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The elimination of free radicals in irradiated UHMWPEs with and without vitamin E stabilization by annealing under pressure

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Abstract

Radiation crosslinking of ultrahigh molecular weight polyethylene (UHMWPE) has been used to decrease the wear of joint implant bearing surfaces. While radiation crosslinking has been successful in decreasing femoral head penetration into UHMWPE acetabular liners *in vivo*, postirradiation thermal treatment of the polymer is required to ensure the oxidative stability of joint implants in the long term. Two types of thermal treatment have been used: (i) annealing below the melting point preserves the mechanical properties but the residual free radicals trapped in the crystalline regions are not completely eliminated, leading to oxidation in the long-term and (ii) annealing above the melting point (melting) eliminates the free radicals but leads to a decrease in mechanical properties through loss of crystallinity during the melting process. In this study, we hypothesized that free radicals could be reduced by annealing below the melting point under pressure effectively without melting due to the elevation of the melting point. By avoiding the complete melting of UHMWPE, mechanical properties would be preserved. Our hypothesis tested positive in that we found the radiation-induced free radicals to be markedly reduced (below the detection limit of state-of-the-art electron spin resonance) by thermal annealing under pressure in radiation crosslinked virgin UHMWPE and UHMWPE/vitamin-E blends without loss of mechanical properties.

Keywords

arthroplasty; bearing surfaces; crystallinity; polyethylene (UHMWPE); radiation

INTRODUCTION

Radiation crosslinking and subsequent thermal treatment of ultrahigh molecular weight polyethylene (UHMWPE) total joint implant bearing surfaces is commonly used to decrease wear volume and increase oxidative stability, respectively.¹ Radiation crosslinking was introduced as a measure to protect against wear particle-induced osteolysis,² one of the major factors currently limiting the longevity of joint implants.³ During irradiation, free radicals are formed in UHMWPE through bond cleavage and most of these free radicals are recombined in the form of crosslinks in the amorphous phase.⁴ However, the free radicals formed in the crystalline phase are long-lived⁵ and cause embrittlement through cascading oxidation reactions.^{6,7} Therefore, the postirradiation thermal treatment step has been used to reduce or eliminate these ‘residual’ free radicals.

One method of thermal treatment is annealing below the peak melting point of the irradiated polymer.^{8,9} In this case, some of the crystalline regions are melted and the free radical content is reduced, but is still detectable.^{10,11} One first generation of highly crosslinked and annealed UHMWPE implants was terminally gamma sterilized and therefore had a significant amount of detectable free radicals, leading to oxidation *in vivo*.^{12,13} The clinical impact of this oxidation is not yet clear.

Another method of postirradiation treatment is melting. Using this method, residual free radicals are reduced to undetectable levels as measured by state-of-the-art electron spin resonance equipment.¹⁴ On the other hand, crystallinity is reduced after the melting step due to the hindrance created by the newly formed crosslinks and therefore, mechanical properties and fatigue resistance are reduced.¹⁵

An alternative method of stabilizing the residual free radicals in UHMWPE is the incorporation of the antioxidant vitamin E in radiation crosslinked UHMWPE.^{16,17} There are two methods of incorporating vitamin E in radiation crosslinked UHMWPE. One is post-irradiation diffusion of vitamin E.¹⁸ While this UHMWPE has detectable free radicals, these free radicals have not caused oxidation up to 3 years *in vitro*.^{19,20} This is presumably due to the vitamin E's ability to break the chain reaction that leads to runaway oxidation by preventing the formation of secondary free radicals and further oxidation reactions.²¹ It has to be noted that this material contained approximately ~1 wt % vitamin E, and vitamin E incorporation by diffusion contained inherent thermal annealing because the process comprised a doping and a homogenization step, both at below but fairly close temperatures (120–130°C) to the peak melting point of irradiated UHMWPE (~140°C).¹⁸ It was also terminally gamma sterilized, introducing more free radicals in the material.

