which are larger in size than the 'folded chain crystals' exhibited by UHMWPE crystallized from the melt at ambient pressure (Fig. 1). In addition, the overall crystallinity of the material is increased, presumably increasing its mechanical strength [15].

We propose that the longevity of joint implants could be improved by improving the fatigue strength of radiation cross-linked UHMWPE using the hexagonal phase and extended chain morphology. One approach is to radiation cross-link high pressure crystallized UHMWPE. Using this method, high radiation doses have to be used to obtain wear resistance due to less amorphous content in high pressure crystallized UHMWPE. Another approach is to high pressure crystallize radiation cross-linked UHMWPE. In this method, cross-linked UHMWPE is first melted, then pressurized to obtain a transition from the melt to the hexagonal phase. Since radiation cross-linked UHMWPE is molten before pressurization, free radicals are eliminated, oxidative stability is gained.

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* Corresponding author. Orthopaedic Biomechanics and Biomaterials Laboratory, Department of Orthopaedic Surgery, Massachusetts General Hospital, 55 Fruit Street, GRJ 1206, Boston, MA 02114, United States. Tel.: +1 617 726 3869; fax: +1 617 643 2521.
E-mail address: omuratoglu@partners.org (O.K. Muratoglu).

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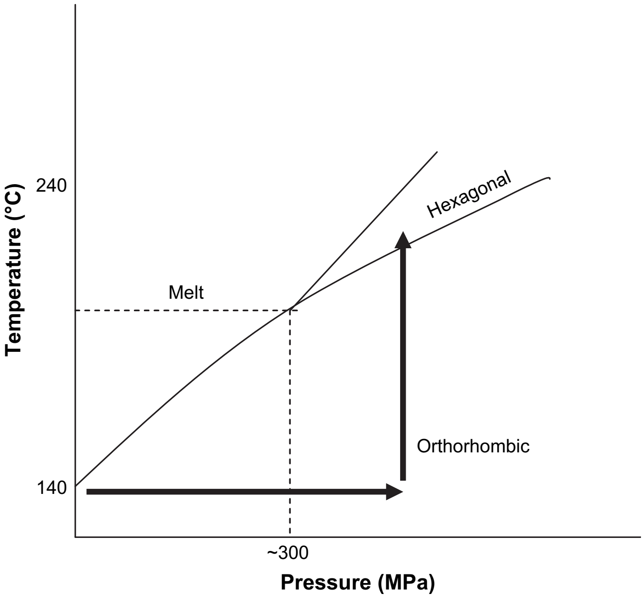

Fig. 1. Schematic phase diagram of UHMWPE. High pressure annealing (HPA) is achieved through pressurizing first, then heating to transition from the orthorhombic to the hexagonal phase.

While this approach works for low to moderate radiation doses in improving mechanical properties, at higher radiation doses the decreased chain mobility due to increased cross-link density inhibits extended chain crystal formation and results in inferior mechanical properties [16]. In this paper, we propose a third approach, in which radiation cross-linked UHMWPE is pressurized first, then heated such that it encounters the hexagonal phase through the orthorhombic phase without going through the melt phase. Rastogi et al. [12,17–19] have reported on the crystal growth behavior and enhanced mobility of uncrosslinked polyethylene chains during this transformation. In addition, it was shown that small samples of solution crystallized, radiation cross-linked UHMWPE can exhibit extended chain morphology [18].

We hypothesized that residual free radicals in cross-linked UHMWPE would have enough mobility during the hexagonal phase transformation to recombine with each other. This would render the cross-linked UHMWPE oxidation resistant. In addition, we further hypothesized that the mechanical properties could be improved due to extended chain crystal formation via this transformation. In this manner, a wear and oxidation resistant UHMWPE joint bearing surface with improved mechanical strength can be obtained without post-irradiation melting.

2. Materials and methods

2.1. Preparation of radiation cross-linked, high pressure annealed UHMWPE

Slab compression molded GUR1050 UHMWPE (Orthoplastics, Lancashire, UK) was packaged in double layer packaging in vacuum. Packaged material was irradiated to 25-kGy by gamma irradiation (Steris Isomedix, Northborough, MA). Cross-linked UHMWPEs irradiated to 65-kGy and 100-kGy by electron beam irradiation at 120 °C and 40 °C, respectively, were obtained from the manufacturer (Zimmer, Inc.).

