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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.

Keywords: Polyethylene; Crystallization; Tensile properties; Ultra-high molecular weight polyethylene

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 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 and thereby alter the crystalline morphology and its consequence of lower toughness and resistance to fatigue crack propagation, is to incorporate an antioxidant, such as α-tocopherol (synthetic vitamin E) into UHMWPE, which is a natural and very effective antioxidant, biocompatible and lipophilic owing to its phenyl tail, 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 hours (CA), melted at 200°C for 10 minutes and subsequently immediately quenched in liquid nitrogen (MQ), melted at 200°C for 10 minutes and then annealed at 127°C for 48 hours (MA).

The same treatments were applied to 4 slices obtained from a sheet of the control material previously irradiated with 50 kGy of gamma radiation in air: CX, CAX, MQX, MAX. Fourier Transform Infrared Spectroscopy was used to inspect the sheets for any oxidation occurring during irradiation. None of the samples showed any significant oxidation.

2.2 Small-angle X-ray scattering (SAXS)

A CuKα rotating anode SAXS instrument (Rigaku S-Max3000) was used to make SAXS measurements. A x-ray source operating at 45kV and 30mA was used and the collimate beam had a diameter of approximately 0.4 mm at the sample position. Data were provided in the form of intensity, *I* (counts), as a function of the scattering vector *q* (nm-1), which is defined as

$$q = (4\pi/\lambda)\sin\theta$$

where λ is the wavelength of X-rays and θ is half of the scattering angle. SAXS scattering intensity was collected by a two-dimensional gas-filled wire array detector at a distance of approximately 1500 mm from the sample with an angular scattering range of q_{min}=0.058 nm^{-1} and q_{max}=1.0 nm^{-1}. The differences in peak positions, and the broad peak of the samples, can be more easily interpreted using the correlation function analyses. The one-dimensional correlation function is related to the scattering curve or the scattering function by the following equation:

$$p(r) = (1/2\pi^2 A)\int_0^\infty q^2 I(q)\cos(qr)dq$$

where p(r) is the paired distance distribution function and, for the case of lamellae, is identical to the one-dimensional correlation function, A is the area of the lamella, I(q) is the experimental scattering function, q is the scattering vector, r is the radial distance perpendicular to the lamellar surfaces in a stack of lamellae, λ is the wavelength of x-rays (=1.543 Å for CuKα) and θ is half the scattering angle. Program ITP [32] was used to obtain the one dimensional correlation functions for each UHMWPE specimen and the first maximum was taken to be the inter-lamellar spacing, as has been previously measured for UHMWPE[2, 5, 33].

2.3 Differential scanning calorimetry

DSC measurements were carried out on all samples (n=3), using a Perkin Elmer Pyris 6 instrument in order to determine the crystallinity. Percent crystallinity was calculated by normalizing the heat of fusion of the sample to the heat of fusion of a pure polyethylene crystal (293 J/g). All DSC samples weighed approximately 4 mg.

2.4 Uniaxial tensile tests

ASTM D638 V dogbone specimens were prepared from each polyethylene (n=5) and subjected to uniaxial tensile testing at room temperature using an Admet universal tensile tester operating at a crosshead speed of 10mm/min. The elastic modulus, yield stress, ultimate tensile stress (UTS), maximum strain at break and Work of Fracture (WOF) were calculated.

2.5 Statistical analysis

The program Statview v5.0 (SAS Institute Inc.) was used to conduct analyses of data, particularly ANOVA with Fisher's protected least significant difference (PLSD) post-hoc test, in which a p-value of less than 0.05 was used to define significance.

3. Results

3.1 *DSC and SAXS*

It is evident from the data present in Tables 1 and 2 that annealing and quenching exhibited opposite behavior - CA had the highest crystallinity, 5.6% more than C, and was not statistically different from MA. In contrast, MQ has the lowest crystallinity, respectively a 19% and 26 % lower compared to C and CA.

