A USAXS Study of the Effects of Crystallization Conditions on the Morphology of UHMWPE

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Introduction

Ultra-high molecular weight polyethylene (UHMWPE) has attained worldwide acceptance as a bearing material used in orthopedic implants. UHMWPE is manufactured primarily by ram extrusion or compression-molding of UHMWPE powder. Both processes involve the use of high temperatures and pressures, followed by slow cooling and a post-processing annealing step. Every aspect of the manufacturing process from the original grade of resin powder used to the resulting stock material and final machining of implant components has been reviewed.[1]

It is well known that the crystalline morphology of polymers has a strong influence on their mechanical properties, such as Young's modulus, yield stress, strain hardening rates, and ultimate tensile properties. These properties vary as a function of cooling rate from the melt temperature (133ºC).[2] Under conditions of rapid cooling (quenching), chain folding is suppressed and the driving force for crystallization is reduced, resulting in a material with an overall lower crystallinity and a high nucleation density. Conversely, slow cooling or isothermal crystallization at low undercooling increases the overall degree of crystallinity with reduced nucleation density, leading to a small number of larger size crystallites compared to quenched polyethylene.

In this study, UHMWPE was subjected to four different thermal histories. The crystalline morphology resulting from these treatments was characterized using ultra-small-angle x-ray scattering (USAXS) at the UNI-CAT beamline of the Advanced Photon Source (APS).

Methods and Materials

Commercially available, ram-extruded GUR 1050 (Ticona, Bayport, TX) rod stock (PolyHi Solidur, Ft. Wayne, IN) was used as the starting material for all experiments. Samples were machined to a 2 mm thickness and subjected to one of four heating and cooling sequences.

In one experiment, isothermal crystallization was performed for 48 h at a low undercooling temperature (125ºC), which is approximately 8º below the melting temperature of UHMWPE (133ºC). In a second experiment, material was slowly cooled from 170ºC to room temperature over a period of 3 h. Samples were raised to 170ºC in a silicone oil bath. Thereafter, samples were slowly cooled to room temperature. Third, samples were heated to 170ºC and then immediately quenched in liquid nitrogen. Finally, UHMWPE quenched in liquid nitrogen was subjected to isothermal crystallization at 80ºC for 2 h in a silicone oil bath. The original rod stock served as a control for all samples.

USAXS was performed on 2-mm-thick specimens using 10-keV x-rays. The beam had a cross-sectional area of 2mm x 0.6 mm. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer Pyris 1 to determine the degree of crystallinity in each sample. Percent crystallinity was calculated by normalizing the heat of fusion of each sample to the heat of fusion of polyethylene crystal (293 J/g). DSC samples weighed 4 mg.

Results

USAXS scattering curves were obtained by plotting the scattered intensity (I) vs. q where

$$q = (4\pi/\lambda)\sin\theta \quad (1)$$

where θ equals one half of the scattering angle, and λ is the wavelength of x-rays (see Fig. 1). The USAXS curves revealed a linear Porod region at ultra-low q values suggesting the presence of large micrometer-size scatterers, such as voids, in all samples, regardless of thermal history. In addition, a broad peak was present in the SAXS region due to scattering from the lamellar morphology.

Void scattering was subtracted from each scattering curve and replotted as Lorentz-corrected intensity to determine the long period or inter-lamellar spacing (see Fig. 2).

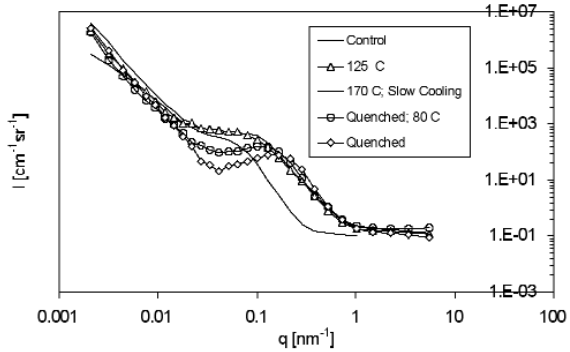

FIG. 1. Scattering plot for UHMWPEs.