Blocks (approximately 5 × 5 × 10 cm) were cut from radiation cross-linked UHMWPEs. One block at each time was placed in a custom-built high pressure chamber (High Pressure Equipment Co., Erie, PA) in deionized water. The chamber was pressurized to about 200 MPa, then heated to about 200 °C. The temperature and pressure were kept steady at 200 °C and 380 MPa for at least 5 h. Then the sample was cooled under pressure to about 25–60 °C and the pressure was released. The samples that have been processed in this manner are called high pressure annealed (HPA) UHMWPE.

Another set of high pressure annealing experiments were performed in the same manner at 220 °C and 380 MPa. Additional samples were melted in argon gas at 200 °C to serve as control irradiated and melted UHMWPE.

2.2. Determination of free radical concentration

A 3 × 3 × 10 mm section was cut from each block. The sections ($n = 2$) were analyzed by a Bruker EMX EPR system (Bruker BioSpin Corporation, Billerica, MA) at the Department of Physics at the University of Memphis (Memphis, TN). The free radical content of all samples was calculated by double integration of the ESR signal over the magnetic field and normalizing by the sample weight.

2.3. Determination of oxidative stability by accelerated aging

Non-HPA and HPA blocks (1 × 1 × 1 cm, $n = 3$) were accelerated aged at 80 °C for 5 weeks in air. Oxidation analysis was performed on thin (~150 μm) sections that were cut from an interior surface using a sledge microtome (Model 90-91-1177, LKB-Produkter AB, Bromma, Sweden) before and after accelerated aging. Infrared spectra were collected across the width of each thin section in 100 μm intervals, with each spectrum recorded as an average of 32 individual infrared scans. An oxidation index was calculated by normalizing the absorbance over 1680–1780 cm^{-1} to the absorbance over 1330–1390 cm^{-1}. The surface oxidation index (SOI) was calculated as the average of the oxidation indices over the first 3 mm of the sample per ASTM F2102-01$^{\varepsilon 1}$.

2.4. Determination of crystalline content

The DSC specimens were weighed 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. 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 here.

2.5. Determination of tensile mechanical properties

Thin sections (3.2 mm) were machined from the non-HPA and HPA UHMWPEs (Eastern Tool, Medford, MA). Dogbone specimens ($n = 5$ each) were stamped from these sections in accordance with ASTM D638, standard test method for tensile properties of plastics. These samples were then tested in accordance with ASTM D638 using an MTS II machine (Eden Prarie, MN) at a crosshead speed of 10 mm/min. The engineering ultimate tensile strength, yield strength, elongation to break and work-to-failure, calculated as the area under the engineering stress–strain curve, are reported.

2.6. Determination of cross-link density

Cross-link density measurements were performed by thermal mechanical analysis (DMA 7e, Perkin Elmer, Wellesley, MA). Thin sections machined from radiation cross-linked HPA UHMWPE were melted at 170 °C under nitrogen purge to remove any stresses residual from the consolidation process that might result in additional swelling during cross-link density measurements.

Small sections were cut out by razor blade from these thin sections to be analyzed (approximately 3 mm by 3 mm). These small pieces were placed under the quartz probe of the DMA (10 mN) and the initial height of the sample was recorded after about 10 min when the creep deformation equilibrated. Then, the probe was immersed in xylene, which was subsequently heated to 130 °C and held for 180 min. The UHMWPE samples swelled in hot xylene until equilibrium was reached. The final height was recorded. A linear equilibrium expansion ratio was calculated by dividing the final height by the initial height and a volumetric equilibrium expansion ratio, q_{eq}, was calculated by cubing the linear expansion ratio assuming that swelling was isotropic. The cross-link density of the samples ($n = 3$ each) was calculated as described previously [20] using the following equations:

$$\mathrm{d}x = \frac{\ln\left(1 - q_{\mathrm{eq}}^{-1}\right) + q_{\mathrm{eq}}^{-1} + Xq_{\mathrm{eq}}^{-2}}{V_1 q_{\mathrm{eq}}^{-1/3}} \tag{1}$$

$$X = 0.33 + \frac{0.55}{q_{\mathrm{eq}}} \tag{2}$$

where the specific volume of xylene, V_1, was 136 cm^3/mol. Measurements were made on radiation cross-linked UHMWPE before and after HPA.