Table 1. Thermal properties and lamellar morphology of various groups of UHMWPE

Thermal history	Tm (°C)	Crystallinity (%)	Inter-lamellar spacing (nm)	Lamellar thickness (nm)	Amorphous region thickness (nm)
C	141	50.8±0.8	49.5	25.1	24.4
CA	142	53.8±0.6	52.9	28.5	24.4
MA	141	53.0±0.7	51.7	27.4	24.3
MQ	135	42.7±0.5	29.0	12.4	16.6

Table 2. Thermal properties and lamellar morphology of various groups of 50-kGy irradiated UHMWPE.

Thermal history	Tm (°C)	Crystallinity (%)	Inter-lamellar spacing (nm)	Lamellar thickness (nm)	Amorphous region thickness (nm)
CX	144	55.3±1.3	49.3	27.3	22.0
CAX	144	56.7±0.3	51.3	29.1	22.2
MAX	144	56.0±0.5	45.9	25.7	22.2
MQX	134	43.2±0.5	23.8	10.3	13.5

Radiation crosslinking increased the melt temperature and crystallinity in all samples; in particular the degree of crystallinity of CX was about 9% higher compared to virgin unaltered sample, followed by the crystallinity of CAX and MAX, which was about 5.5% more than CA and MA, respectively. In general, the effect of the thermal treatments on irradiated samples followed a similar trend as for the non-irradiated UHMWPEs: CAX and MAX were not significantly different and had the highest crystallinity, about 28% more than MQX.

