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

M. Turell and A. Bellare
Department of Orthopedic Surgery, Brigham and Women's Hospital, Harvard Medical School, Boston, MA, U.S.A.

Introduction

Ultrahigh-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 postprocessing 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 morphologies of polymers have 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 six different thermal histories. The crystalline morphology resulting from these treatments was characterized by using ultrasmall-angle x-ray scattering (USAXS) at the UNI-CAT beamline of the 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. Rod stock was machined into discs with a diameter of 76 mm and a 1-mm thickness. These samples were subjected to one of six heating and cooling sequences. In one experiment, samples were heated to 170ºC and then immediately quenched in liquid nitrogen. In five subsequent experiments, UHMWPE that had been quenched in liquid nitrogen was subjected to isothermal crystallization at one of five crystallization temperatures (60º, 80º, 100º, 110º, or 120ºC) for 48 h by using a silicone oil bath with precise temperature control. The original rod stock served as a control for all samples.

USAXS was performed on 1-mm-thick specimens at the UNI-CAT beamline of the APS by using 10-keV x-rays. The beam's cross-sectional area was 2×0.6 mm. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer Pyris 1 instrument 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:

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

such that θ = one-half of the scattering angle and λ = the wavelength of x-rays (Fig. 1). The USAXS curves revealed a linear Porod region at ultralow *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 because of scattering from the lamellar morphology.

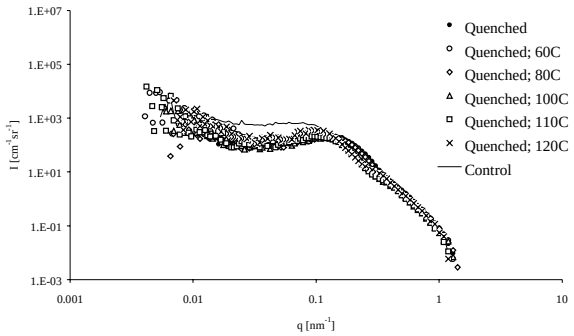

FIG. 1. Scattering plot for all UHMWPE samples.

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

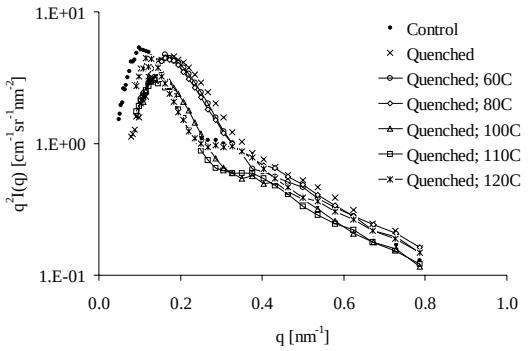

FIG. 2. Plot of q^2I vs. q for all heat-treated samples and untreated control.

Because of the presence of broad peaks, it was necessary to obtain long periods from paired distance distribution functions (PDDFs) or *p(r)*, which were identical to the 1-D correlation function for lamellar systems. The scattering functions were converted to PDDFs by using the computer program ITP developed by Glatter [3]. PDDF is related to the scattering function *I(q)* by the following equation:

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

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

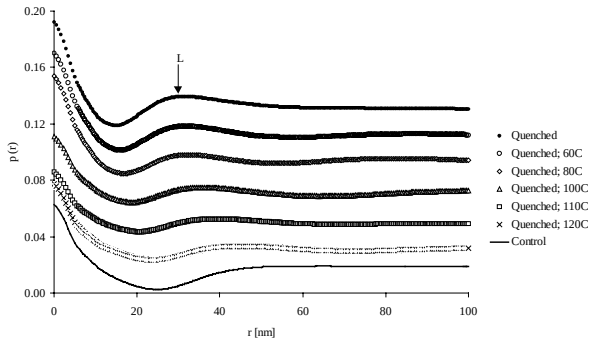

FIG. 3. Paired distance distribution functions p(r). (Values of p(r) have been offset for clarity.)

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

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

where D = the lamellar thickness, X_c = the degree of crystallinity (%) measured by DSC, and L = the USAXS long period (interlamellar spacing). The thickness of the amorphous region *A* was also calculated by taking the difference between the interlamellar spacing and the lamellar thickness (Table 1).

Table 1. Characterization of crystalline morphology of UHMWPE samples.

Treatment	X_c (%) (DSC)	L (nm) (USAXS)	D (nm)	A (nm)
Control	48.3	65.2	31.5	33.7
Quenched	34.6	31.4	10.9	20.5
Quenched, 60C	36.0	31.6	11.4	20.2
Quenched, 80C	42.9	32.2	13.8	18.4
Quenched, 100C	55.8	36.1	20.1	16.0
Quenched, 110C	57.8	39.2	22.7	16.5
Quenched, 120C	62.6	44.5	27.9	16.6

Discussion

This study revealed that the crystalline morphology of UHMWPE can be elucidated by using USAXS. It is difficult to measure the large interlamellar spacings of UHMWPE by 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 micrometer-length scales (voids) and nanometer-length scales (lamellae). 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 mechanical properties of UHMWPE. A structure-property-processing study involving different thermal histories and morphological characterization that uses USAXS and mechanical properties measurement would greatly help in guiding the development of UHMWPE orthopedic implants with superior mechanical performance.

Acknowledgments

Funding was provided through a biomedical engineering grant by the Whitaker Foundation. We thank Dr. P. Jemian and Dr. J. Ilavsky for their expert assistance with USAXS measurements. The UNI-CAT facility at the APS is supported by the University of Illinois at Urbana-Champaign, Materials Research Laboratory (U.S. Department of Energy [DOE], State of Illinois-IBHE-HECA, and National Science Foundation), Oak Ridge National Laboratory (DOE), National Institute of Standards and Technology (U.S. Department of Commerce), and UOP LLC. Use of the APS is supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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