In all studies in which there were at least three samples, statistical analysis was performed and p values were calculated using Student's t-test for two-tailed distributions with unequal variance.

3. Results

High pressure annealing reduced the free radical content to very low or negligible levels in all irradiated UHMWPEs compared to non-HPA UHMWPE (Fig. 2a–c). The non-HPA irradiated samples exhibited allyl/alkyl radicals with some oxygen induced free radicals as observed by the singlet at 3500 Gauss (Fig. 2a–c). All irradiated HPA samples exhibited a small peak at 3500 Gauss.

While all non-HPA irradiated UHMWPEs oxidized heavily under accelerated aging conditions, none of the irradiated HPA UHMWPE showed oxidation above an SOI of 0.12 (Fig. 3a–c). For 25-kGy irradiated UHMWPE, the surface oxidation index for 25-kGy, 65-kGy and 100-kGy irradiated UHMWPEs was increased significantly upon accelerated aging. In contrast, the irradiated samples that were subjected to HPA showed no significant increase in oxidation after accelerated aging except the 100-kGy irradiated UHMWPE that was annealed at 200 °C and 380 MPa.

The cross-link density of radiation cross-linked UHMWPE was not detrimentally affected by high pressure annealing. The cross-link density was unchanged after annealing at 200 °C (Table 1; $p = 0.81$, 0.85 and 0.33, respectively, for 25-, 65- and 100-kGy irradiated UHMWPEs). The cross-link density was lower for 25-kGy irradiated UHMWPE ($p = 0.02$), did not change significantly for 65-kGy irradiated UHMWPE ($p = 0.74$) and was higher for 100-kGy irradiated UHMWPE ($p = 0.02$) after annealing at 220 °C.

The changes in mechanical properties are summarized in Fig. 4–7. At 25-kGy of radiation, HPA treatment increased the ultimate tensile strength (UTS) and work-to-failure (WF) of irradiated UHMWPE (Figs. 4 and 5). At this dose, yield strength (YS) remained unchanged (Fig. 6) while the elongation at break (EAB) decreased (Fig. 7). At 65-kGy, the changes in the UTS and WF after HPA were negligible. At this dose, there was a slight increase in YS and a slight decrease in EAB. At 100 kGy, HPA decreased both UTS and WF, increased YS while EAB decreased for the sample annealed at