Due to the presence of broad peaks, it was necessary to obtain long periods from paired distance distribution functions

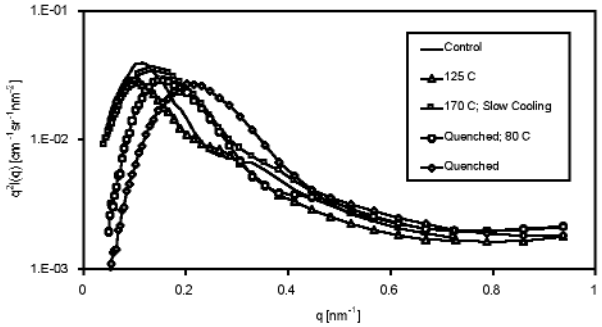

FIG. 2. Plot of q^2I vs. q for all heat-treated samples and untreated control.

(PDDF) or p(r) which were identical to the one and untreated control. dimensional correlation function for lamellar systems. The scattering functions were converted to PDDFs using the computer program ITP developed by Glatter.[3] PDDF is related to the scattering function I(q) by the following equation:

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

where p(r) is the paired distance distribution function, A is the area of the lamella, I(q) is the experimental scattering function, q is the scattering vector, and r is the radial distance perpendicular to lamellar surfaces within a stack of lamellae. The USAXS long period for all samples was measured from the first maximum of p(r) (Fig. 3).

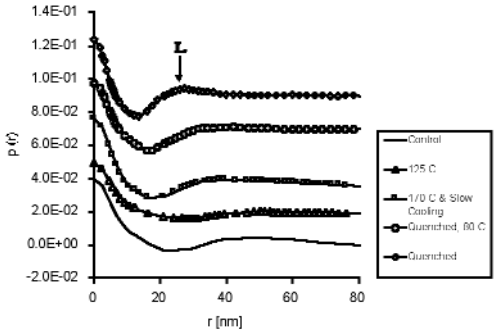

FIG. 3. Paired distance distribution functions p(r). Values of p(r) have been offset for clarity.

Together, the long period and DSC crystallinity were used to calculate the lamellar thickness using the following equation:

$$D = X_c L \qquad (3)$$

where D is the lamellar thickness, X_c is the degree of crystallinity (%) measured by DSC, and L represents the

USAXS long period (inter-lamellar spacing). The thickness of the amorphous regions (A) was also calculated by taking the difference between the inter-lamellar spacing and the lamellar thickness (see Table 1).

Discussion

This study revealed that the crystalline morphology of UHMWPE can be elucidated using USAXS. It is difficult to measure the large interlamellar spacings of UHMWPE using conventional SAXS. The large range of scattering angles of the USAXS camera of the UNI-CAT beamline enables the morphology of UHMWPE to be measured at both the micrometer (voids) and the nanometer (lamellae) length scales. USAXS revealed the presence of voids in bulk UHMWPE due to incomplete consolidation of the resin powder during processing. There was a vast difference in the interlamellar spacing depending on the crystallization conditions, which is expected to strongly affect the mechanical properties of UHMWPE. A structure-property-processing study involving different thermal histories, morphological characterization using USAXS, and mechanical properties measurement would greatly assist in guiding the development of UHMWPE orthopedic implants with superior mechanical performance.

Table 1. Characterization of crystalline morphology of UHMWPE samples.

Treatment	X_c	L	D	A
[%] (DSC)	[nm] (USAXS)	[nm]	[nm]	
125°C	50.6	59.9	30.3	29.6
170°C	47.3	38.4	18.2	20.2
N_2	35.3	27.2	9.6	17.6
N_2; 80°C	44.6	41.6	18.6	23.4
Control	54.3	49.0	26.6	22.4

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References

[1] S.M. Kurtz et al., Biomat. **20**, 1659-1688 (1999).

[2] R.W. Truss et al., Polym. Eng. Sci. **20**, 747-755 (1980).

[3] Glatter, Acta Phys. Austriaca **47**, 83-102 (1977).