Another method of incorporating vitamin E in UHMWPE is by blending into powder before consolidation into solid form and subsequent radiation crosslinking.^{22–24} In this case, the vitamin E concentration and radiation dose have to be optimized carefully since vitamin E hinders crosslinking when present during irradiation. Furthermore, vitamin E loses activity during irradiation, decreasing the amount available to protect the material against oxidation after implantation. These irradiated blends contain up to 0.2 wt % vitamin E,²⁵ which is further reduced due to irradiation. This material also contains detectable free radicals, the reduction of which by a complimentary method such as the one proposed here may be beneficial in enhancing its oxidative stability provided by vitamin E in the longer term.

Radiation crosslinked UHMWPE, which has been diffused with vitamin E as described above and terminally gamma sterilized, has been in clinical use in total joint replacement since 2007. There are ongoing prospective, randomized clinical studies investigating the clinical performance of this material, but results are not yet published.

Several other methods for eliminating free radicals by inducing mobility in the crystalline domains without complete melting of the domains have been proposed to preserve the mechanical properties otherwise lost during melting. One method was the mechanical deformation of irradiated UHMWPE followed by thermal annealing for dimensional recovery.²⁶ Another was applying high pressure and temperature to induce the phase transformation from orthorhombic to hexagonal crystal structure without going through the melt phase, again enhancing mobility and demonstrating the elimination of free radicals.²⁷

In this study, we hypothesized that elevation of the melting point of irradiated UHMWPE by annealing under pressure would enhance the elimination of free radicals at low pressures (~70 MPa) where a crystalline phase transformation was not induced. The increase in the energy of the chains will increase as a function of the increase in the annealing temperature commensurate with the increase in the peak melting temperature under pressure.

In order to test our hypotheses, we annealed radiation crosslinked virgin and 0.2 wt % vitamin E blend of UHMWPE under pressure at below, at and above the peak melting point. We measured the changes in crystallinity, free radical content, and mechanical properties.

MATERIALS AND METHODS

Preparation of radiation crosslinked, pressure annealed UHMWPEs

Slab compression molded virgin UHMWPE (GUR1050 medical grade, Orthoplastics, Lancashire, UK) was irradiated to 100 kGy by electron-beam irradiation using a 10 MeV beam line (Iotron, Vancouver, BC). The stock was cut into approximately $5 \times 5 \times 10$ cm blocks and placed in deionized water in a custom-built high pressure chamber. The samples were pressurized to about 70 MPa and heated to the desired temperature. The pressure was released to within ~ 3.5 MPa during the heating process. The temperature and pressure readings were recorded. The temperature and pressure were kept constant for 5 hours. The samples were then cooled down to room temperature and subsequently the pressure was released. The list of all samples prepared for this study is given in Table I.

Vitamin E blended UHMWPE (GUR1050 medical grade consolidated by compression molding) was procured from Orthoplastics (0.2 wt %). One-cm thick samples were machined from 0.2 wt % vitamin E-blended UHMWPE blocks and irradiated to 200 kGy at 25 kGy/pass using a 2.5 MeV beam line (High Voltage Research Laboratories, Massachusetts Institute of Technology, Cambridge, MA). The processing conditions used with vitamin E-blended, irradiated UHMWPE are also shown in Table I.

All further analysis was made on samples machined at least 0.5 cm away from the surface of the annealed blocks.

Determination of crystallinity

Specimens were weighed with a Sartorius CP 225D balance to a resolution of 0.01 milligrams 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 $10^\circ\text{C}/\text{min}$ 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.

Determination of free radical content

A $30 \times 30 \times 10$ 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) within 4 days of preparation. 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.

Tensile mechanical testing

Two coplanar thin sections (3.2 mm) were machined (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 D-638 using a MTS II machine (Eden Prairie, MN) at a crosshead speed of 10 mm/min. The engineering ultimate tensile strength (UTS) is reported. In addition, the true elongation at break (EAB) was determined using a laser extensometer.

