USAXS characterization of the microstructure & nanostructure of polyethylene used in orthopaedic implants

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INTRODUCTION

- Ultra-high molecular weight polyethylene (UHMWPE) has attained worldwide acceptance as a bearing material used in patellar components of total knee replacement prostheses. (Figure 1) Each year, over 500,000 total joint replacement prostheses are implanted in the U.S. costing the US Healthcare $2 billion annually.

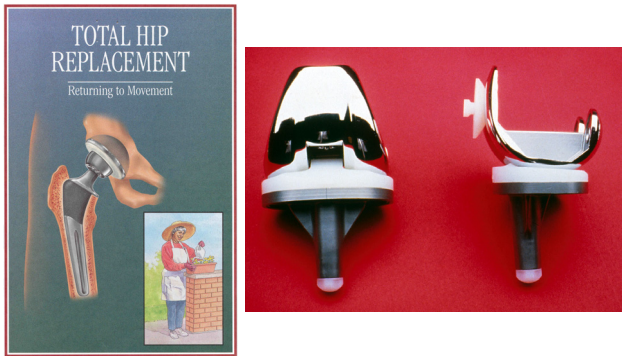

Fig 1.: Total hip replacement (left) and total knee replacement (right) prostheses

- The lifetime of UHMWPE components is limited by their wear resistance as they articulate against a metallic of ceramic counterface since particulate wear debris leads to biological complications such as bone loss or osteolysis [1, 2]. In addition, mechanical damage can also decrease their longevity.

- Radiation crosslinked UHMWPE has a very high resistance to wear but has lower mechanical properties than uncrosslinked UHMWPE [3, 4].

- In this study, high pressure crystallization was used to increase crystallinity and lamellar thickness of UHMWPE and characterized using ultra-small angle x-ray scattering (USAXS) and scanning electron microscopy.

MATERIALS AND METHODS

- Starting material was a GUR 1050 (Hoechst-Ticona, Bayport, TX) ram-extruded rod stock (PolyHi Solidur, Ft. Wayne, IN), crystallinity 57.8%. A custom built high pressure cell was used to crystallize UHMWPE at various temperatures at constant pressure and at various pressures at constant temperature.

- Samples were characterized using a combination of differential scanning calorimetry (DSC) using a Perkin Elmer Pyris 1 calorimeter, low voltage scanning electron microscopy (LVSEM) using a JEOL 6320FV low voltage microscopy and ultra-small angle x-ray scattering (USAXS) at the UNICAT beamline of the Advanced Photon Source using 10kEV x-rays and a rectangular slit geometry of 2mm x 2mm. For DSC, the percent crystallinity was calculated by normalizing the heat of fusion of each sample to the heat of fusion of polyethylene crystal (293 J/g).

RESULTS AND DISCUSSION

•LVSEM on permanganic etched freeze fracture cross section of UHMWPE showed tortuous lamellae in a range of 20nm to 0.2 µm thickness depending on crystallization pressures and temperatures (see Figure 2).

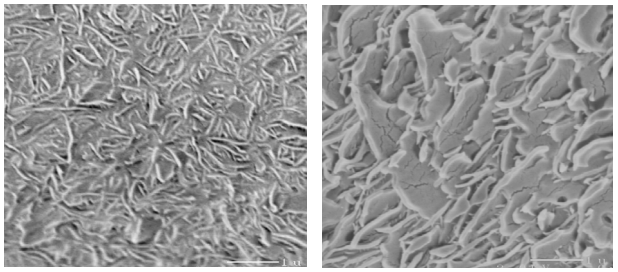

Fig 2.: Lamellar morphology of atmospheric pressure crystallized UHMWPE (left) and UHMWPE crystallized at 500 MPa pressure and 240C temperature (right).

•USAXS showed that the peak associated with inter-lamellar spacing shifted to low angles with increase in crystallization temperature and pressure (see Figure 3)

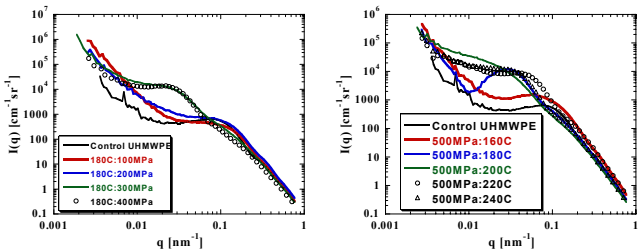

Fig 3.: USAXS plots of UHMWPE crystallized at various pressures at 180C (left) and UHMWPE crystallized at various temperatures at 500MPa (right).

•Due to the presence of broad peaks it was necessary to obtain long periods from paired distance distribution functions (PDDF) or p(r) which were identical to the one dimensional correlation function for lamellar systems. The scattering functions were converted to PDDFs using the computer program ITP developed by Glatter [5]. PDDF is related to the scattering function I(q) by the following equation:

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

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 (= $(4\pi/\lambda)\sin\theta$ where λ is the scattering wavelength and θ is one-half of the scattering angle), 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) (Figure 4).

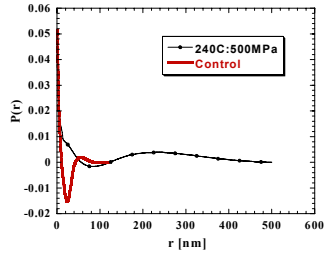

Fig 4.: Representative PDDFs of atmospheric pressure crystallized UHMWPE and UHMWPE crystallized at a temperature of 240C and pressure of 500 MPa

•Long period and crystallinity depended on the crystallization conditions (see Table 1)

Table 1. Long period (L), melting temperature (Tm) degree of crystallinity (Xc) at various crystallization temperatures (Tc) and pressures (P).

T_C (C)	P (MPa)	T_M (C)	X_C %	L [nm]
rodstock	0	136.2	57.8	55
160	500	144.3	78.1	62
180	500	145.2	82.8	156
200	500	146.4	86.6	214
220	500	147.0	90.7	103
240	500	146.4	91.1	141
180	100	136.2	59.7	43
180	200	136.8	56.5	49
180	300	146.0	70.9	185
180	400	147.1	77.8	187

•In conclusion, high pressure crystallization can be used to increase crystallinity of UHMWPE substantially by thickening of lamellae, resulting in an increase in USAXS long period. This has the potential to increase clinically relevant mechanical properties of UHMWPE such as fatigue strength and resistance to creep deformation.

REFERENCES

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