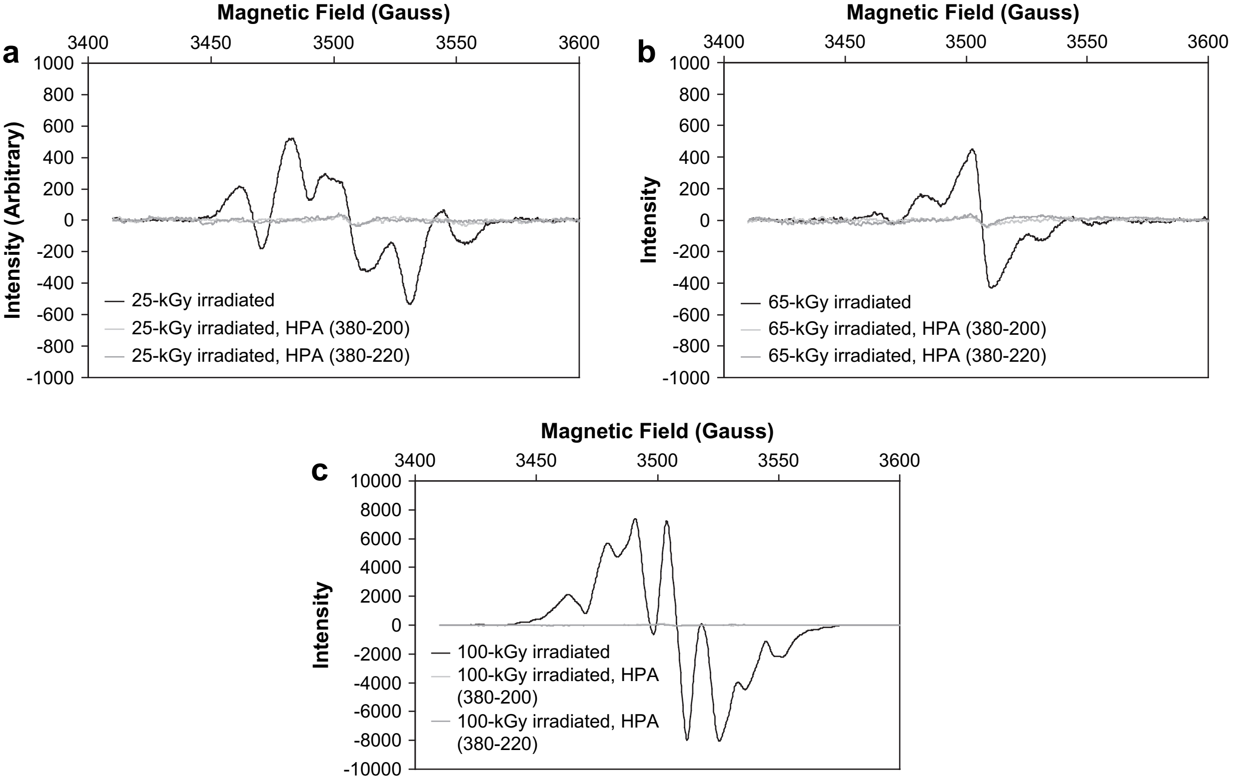

Fig. 2. Free radical signal of (a) 25-kGy irradiated, (b) 65-kGy irradiated, (c) 100-kGy irradiated and subsequently high pressure annealed UHMWPE.