Pin-on-disc (POD) wear 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 bidirectional POD tester²⁸ under constant load (a nominal pressure of 2.56 MPa per pin) at a frequency of 2 Hz for 1 million cycles (MC) with gravimetric assessment of wear at approximately every 0.25MC. The counterfaces used were cobaltchrome discs polished to a surface roughness, R_a , of 0.02 μm . The bidirectional motion was rectangular, 5×10 mm. 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 1 MC. Irradiated UHMWPE annealed at 70 ksi and 150°C ($n = 3$) was tested at the same time as irradiated control UHMWPE ($n = 3$).

In all studies in which there were at least three samples, statistical analysis was performed using a Student's t -test for two-tailed distributions with unequal variance. Significance was assigned to $p < 0.05$.

RESULTS

Melting of 100-kGy irradiated UHMWPE at ambient pressure and at 150°C decreased both the crystallinity and peak melting point ($p = 0.007$ and $p = 0.002$, respectively; Table II). In contrast, there was no significant difference in the crystallinity ($p = 0.43$) or the peak melting point of the 100-kGy irradiated UHMWPE annealed under 70 MPa at room temperature compared to before annealing ($p = 0.07$; Table II). The single melting peak displayed by the 100-kGy irradiated UHMWPE was similar to the sample that was annealed under pressure at room temperature, while melting at ambient pressure caused the peak to broaden in shape and shift to lower melting temperatures (Figure 1, Table II).

Melting at ambient pressure decreased the ultimate tensile strength of 100-kGy irradiated UHMWPE ($p = 0.009$; Table II). The ultimate tensile strength of 100-kGy irradiated UHMWPE annealed under pressure at room temperature was comparable to that before annealing UHMWPE ($p = 0.06$; Table II). There was a detectable free radical signal in the 100-kGy irradiated UHMWPE and irradiated UHMWPE that was annealed under pressure at room temperature (Figure 2). Both contained multiple peaks. The 100-kGy irradiated and ambient-pressure melted UHMWPE had no detectable free radicals.

Of the 100-kGy irradiated UHMWPEs that were annealed at 70 MPa close to the melting point, UHMWPE annealed at 140°C had comparable crystallinity to that of the untreated sample ($p = 0.91$); those of the UHMWPEs annealed at 150°C and 160°C were lower ($p = 0.07$ and 0.02 , respectively; Table III). The crystallinity of the UHMWPE annealed at 160 MPa and 150°C was higher than the untreated irradiated UHMWPE ($p = 0.06$). The sharp melting peak of 100-kGy irradiated UHMWPE was largely preserved after annealing at 70 MPa /140°C and 160MPa/150°C (Figure 3). In contrast, the melting peak of the sample that was annealed at 70 MPa/150°C contained two distinct peaks, one coinciding with the untreated material and a broad one that shifted to lower melting temperatures. The melting peak of the sample annealed at 70 MPa/160°C showed a single broad peak at lower temperatures than the untreated sample (Figure 3).

The free radical content of all annealed UHMWPEs were reduced compared to untreated 100-kGy irradiated UHMWPE (Figure 4, inset). The irradiated UHMWPEs annealed at 70 MPa/140°C and 160 MPa/150°C contained detectable free radicals while neither of the UHMWPEs annealed at 70 MPa/150°C and 70 MPa/160°C contained detectable free radicals (Figure 4).

The ultimate tensile strength of the 100-kGy irradiated UHMWPEs annealed at 70 MPa/140°C and 70 MPa/150°C was decreased compared to that of untreated irradiated UHMWPE ($p = 0.014$ and 0.002 , respectively) but was higher than irradiated UHMWPE melted at ambient pressure ($p = 0.04$ and 0.03 ; Tables II and III). The irradiated UHMWPE annealed at 70 MPa/160°C had comparable strength to that of irradiated UHMWPE melted at ambient pressure ($p = 0.68$). The wear rate of 100-kGy irradiated UHMWPE annealed at 70 MPa/150°C was comparable to that of 100-kGy irradiated UHMWPE ($p = 0.77$) and 100-kGy irradiated UHMWPE melted at ambient pressure ($p = 0.37$; Table IV).