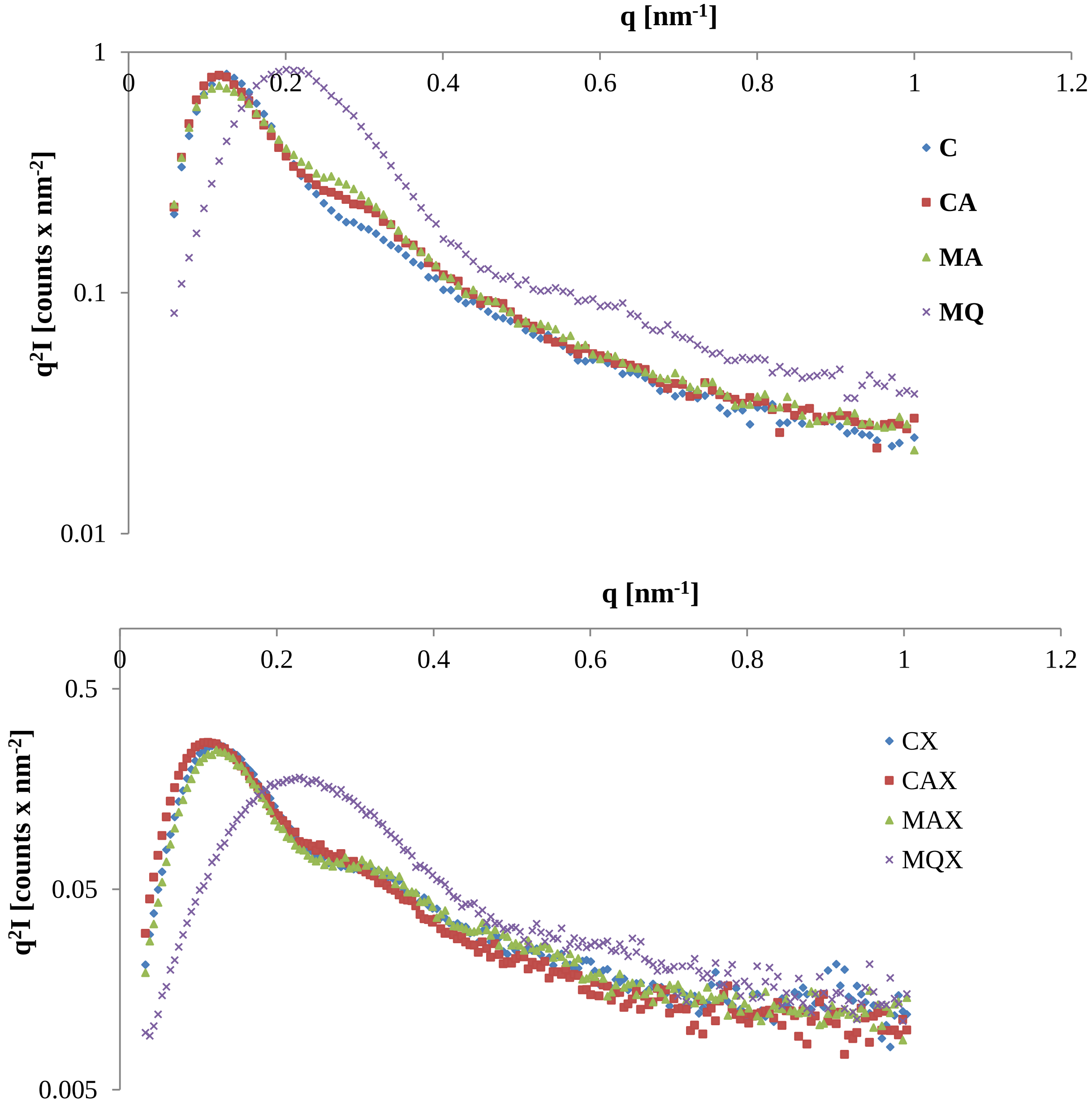

Figure 1. Lorentz-corrected Scattering functions of UHMWPE subjected to various thermal treatments (top) and corresponding 50 kGy radiation crosslinked UHMWPE (bottom).

The SAXS plots in Figure 1 showed that all of the samples except for MQ and MQX had a broad peak almost the same scattering angle whereas MQ and MQX peaks were at significantly higher scattering angle, q.