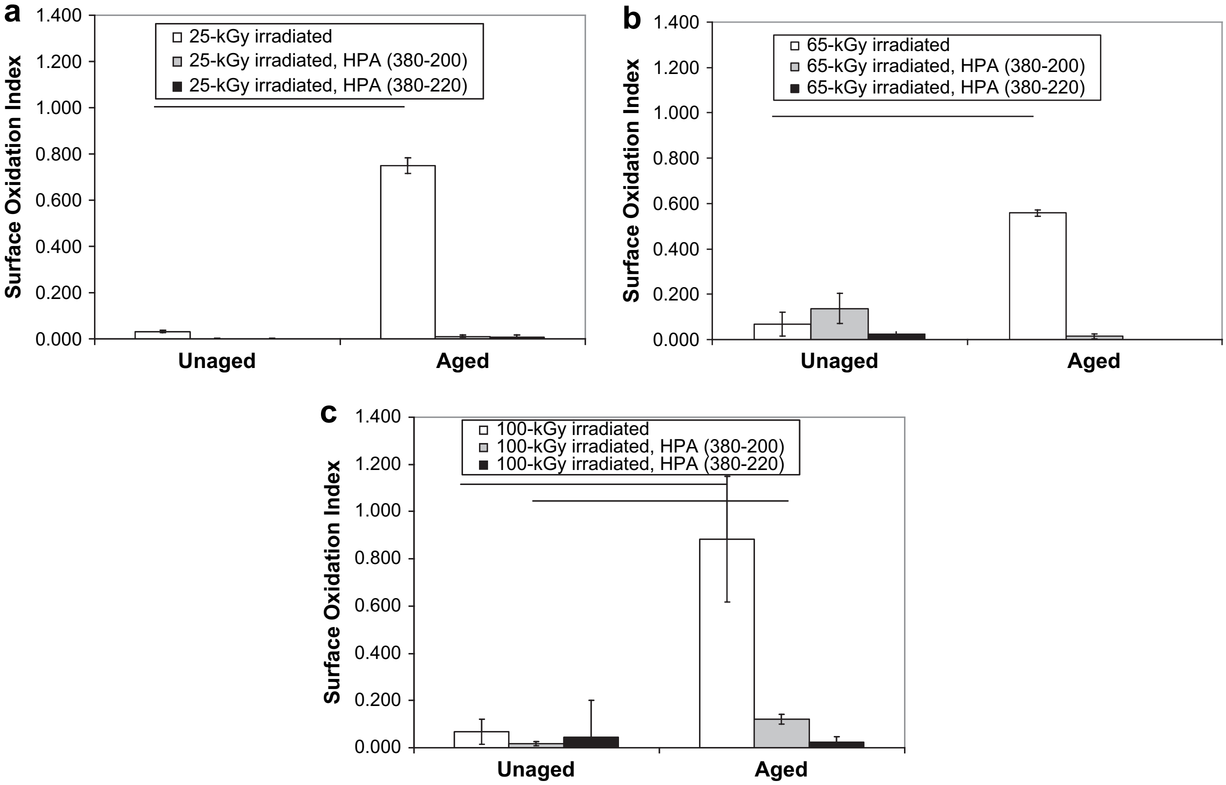

Fig. 3. Surface oxidation index of (a) 25-kGy irradiated, (b) 65-kGy irradiated, (c) 100-kGy irradiated and subsequently high pressure annealed UHMWPE after oven aging at 80 °C for 5 weeks. The lines between data sets show statistically significant differences ($p < 0.05$).

200 °C and 380 MPa and increased for the sample annealed at 220 °C and 380 MPa.

The crystallinity of irradiated UHMWPEs decreased significantly after melting at 200 °C for 65 and 100-kGy radiation doses (Table 2; $p = 0.13$, 0.006 and 0.0002 for 25-, 65- and 100-kGy irradiated UHMWPEs, respectively). Compared to their irradiated counterparts, only 25-kGy irradiated HPA UHMWPE annealed at 200 °C showed significantly higher crystallinity ($p = 0.02$, 0.12 and 0.89 for 25-, 65- and 100-kGy irradiated UHMWPEs, respectively). Both 25- and 65-kGy irradiated HPA UHMWPEs annealed at 220 °C showed significantly higher crystallinity ($p = 0.04$, 0.01 and 0.37 for 25-, 65- and 100-kGy irradiated UHMWPEs, respectively). Also, the crystallinity of irradiated HPA UHMWPE annealed at 200 °C and 220 °C was not significantly different from each other ($p = 0.54$, 0.17 and 0.26 for 25-, 65- and 100-kGy irradiated UHMWPEs, respectively). Compared to irradiated, melted UHMWPE, all irradiated HPA UHMWPEs showed higher crystallinity ($p = 0.02$, 0.01 and 0.00002 for 25-, 65- and 100-kGy irradiated UHMWPEs annealed at 200 °C and $p = 0.01$, 0.003 and 0.01 for, 25-, 65- and 100-kGy irradiated UHMWPEs annealed at 220 °C, respectively).

The peak melting point (PMT) of irradiated HPA UHMWPEs was not different from non-HPA UHMWPE at all radiation doses studied (Table 3). The peak melting point of all 25-kGy and 100-kGy irradiated HPA UHMWPEs was higher when compared to that of irradiated and melted UHMWPE while 65-kGy irradiated UHMWPE showed a peak melting point comparable to that of 65-kGy irradiated and melted UHMWPE (Table 3).

Table 1
Cross-link density (mol/m^3) of radiation cross-linked, high pressure annealed UHMWPE.

Radiation dose (kGy)	Irradiated	Irradiated, HPA (380 MPa, 200 °C)	Irradiated, HPA (380 MPa, 220 °C)
25	93 ± 3	92 ± 3	84 ± 3
65	162 ± 6	161 ± 11	161 ± 2
100	189 ± 9	198 ± 16	221 ± 3

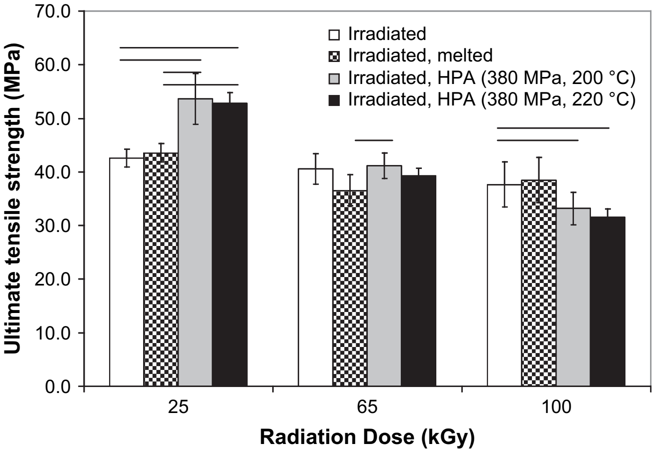

Fig. 4. Ultimate tensile strength of irradiated, irradiated and melted and high pressure annealed UHMWPEs as a function of radiation dose. The lines between data sets show statistically significant differences ($p < 0.05$).