The crystallinity of 0.2 wt % vitamin E-blended and 200-kGy irradiated UHMWPE (VE) was decreased slightly after annealing at 70 MPa/150°C ($p = 0.11$) and 70 MPa/160°C ($p = 0.002$; Table V). The peak melting point was reduced for the sample annealed at 70 MPa/160°C ($p = 0.004$) but not for that annealed at 70 MPa/150°C compared with before annealing ($p = 0.11$; Table V). A single sharp melting peak was displayed by VE while VE annealed at 70 MPa/150°C displayed two distinct melting peaks. VE annealed at 70 MPa/160°C had a broad single melting peak that was lower than the melting temperature of untreated VE (Figure 5). While vitamin E-blended and irradiated UHMWPE had detectable free radicals, VEs annealed at 70 MPa/150°C and 70 MPa/160°C did not contain detectable free radicals (Figure 6). The tensile strength of VE annealed at 70 MPa/150°C was preserved ($p = 0.89$) after annealing while that of VE annealed at 70 MPa/160°C was slightly reduced ($p = 0.12$; Table V).

DISCUSSION

Our ultimate goal in manipulating the morphology of UHMWPE is to obtain a simultaneously wear and oxidation resistant bearing material with maximized mechanical strength. Currently, post-irradiation melting provides wear resistance and increased oxidative stability. However, because postirradiation melting decreased the mechanical strength of crosslinked UHMWPE, the specific goal was to eliminate the oxidation-prone, radiation-induced free radicals by avoiding postirradiation melting.

The approach was to anneal irradiated UHMWPE under pressure allowing the use of elevated annealing temperatures without melting the polymer. Irradiated UHMWPE annealed at ambient pressure close to but below its melting point still has detectable free radicals,²⁹ which lead to oxidation in the long term.^{12,30} We hypothesized that the free radicals would be more effectively quenched and could be reduced to undetectable levels by increasing the annealing temperature. In order to prevent the crystals from melting during annealing at the elevated temperature, pressure was increased. Thus, we further hypothesized that free radicals would be eliminated without decreasing mechanical strength since we avoided postirradiation melting. Our hypotheses tested positive and we were able to decrease the free radicals in virgin, irradiated UHMWPE and vitamin E-containing, irradiated UHMWPE to undetectable levels by low pressure annealing without sacrificing mechanical strength.

We first determined the decoupled effects of heating and the application of pressure on the concentration of free radicals. As mentioned above, while heating above the melting point at ambient pressure is commonly used to eliminate free radicals in UHMWPE,^{14,31} the effects of the application of pressure alone were not known. The melting thermograms of irradiated and melted UHMWPE compared with irradiated UHMWPE annealed under pressure at room temperature demonstrated that the irradiated UHMWPE annealed under pressure had not undergone a melt transition showing a similar shape and location of the melting peak when compared with the untreated irradiated UHMWPE (Figure 1). In fact, while irradiated and melted UHMWPE lost some of its crystallinity due to the hindrance of its crosslinks on

recrystallization, the crystallinity of irradiated UHMWPE annealed under pressure was maintained (Table II). Presumably due to the retention of crystallinity, the mechanical properties of irradiated UHMWPE annealed under pressure at room temperature were retained (Figure 2).

In this study, we present tensile mechanical properties as a general indicator of the strength of these radiation crosslinked UHMWPEs. The ultimate tensile strength is positively correlated to the fatigue strength of crosslinked UHMWPEs,^{15,32,33} which is an important property believed to affect the longevity of joint implants.³⁴⁻³⁷ A UHMWPE with increased fatigue strength is believed to be less prone to delamination, which is a fatigue-induced wear mechanism,^{34,38} and also have less risk for fracture under adverse loading conditions such as rim impingement and edge loading.