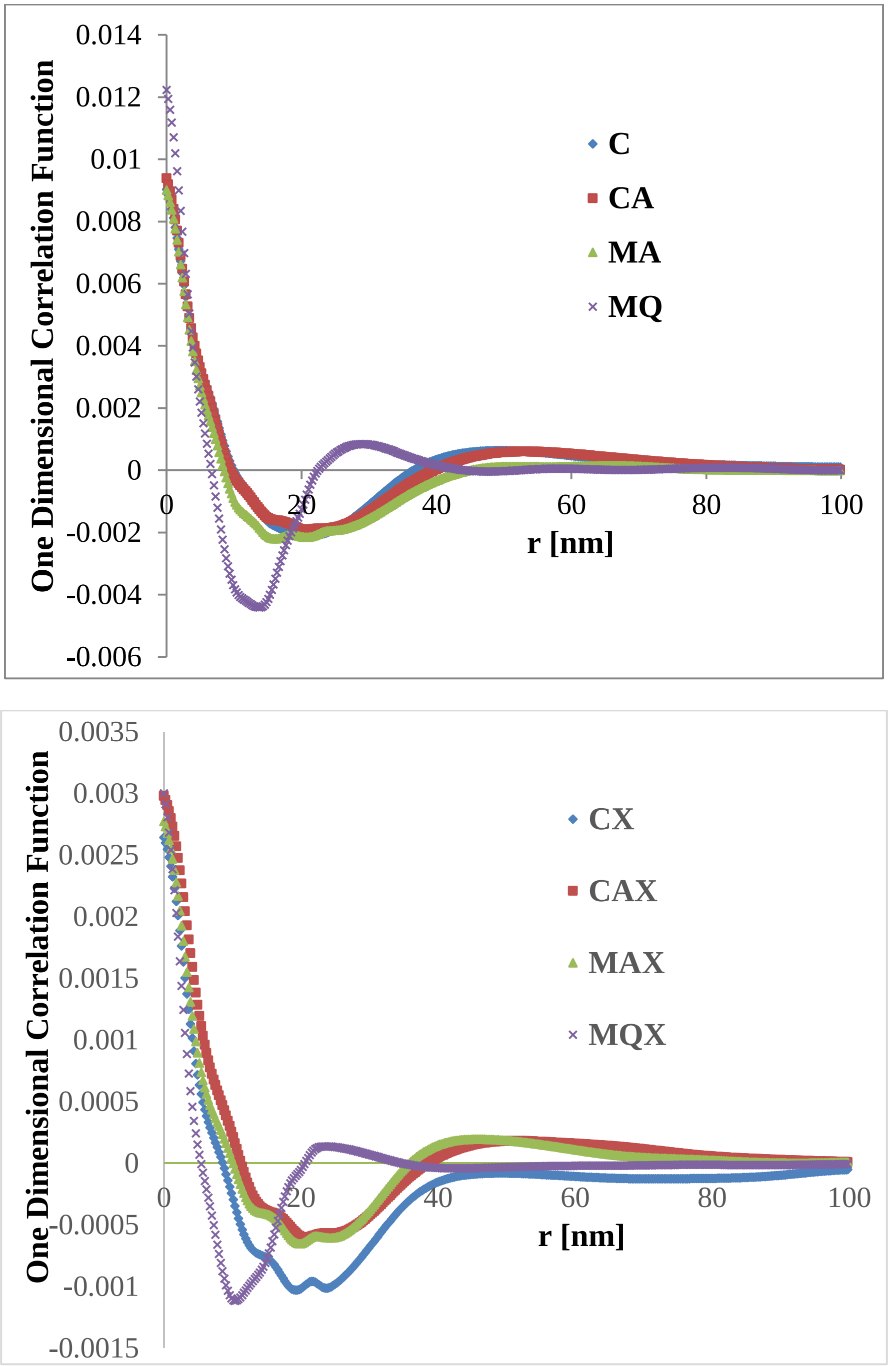

Figure 2. One Dimensional Correlation functions of UHMWPE subjected to various thermal treatments (top) and corresponding 50 kGy radiation crosslinked UHMWPE (bottom).

The One-dimensional correlation functions in Figure 2 showed small but subtle differences in the first maximum but again, as expected, the MQ and MQX peak was present at a much lower radial distance, indicating a much lower inter-lamellar spacing. The thickness of crystalline lamellae and the amorphous regions were determined through a combination of DSC crystallinity and SAXS inter-lamellar spacing: lamellar thickness was calculated multiplying the degree of crystallinity (%) measured by DSC for the SAXS inter-lamellar spacing and the thickness of the amorphous region was obtained the difference between the inter-lamellar spacing and the lamellar thickness. The data in Tables 1 and 2 show that a higher crystallinity correlated with a higher lamellar thickness. CA had the highest lamellar thickness, which was slightly higher than that of C and MA but more than twice that of MQ. The irradiated samples show the same trend, but in this case the lamellar thickness of MQX was almost three times lower than that of CAX. The amorphous layer thicknesses for all non-irradiated and irradiated UHMWPEs were the same, except for the case of the quenched specimens which were much lower. In addition, the amorphous layer thicknesses of the irradiated groups were slightly lower than those of the non-irradiated UHMWPEs.

3.2 Mechanical tests

It is evident from Table 3 and Figure 3 (top) that CA had the highest tensile modulus: 64%, 26% and 8% more than MQ, C and MA, respectively. MQ had the lowest yield stress and UTS, with significant differences between all samples. On the other hand, the maximum strain or strain-to-break of MQ was the highest, 19% and 25% higher than MA and CA respectively.

Table 3. Tensile properties of various groups of UHMWPE.

Thermal history	Tensile modulus (MPa)	Yield stress (MPa)	Ultimate tensile stress (MPa)	Strain at break (mm/mm)	Work-of-fracture (MJ/mm3)
C	120.67±5.98	24.41±0.76	43.13±2.68	8.66±0.20	268.06±11.26
CA	152.00±7.98	23.92±0.36	44.33±1.36	9.14±0.28	283.62±13.01
MA	141.67±5.92	22.77±0.48	42.41±1.73	9.63±0.39	260.65±9.52
MQ	70.89±1.90	16.97±0.64	35.30±3.04	11.43±0.94	262.55±10.68