4. Discussion

One aim of high pressure annealing of cross-linked UHMWPE was to eliminate the residual free radicals in highly cross-linked UHMWPE. The free radicals formed in the crystalline regions are trapped over long period of time [1,2] because the lattice spacing is

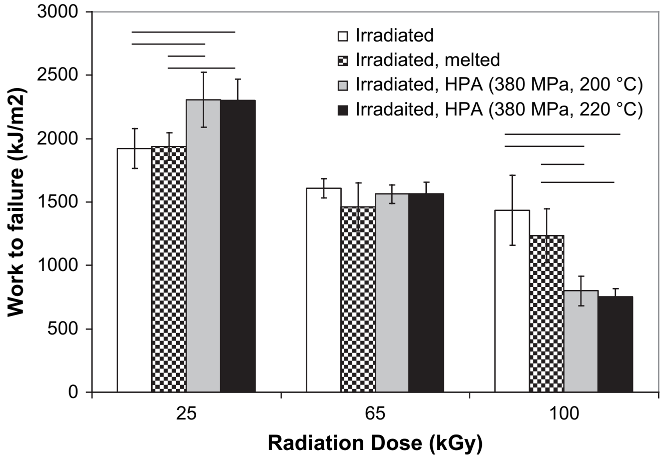

Fig. 5. Work-to-failure of irradiated, irradiated and melted and high pressure annealed UHMWPEs as a function of radiation dose. The lines between data sets show statistically significant differences ($p < 0.05$).

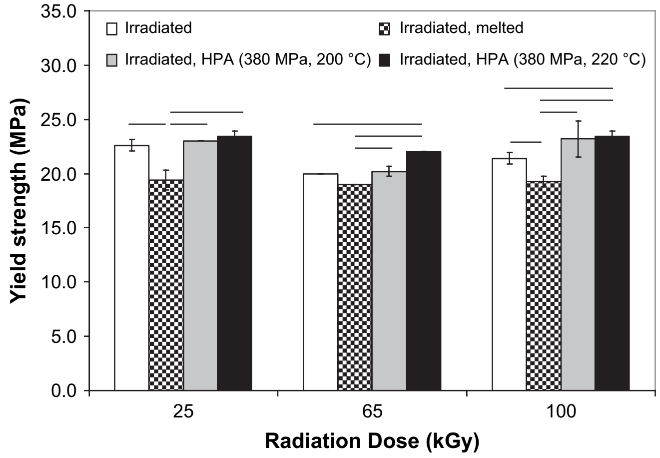

Fig. 6. Yield strength of irradiated, irradiated and melted and high pressure annealed UHMWPEs as a function of radiation dose. The lines between data sets show statistically significant differences ($p < 0.05$).

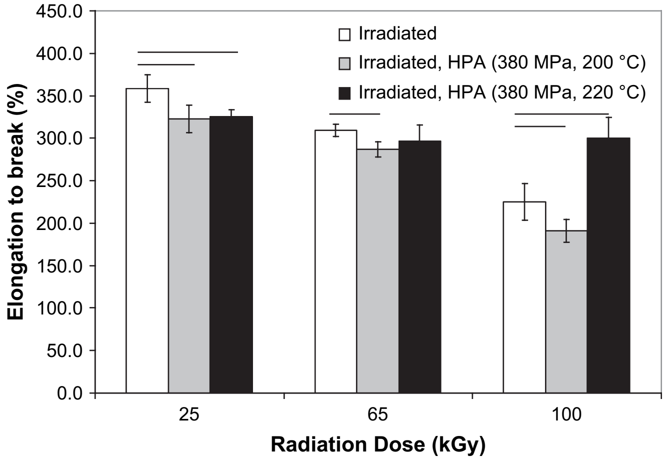

Fig. 7. Elongation to break of irradiated, irradiated and melted and high pressure annealed UHMWPEs as a function of radiation dose. The lines between data sets show statistically significant differences ($p < 0.05$). Data for irradiated and melted UHMWPE could not be reported due to equipment malfunction during testing.