As expected, melting at ambient pressure reduced the free radical concentration to undetectable levels (10^{14} spins/g) while that of irradiated UHMWPE annealed at 70 MPa at room temperature was comparable to untreated irradiated UHMWPE (2.6×10^{16} spins/g compared to 2.8×10^{16} spins/g; Figure 2). Irradiated UHMWPE melted at ambient pressure with undetectable level of residual free radicals has been shown to be more oxidation resistant than irradiated UHMWPEs with free radicals such as conventional, gamma sterilized UHMWPE and irradiated/annealed UHMWPE.^{14,29} Similarly, the free radical signature of irradiated UHMWPE and irradiated UHMWPE annealed under pressure at room temperature displayed similar peaks, a combination of allyl, alkyl, and polyenyl free radicals.^{39,40} These results showed that pressure treatment of 100-kGy irradiated UHMWPE alone did not induce enough mobility in the free radicals trapped in the crystalline regions to recombine and be extinguished. Therefore, irradiated UHMWPE annealed under pressure at room temperature would be expected to oxidize in the long-term.

The temperatures used in this study for heat treatment in combination with pressure annealing were estimated assuming that the temperature increase due to the pressure was linear. We estimated this rate to be ~ 7.5 MPa/ $^{\circ}\text{C}$ by linear regression between the peak melting temperature of UHMWPE at ambient pressure (140°C) and the orthorhombic to hexagonal phase transition we observed at 310 MPa (180°C).⁴¹ We performed our studies at 70 MPa because this was a high enough pressure to substantially increase the peak melting point of UHMWPE (to approximately 150°C) and a low enough pressure to be attainable in a typical bench-top pressure vessel.

We ascertained whether the low pressure annealed UHMWPEs had been melted during processing by looking at their melting behavior; broadening of the peaks and shift to lower melting temperatures were indicative of melting.⁴² The presence of a broad shoulder at lower melting temperatures was indicative of partial melting. From the shape and location of the melting point, we assessed that at 70 MPa, heating of 100-kGy irradiated UHMWPE to 160°C caused complete melting, heating to 150°C caused partial melting, and heating to 140°C caused minimal melting (Figure 3). At 150°C , at the higher pressure of 160 MPa, there was no melting, suggesting that by moving to higher pressure, the processing condition moved away from the phase transition line. In this manner, the location of all processing conditions was estimated with respect to the UHMWPE phase diagram (Figure 7).

The free radical concentration after pressure annealing at temperatures around the melting point decreased the closer the processing condition (temperature and pressure) was to the phase transition line. Thus, 100-kGy irradiated UHMWPEs treated at 160 MPa/ 150°C and 70 MPa/ 140°C in addition to the already discussed 70 MPa/room temperature annealed UHMWPE contained the highest amount of free radicals due to their location away from the phase transition (Figure 4). More importantly, the partial melting at 70 MPa/ 150°C caused

the free radical concentrations to be reduced to undetectable levels similar to those of the completely melted UHMWPE at 70 MPa/160°C without the accompanying decrease in mechanical strength (Table III).

Partial melting at 70 MPa caused a comparable decrease in free radical concentration as that of melting at ambient pressure without the decrease in mechanical properties. This is presumably due to the mobility induced in the free radicals in the crystalline domains^{43,44} by partial melting at higher temperatures due to the elevation of the melting point of the UHMWPE under pressure and the increased reaction rates of the free radicals at higher temperatures.

Radiation crosslinking is used to increase the wear resistance of UHMWPE through the decrease in plastic deformation¹⁵ and articulation-induced strain hardening on the surface of implants.⁴⁵ The wear of UHMWPE is believed to occur due to the failure of the material in the weakened transverse direction when the material oriented in the principal direction of motion is subjected to shear loading in other directions. Therefore, wear is dependent on the elongation and the ultimate strength, which in turn are sensitive to changes in crosslink density.^{15,33,46} We assessed the wear resistance of 100-kGy irradiated UHMWPE low pressure annealed at 70 MPa/150°C (Table IV). Presumably due to the comparable tensile mechanical properties of this irradiated UHMWPE to that before annealing, the elimination of the free radicals was achieved without detrimentally affecting the wear resistance.

While we have not performed a simulator study with this particular material, the bidirectional POD wear test used here²⁸ has correlated well with simulator wear in our laboratory^{14,46-48} for highly crosslinked UHMWPEs with similar crosslink density. The similar wear rate of the cross-linked UHMWPE after annealing at low pressure suggested that there was no unexpected change in its crosslink density or crosslink structure affecting its wear behavior. Clinically more relevant wear information would be obtained from further wear studies involving joint simulators.