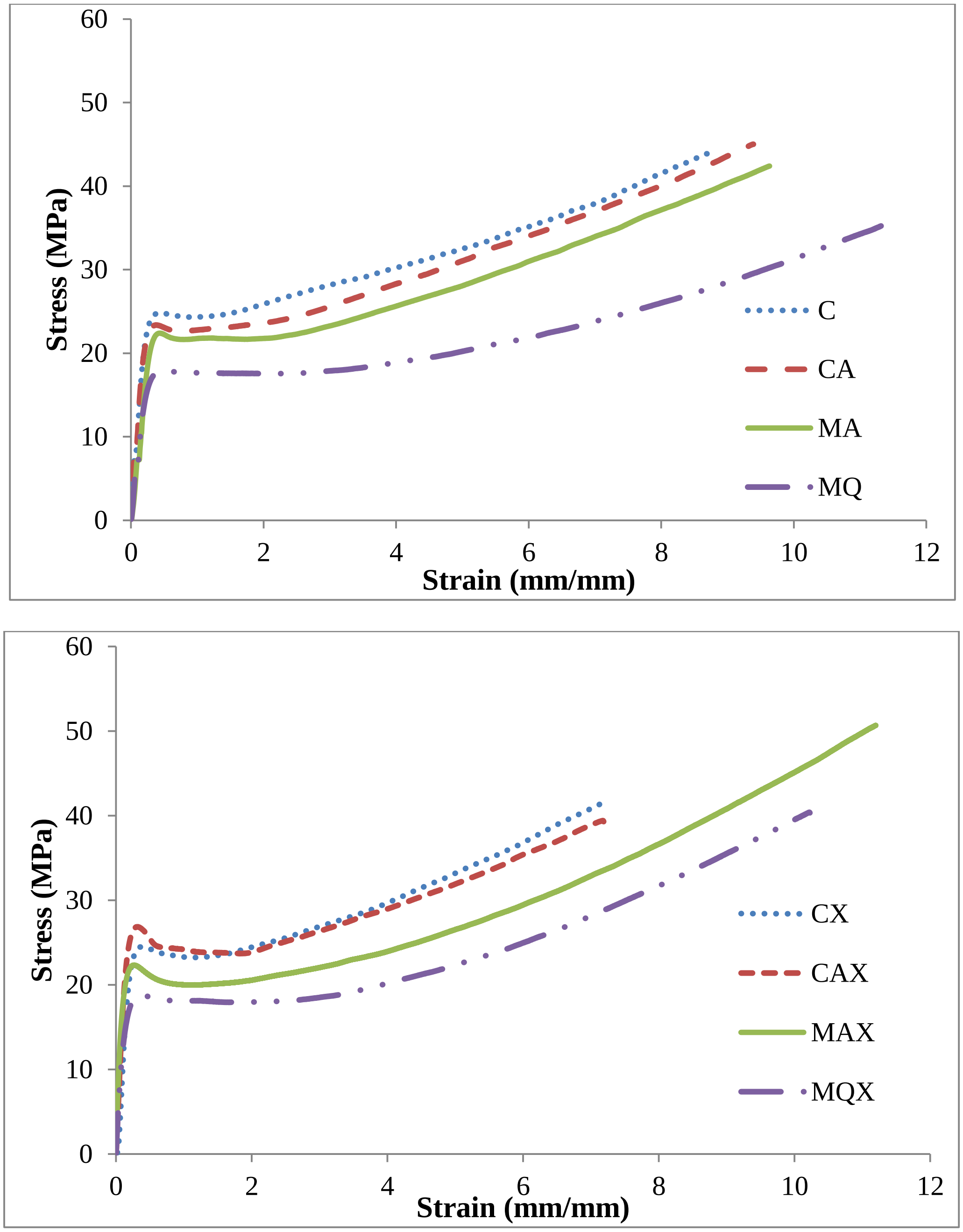

Fig 3. Representative stress-strain curves obtained by tensile test on various groups of non-crosslinked UHMWPE (top) and 50 kGy radiation crosslinked UHMWPE (bottom).

Table 4 and Figure 3 shows that CAX had the greatest tensile modulus among all irradiated samples, 6% more than MAX, 13% more than CX and twice that of MQX. The highest yield stress was observed for CX and CAX. MAX had the highest ultimate tensile stress and strain to break: the ultimate tensile stress of this sample was 16%, 19 and 30% higher than that of CX, MQX and CAX, respectively. Comparing non-irradiated and irradiated samples subjected to the same thermal treatment, there were statistically significant differences for almost all tensile properties; irradiated samples had in general a higher elastic modulus and yield stress ($p \leq 0.05$; ANOVA with Fisher's PLSD post-hoc test).