Table 2
Crystallinity (%) of radiation cross-linked and high pressure annealed UHMWPE.

Radiation dose (kGy)	Irradiated	Irradiated, melted	Irradiated, HPA (380 MPa, 200 °C)	Irradiated, HPA (380 MPa, 220 °C)
25	61 ± 2	55 ± 4	71 ± 1	70 ± 2
65	59 ± 1	51 ± 1	62 ± 2	65 ± 1
100	59 ± 1	51 ± 1	63 ± 2	65 ± 3

larger than the length of carbon–carbon bond, not allowing recombination of the free radicals on adjacent chain segments. During the transition to the hexagonal phase, the crystalline chains become more mobile than they are in the orthorhombic phase, allowing additional crystal growth. In the hexagonal phase, the unit cell dimensions along the *b* and *c*-axes are reduced. Our first hypothesis was that the mobility in the chains during the phase transition would aid in the recombination and escape of the free radicals into the amorphous phase, effectively resulting in the elimination of the trapped free radicals without complete melting of the crystals.

Our first hypothesis tested positive. The free radicals in all irradiated UHMWPEs were reduced to negligible or very low levels following high pressure annealing (Fig. 2a–c). Since the detection limit of ESR is considered to be 10^{14} spins/g and the values for 65- and 100-kGy irradiated HPA UHMWPEs were very close to this detection limit (not shown), we performed accelerated aging on irradiated HPA UHMWPE to ascertain that these materials were oxidatively stable. The only irradiated HPA UHMWPE which showed small but significant oxidation compared to its unaged state was 100-kGy irradiated HPA UHMWPE annealed at 200 °C and 380 MPa.

Although the free radical signal in all irradiated UHMWPEs were very low, the slight oxidation in 100-kGy irradiated UHMWPE annealed at 200 °C (Fig. 3c) suggested that the free radicals may not have been completely eliminated in this sample. This was presumably due to the 100-kGy irradiated UHMWPE having a high cross-link density (Table 1), and the polymer chains in this network being the least mobile. This prompted us to increase the annealing temperature to 220 °C to increase the chain mobility in this UHMWPE during annealing. As a result, the free radicals in this more highly cross-linked UHMWPE were reduced to undetectable levels as well. Also in support of the oxidative stability of irradiated HPA material, accelerated aging did not result in any significant oxidation in annealed UHMWPEs (Fig. 3a–c). This suggested that high pressure annealing can be used as an alternative method to oxidatively stabilize cross-linked UHMWPE without melting the polymer.

Our second hypothesis was that the mechanical strength of radiation cross-linked UHMWPE could be improved through high pressure annealing. This hypothesis tested positive for 25-kGy and 65-kGy irradiated UHMWPEs evidenced by the increase in their yield and ultimate tensile strengths when compared to their oxidatively stable irradiated and melted non-HPA counterparts (Figs. 4 and 5). For 100-kGy irradiated UHMWPE, despite an increase in the yield strength, the ultimate tensile strength was reduced. We have shown previously that the improvement of mechanical properties due to extended chain growth in radiation

Table 3
Peak melting temperature (°C) of radiation cross-linked and high pressure annealed UHMWPE.

Radiation dose (kGy)	Irradiated	Irradiated, melted	Irradiated, HPA (380 MPa, 200 °C)	Irradiated, HPA (380 MPa, 220 °C)
25	138.4 ± 0.2	132.5 ± 0.2	141.2 ± 0.1	141.2 ± 0.1
65	141.0 ± 0.3	139.1 ± 0.2	139.6 ± 0.3	141.6 ± 0.7
100	140.8 ± 0.2	135.6 ± 0.4	140.1 ± 0.7	141.9 ± 0.6

cross-linked UHMWPE was dependent on chain mobility in the amorphous phase and thus was affected by radiation dose [16], with UHMWPE with lower cross-link density showing better property improvement. This is because cross-linking results in a less mobile amorphous phase with more junction points, limiting the extent to which polymer chains can crystallize or contribute to lamellar growth and extended chain formation in highly cross-linked UHMWPE during high pressure crystallization. In the previous study, we had initially melted irradiated polyethylene, and subsequently pressurized it to achieve the melt to hexagonal phase transition, whereas in this study, we pressurized the cross-linked UHMWPE first, therefore achieving a solid-state transition from the orthorhombic to the hexagonal phase. We had observed better improvement in the properties of 65-kGy irradiated UHMWPE during high pressure crystallization through the melt compared to high pressure annealing, which suggests that amorphous chain confinement may be more effective in decreasing the extent of lamellar growth in highly cross-linked UHMWPE during hexagonal transition from the orthorhombic phase.