Another type of UHMWPE that can benefit additionally from low pressure annealing close to the melting point is vitamin E-blended and subsequently irradiated UHMWPE. The presence of vitamin E significantly increased the oxidative stability of UHMWPE under *in vitro* accelerated and real-time aging conditions.^{17,19,25,49} When present during radiation crosslinking, vitamin E is consumed as a function of increasing radiation dose.⁵⁰ After irradiation, it hinders the cascading oxidation reactions in UHMWPE presumably by reacting with the macroalkyl radicals and with the peroxy free radicals caused as a result of reactions of these with oxygen, thereby minimizing polymer oxidation.²¹ Our long-term hypothesis is that if the radiation induced free radicals in vitamin E-stabilized UHMWPE could be quenched, then the antioxidant incorporated in the irradiated UHMWPE would be effective against oxidation for a longer period of time. Therefore, we investigated the effect of low pressure annealing on irradiated vitamin E-blended UHMWPE. While vitamin E itself is being consumed during irradiation, it also acts as a free radical scavenger and hinders crosslinking in UHMWPE,²⁴ leading to increased wear.²² It has been shown that the radiation dose has to be increased when crosslinking vitamin E-stabilized UHMWPE to obtain a desired crosslink density compared to virgin UHMWPE.⁵¹ It has also been shown that for vitamin E concentrations equal to and above 0.3 wt %, it may not be possible to achieve the crosslink density of 100-kGy irradiated virgin UHMWPE even at a radiation dose of 200 kGy.⁵¹ Thus, in this study, we chose to study a 0.2 wt % vitamin E blend irradiated to 200 kGy as a feasible irradiated vitamin E blend of UHMWPE for future clinical use.

We showed that it is possible to use these two complimentary methods; i.e. antioxidant stabilization of irradiated UHMWPE by vitamin E and annealing below the melting point under pressure to reduce the oxidative burden of radiation crosslinked UHMWPE in the longer term. The effects of low pressure annealing on the irradiated vitamin E blend were similar to those obtained for virgin, irradiated UHMWPE (Figure 4 and Table III) in terms of the free radical content and mechanical strength. Partial melting at 70 MPa (Figure 5) resulted in the preservation of tensile mechanical strength (Table V) while the free radical concentration was reduced to undetectable levels (Figure 6).

CONCLUSIONS

Thermal annealing under pressure at 70 MPa at 150°C caused partial melting of 100-kGy irradiated UHMWPE and 0.2 wt % vitamin E-blended and 200-kGy irradiated UHMWPE; the mechanical strength of irradiated UHMWPEs were maintained while the free radical concentration was reduced to undetectable levels. This could be a method to decrease the oxidative burden of radiation crosslinked UHMWPEs without a decrease in mechanical properties.

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FIGURE 1.

The effect of pressure treatment alone at room temperature and the effect of heat treatment alone without applying pressure on the melting behavior of 100-kGy irradiated UHMWPE.

FIGURE 2.

Electron spin resonance signals of 100 kGy irradiated, unmelted UHMWPE, 100 kGy irradiated UHMWPE pressure treated at room temperature, and 70 and 100 kGy irradiated UHMWPE melted at 150°C at ambient pressure. The spectra were normalized to sample weight and moved arbitrarily for clarity.

FIGURE 3.

The effect of low pressure annealing close to the melting temperature on the melting behavior of 100-kGy irradiated UHMWPE.

FIGURE 4.

Electron spin resonance signals of 100 kGy irradiated UHMWPEs pressure treated close to the melting point. The spectra of 100-kGy irradiated UHMWPE without further treatment is shown inset. The spectra were normalized to sample weight and moved arbitrarily for clarity.

FIGURE 5.

The effect of low pressure annealing close to the melting temperature on the melting behavior of vitamin E-blended, irradiated UHMWPE.

FIGURE 6.