Table 4. Tensile properties of various groups of 50-kGy irradiated UHMWPE.

Thermal history	Tensile modulus (MPa)	Yield stress (MPa)	Ultimate tensile stress (MPa)	Strain at break (mm/mm)	Work-of-fracture (MJ/mm3)
CX	160.12±1.96	26.85±1.05	43.41±1.22	7.26±0.57	233.32±17.80
CAX	180.25±2.55	25.66±1.16	38.72±2.10	7.22±0.26	204.68±9.41
MAX	170.72±4.02	21.63±0.4	50.15±0.6	11.20±0.01	336.29±4.3
MQX	75.13±2.36	18.72±0.64	42.11±3.11	10.44±0.79	255.26±29.66

4. Discussion

One of the goals of this study was to determine whether significant differences in the lamellar morphology and tensile properties of UHMWPE blended with vitamin E could be achieved by use of various thermal treatments, and to also determine whether irradiation would alter the morphologicy and tensile properties to a different extent compared to non-irradiated UHMWPE.

We have demonstrated that annealing of both unaltered and melted samples increased the crystallinity of PE due to the formation of an overall smaller number of thick lamellae. In the case of isothermal annealing of the control (CA and CAX), as the polymer is heated to the annealing temperature, it is expected that thin lamellae melt and recrystallization occur until the isothermal crystallization temperature is achieved since polyethylene is known to rapidly crystallize until 120°C above which the crystallization rate decreases [34]. Thereafter, at the annealing temperature of 127°C lamellar thickening is to be expected, resulting in an increase in crystallinity over that of the untreated control. In the case of melting followed by isothermal crystallization, all of the morphology of the control is replaced by one characterized by a low nucleation density and slow crystal growth and thickening, resulting in a small number of thick lamellae. The process of annealing at a temperature slightly below the melting point provides more time for the chains to organize themselves into the lamellar crystals. In contrast, rapid quenching provides a large number of thin lamellae characterized by a high nucleation density.