We have attributed the increase in the UTS, YS and WF of high pressure crystallized unirradiated UHMWPE largely to the formation of extended chain crystals [15]. The fact that we observed mechanical property improvements with UHMWPE crystallized at high temperatures and pressures [15] below the previously reported triple point [12,21] corroborated that there is a region below and close to the hexagonal phase where chain mobility and lamellar growth are enhanced. This may also be valid for radiation cross-linked UHMWPE. In addition, although there is a positive correlation between the crystallinity and strength (unpublished data), the effect of the state of the amorphous phase on the mechanical strength of high pressure crystallized or high pressure annealed UHMWPE has not been studied and may have a significant effect on the properties. The higher mechanical properties for 25-kGy irradiated HPA UHMWPE compared to irradiated UHMWPE (Figs. 4–6) were accompanied by a significant increase in crystallinity (Table 2), but the peak melting point was not significantly increased (Table 3). This suggests that when the cross-linked UHMWPE transitioned through the hexagonal phase from the orthorhombic phase, crystal growth was dominated by folded chain crystals rather than extended chain crystals. It is also possible that extended chain growth could not be completed in cross-linked UHMWPE due to the intrinsic lack of mobility and decreased molecular weight between crosslinks.

It is clear that there is a large effect of radiation dose and cross-link density on crystal growth and mechanical strength improvement during high pressure annealing. As expected, less cross-linked UHMWPE, which contains more mobile chains with intrinsically larger molecular weight between cross-links showed more improved strength. It is most appropriate to compare the mechanical properties of cross-linked HPA UHMWPE to irradiated and melted UHMWPE because the goal is to achieve a wear and oxidation resistant cross-linked UHMWPE. The irradiated HPA UHMWPEs without detectable free radicals and the non-HPA irradiated and melted UHMWPEs would be expected to have similar oxidative stability. Cross-link density of a network has been directly related to wear [20], therefore, it can be deduced that since cross-linked HPA UHMWPE has similar cross-link density to non-HPA UHMWPE (Table 1), it will also show similar wear behavior. However, unless it is oxidatively stabilized by subsequent melting, irradiated non-HPA UHMWPE contains residual free radicals and oxidizes (Fig. 3a–c), whereas irradiated HPA UHMWPEs, except 100-kGy irradiated UHMWPE annealed at 380 MPa and 200 °C, were oxidatively stable.

The ultimate tensile strength (Fig. 4) and plasticity of 100-kGy irradiated UHMWPE, as reported by the work-to-failure (Fig. 5), were reduced after high pressure annealing. This may suggest chain scissioning of tie-chains between crystalline regions placed under stress due to the phase transformation. The drastic increase in the EAB (Fig. 7) after high pressure annealing at 380 MPa and 220 °C may also support this explanation. This behavior was in contrast to decreasing EAB in 25 and 65-kGy irradiated HPA UHMWPEs, which would be expected due to the higher crystallinity without network degradation. Also, since the increase in the yield strength is not accompanied by an increase in the ultimate tensile strength, it is possible that the slight increase in the crystallinity of this highly cross-linked HPA UHMWPE (Table 2) may be due to the recrystallization of degraded chains rather than the formation of any new crystals. A decrease in cross-link density would be expected to accompany such degradation and recrystallization but is not present. Therefore, the mechanism by which the mechanical properties were decreased for highly cross-linked HPA UHMWPE remains unknown, but these results point to a low limit of chain mobility associated with high cross-link density where high pressure annealing can be used without sacrificing mechanical properties.

5. Conclusions

High pressure annealing could be used to eliminate free radicals in radiation cross-linked UHMWPE without the need for melting. Concomitantly, the mechanical properties of irradiated UHMWPE, mobile enough to form additional crystals in the hexagonal phase, could be improved for UHMWPEs with low to moderate cross-link density.

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