Electron spin resonance signals of vitamin E-blended, irradiated UHMWPE pressure treated close to the melting point. The spectra were normalized to sample weight and moved arbitrarily for clarity.

FIGURE 7.

The approximate location of processing conditions on the phase diagram of cross-linked UHMWPE. The empty circles represent conditions at which the residual free radicals in 100-kGy irradiated UHMWPE are reduced to undetectable levels.

TABLE I
A List of Processed Samples and Processing Conditions

Sample name	Vitamin E Content (wt %)	Radiation Dose (kGy)	Annealing Temperature (°C)	Annealing Pressure (MPa)
100 kGy	–	100	–	–
100 kGy melted	–	100	150	Ambient
100 kGy LPA 70 MPa/RT	–	100	22 ± 0.5	70.3 ± 6.2
100 kGy LPA 70 MPa/140°C	–	100	143 ± 5.9	73.1 ± 9.6
100 kGy LPA 70 MPa/150°C	–	100	153 ± 7.6	81.4 ± 14.4
100 kGy LPA 160 MPa/150°C	–	100	149 ± 7.4	158.6 ± 11.7
100 kGy LPA 70 MPa/160°C	–	100	162 ± 8.3	83.4 ± 13.1
0.2 wt % + 200 kGy (VE)	0.2 wt %	200	150	Ambient
VE LPA 70 MPa/150°C	0.2 wt %	200	152 ± 6.2	69.6 ± 9.7
VE LPA 70 MPa/160°C	0.2 wt %	200	162 ± 8.1	70.3 ± 11.7

LPA stands for low pressure annealing. The average temperature and pressure were calculated over the dwell period of the experiment when the temperature increased above 130°C until it decreased below 130°C in the cool-down. The temperature at which the samples were melted at ambient pressure was not recorded in situ and is given by the single reading before the samples were placed in the oven.

TABLE II
The Effect of Pressure Treatment Alone at Room Temperature and Heat Treatment Alone at Ambient Pressure on the Crystallinity and the Peak Melting Point of 100 kGy Irradiated UHMWPE

	Crystallinity (%)	Peak Melting Point (°C)	Ultimate Tensile Strength (MPa)
100 kGy	61 ± 2	140.7 ± 0.7	49.6 ± 3.8
100 kGy melted at 150°C at ambient pressure	52 ± 1	135.4 ± 0.4	38.7 ± 3.2
100 kGy annealed at room temperature at 70 MPa	60 ± 0	139.9 ± 1.1	53.0 ± 2.9

TABLE III
The Effect of Low Pressure Annealing Close to the Melting Point on the Crystallinity and Peak Melting Point of 100 kGy Irradiated UHMWPE

	Crystallinity (%)	Peak Melting Point (°C)	Ultimate Tensile Strength (MPa)
100 kGy LPA 70 MPa/140°C	61 ± 1	139.9 ± 0.5	43.4 ± 4.1
100 kGy LPA 70 MPa/150°C	56 ± 2	140.2 ± 0.2	43.3 ± 2.9
100 kGy LPA 70 MPa/160°C	54 ± 1	136.6 ± 0.4	37.4 ± 3.3

TABLE IV
Pin-on-Disc Wear Rates of 100-kGy Irradiated, Low Pressure Annealed UHMWPE

	Wear Rate (mg/MC)
100 kGy	-1.4 ± 0.6
100 kGy melted	-1.5 ± 0.5
100 kGy LPA 70–150	-1.2 ± 0.7

TABLE V
The Effect of Low Pressure Annealing Close to the Melting Point on the Crystallinity and Peak Melting Point of Vitamin E-Blended, Irradiated UHMWPE

	Crystallinity (%)	Peak Melting Point (°C)	Ultimate Tensile Strength (MPa)
0.2 wt % + 200 kGy (VE)	61 ± 1	141.1 ± 0.5	40.3 ± 4.3
VE LPA 70 MPa/150°C	57 ± 3	141.9 ± 0.3	39.8 ± 5.1
VE LPA 70 MPa/160°C	57 ± 1	137.5 ± 0.2	35.8 ± 1.5