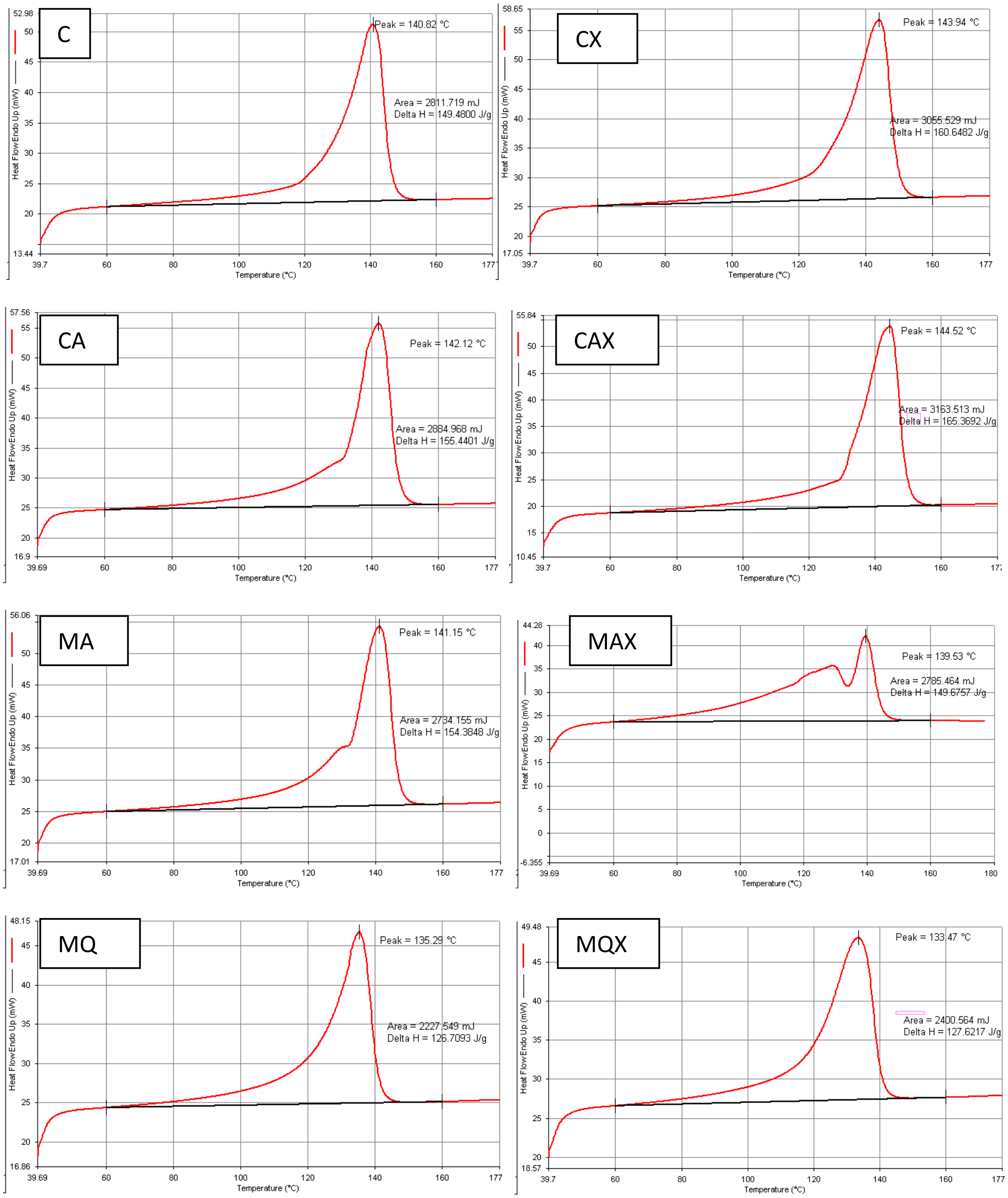

Figure 4. DSC thermograms of various groups of non-crosslinked UHMWPE (left) and corresponding 50-kGy crosslinked UHMWPE (right).

The shape of the DSC curves obtained is typical of semi-crystalline polyethylenes (Figure 4). The melting endotherm was a broad peak, indication the presence of crystals of very different size - the smaller crystals melt at lower temperature whereas the thicker crystals melt at higher temperatures. This is especially noticeable in the annealed samples, in which the main melting peak was superimposed on another much smaller but distinct peak, at a lower temperature. This double-peak behavior is due to the simultaneous presence of two crystallite populations: smaller crystallites formed during the thermal treatment and larger crystallites already present in the initial samples. The presence of a double-peak is also evident in SAXS curves of CA, MA, CAX and MAX (Figure 1) that have a small but distinct second peak at higher q, which resulted in the presence of small maxima superimposed on the broad peak in the corresponding one-dimensional correlation functions (Figure 2).

Crosslinked UHMWPEs were characterized by a higher melting temperature and crystallinity than the non-crosslinked UHMWPEs. However, the higher crystallinity did not necessarily result in a higher lamellar thickness and in fact lamellar thicknesses were generally the same or lower for the crosslinked UHMWPEs. This is probably due to a propensity for crosslinked UHMWPEs to have a higher nucleation density than non-crosslinked UHMWPEs subjected to an identical thermal history. A higher melting temperature is likely the result of lower mobility of the amorphous regions that influence the melting temperature of the lamellar regions. If the material did not contain vitamin E, a post-irradiation thermal treatment would have been necessary to increase the oxidation resistance of the PE and provide a stable material, with consequent lowering of crystallinity. Indeed, Bistolfi et al [2] observed that the post-irradiation melting of 50-kGy irradiated UHMWPE causes a reduction of crystallinity and lamellar thickness of about 9-11% in comparison to the virgin material.

The tensile test showed how various thermal processing methods are able to enhance or maintain the tensile properties of UHMWPE. An increase in crystallinity resulted in an increase in the small strain properties (Young’s modulus and Yield Stress) whereas quenching resulted in the opposite effect. This is to be expected due to the higher modulus of lamellae compared to the liquid like amorphous layers between the lamellae. A larger overall crystallinity (and consequently a lower amorphous content) would then increase modulus and yield stress whereupon there is an onset of plastic deformation. Quenching from the melt state (MQ) is able to increase the ductility of the material substantially whilst decreasing ultimate tensile stress. This has been attributed to the increase in tie molecules between lamellae since rapid crystallization does not provide sufficient time for macromolecules to form chain folds, resulting in more tie molecules per lamella [35]. A consequence of such macromolecular organization is the decrease in strain hardening behavior allowing the polymer to stretch to a higher strain-to-break but with a lower ultimate tensile stress resulting from less strain hardening. This effect was however negated in the crosslinked, quenched UHMWPE (MQX), which did not have a higher strain-to-break compared to MAX, probably due to the presence of crosslinks. The crosslinks result in a higher strain hardening rate evident from the rapid increase in applied stress with strain compared to the non-crosslinked group (see Figure 3).

The observation of the influence of thermal treatments on already irradiated, crosslinked 0.1% α-tocopherol blended PE showed that they can be efficiently used to obtain high mechanical properties without decreasing the oxidation resistance. In general, the increase in the degree of crosslinking and the molecular weight induces an improvement in some tensile properties of polyethylene which are very important in the field of materials for prosthetic use, especially since crosslinking is required for high wear resistance. On the other hand, irradiation caused a decrease in other properties such as elongation at break. In our experiments, some of the thermal histories enabled the crosslinked groups to have a high tensile modulus and yield stress, thus the ability of the material to resist to elastic deformations. These effects are more evident in CX, CAX and MAX elastic moduli, which increased of 30-20%, while all yield stress increase of about 10%. On the other hand, irradiation has also decreased the strain at break and work of fracture of the control and annealed only samples (C and CA vs. CX and CAX). Significant is the case of MAX that, after irradiation and thermal treatment, led to the highest ultimate tensile stress, strain at break and work of fracture. This sample was subjected to both melting and annealing close to the melting temperature, which should have also released free radicals from the crystalline phase. Actually, it is not clear what the fate of these radicals is. Some studies hypothesized that post-irradiation heating could release the free radicals trapped in the crystalline lamellae of PE and allow them to recombine to form additional crosslinks [21, 22]. But this should further decreased strain at break and work of fracture. Most probably, the fast melting and long annealing after cross-linking induced a lamellar morphology, with an ideal balance between overall crystallinity and nucleation density. A secondary benefit of raising the crystallinity through thermal treatments after irradiation was that we were able to potentially limit the concentration of free radicals generated during irradiation and trapped in the crystallites.

Tensile properties are closely related to impact strength, fracture toughness and resistance to fatigue crack propagation, all of which are a measure of the resistance of the material to crack growth in different modes, which occurs by tensile deformation of the polymer ahead of the crack tip. Thus, manipulation of tensile properties by altering the thermal history of irradiated, vitamin E stabilized UHMWPE has the potential to provide an oxidation resistant, wear resistant UHMWPE with superior toughness. While this study helped to elucidate that morphology can be systematically modified by controlling crystallization conditions, a more comprehensive structure-property-processing study would be necessary, involving a host of mechanical test methods, in order to determine the ideal crystallization conditions required to develop orthopedic implants with superior mechanical performance.

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FIGURE and TABLE Captions

Table 1. Thermal properties and lamellar morphology of various groups of UHMWPE.

Table 2. Thermal properties and lamellar morphology of various groups of 50-kGy irradiated UHMWPE.

Table 3. Tensile properties of various groups of UHMWPE.

Table 4. Tensile properties of various groups of 50-kGy irradiated UHMWPE.

Figure 1. Lorentz-corrected Scattering functions of UHMWPE subjected to various thermal treatments (top) and corresponding 50 kGy radiation crosslinked UHMWPE (bottom).

Figure 2. One Dimensional Correlation functions of UHMWPE subjected to various thermal treatments (top) and corresponding 50 kGy radiation crosslinked UHMWPE (bottom).

Figure 3. Representative stress-strain curves obtained by tensile test on various groups of non-crosslinked UHMWPE (top) and 50 kGy radiation crosslinked UHMWPE (bottom).

Figure 4. DSC thermograms of various groups of non-crosslinked UHMWPE (left) and corresponding 50-kGy crosslinked UHMWPE (right).