

Effects of Annealing on UHMWPE Molecular Orientation

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Introduction Ultra-high molecular weight polyethylene (UHMWPE) is the dominant material used in artificial joints due to its outstanding wear resistance. At the same time, UHMWPE wear debris has been found to contribute to the loosening of the implants. As human life expectancy increases, there is an urgent need to improve the life of implants. Hubbard et al. (1) and Hastings et al. (2) have demonstrated that the molding and annealing the UHMWPE at a safe elevated temperature resulted in increased mechanical strength. Also, cross-linking of UHMWPE has been demonstrated to reduce wear significantly. We have previously measured molecular orientation as a function of wear motion (4). While the link between molecular orientation and wear has not been clearly established, molecular orientation has been recognized as an important parameter in wear resistance. This paper examines the change of molecular orientation caused by annealing UHMWPE. Our technique utilizes soft x-ray absorption spectroscopy at a synchrotron beamline to characterize the molecular orientation of the UHMWPE surface layer (3). The amount of soft x-ray absorption is very sensitive to the average molecular chain angle with respect to the electric field vector (E) of the incident x-ray beam.

Experimental Three different UHMWPE materials were employed in this study: 1) Himont[§] resin (ca. 1989), compression molded, gamma sterilized in nitrogen by ca. 37 kGy; 2) extruded GUR 1050, gamma sterilized in nitrogen by ca. 100 kGy, followed by free radical reduction protocol; and 3) virgin extruded GUR 1050. Cylindrical pins were machined from these three materials to have nominal dimensions of 6.35 mm in diameter and 19.05 mm in length. The compression molded pins were machined to dimensions with one end face being the original molded face and the other face being cut by using a fly cutter. The two GUR 1050 materials were machined by using a lathe. One of the end faces of these GUR 1050 pins was finished by using a diamond tooling.

The pins were mounted with a reference line on the cylindrical sample surface parallel to the electric field polarization plane in an x-ray beamline. Soft x-ray absorption of UHMWPE near the carbon K-edge was measured by surface sensitive (10 nm) electron yield detection (3). Then the sample was rotated 90° such that the reference line on the pin was perpendicular to the electric field polarization plane. Then these pins were annealed at ca. 130 °C in N₂ and reanalyzed with x-ray absorption method. The sample reference line was maintained and hence clear comparisons of effects of annealing in sets of UHMWPE blanks were possible.

Results and Discussion The x-ray absorption of UHMWPE is sensitive to the chemical bonding and the orientation of the bonds near the carbon atom. For the three samples described above, x-ray absorption spectra were obtained at normal incidence (when E is parallel to the sample) and at glancing incidence (when E is perpendicular to the sample). The x-ray absorption spectrum of UHMWPE (shown previously (4)) exhibits C-H resonance peak (288 eV) and C-C resonance peak (293 eV). In order to compare the degree of preferential molecular orientation each spectrum was normalized to the carbon-edge jump of unity and the spectrum of E-perpendicular was subtracted from E-parallel as shown (solid lines) in Fig. 1. A similar analysis procedure was applied to the annealed blanks

and subtraction spectrum for the same sample is plotted in dashed curve along with the un-annealed blanks (solid lines).

The subtraction spectrum highlights the bonds having preferred orientations (a spectral feature with no preferred orientation subtracts to zero). It can be clearly noted that in all the three types of blanks (compression molded, highly cross-linked and virgin blank) before annealing we observed high magnitude in the subtraction spectra which implies high degree of orientation due to machining. The methodology to compute the degree of orientation has been described by Outka et al. (5). The degree of orientation before and after annealing is summarized in Table 1.

Figure 1: Difference X-ray Absorption Spectra

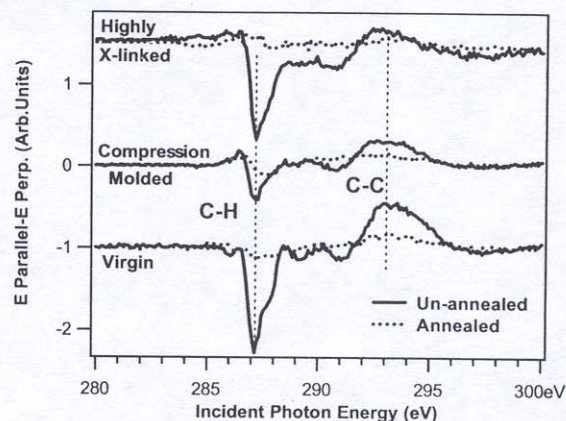


Table 1: Molecular Orientation

UHMWPE Sample Type	Orientation (C-H) before Annealing, %	Orientation (C-H) after Annealing, %
Highly X-linked (GUR 1050)	54 ± 5	5 ± 5
Compression Molded (Himont)	19 ± 5	5 ± 5
Virgin UHMWPE (GUR 1050)	59 ± 5	6 ± 5

Our study has clearly shown that the average molecular orientation in UHMWPE has significantly decreased after annealing the sample at 130 °C in nitrogen. On repeating these experiments the orientation values were within ±5 % (range) which implies that this method of directly measuring surface molecular orientation using the resonant absorption of linearly polarized soft x-rays is quite reliable.

References

- (1) Hubbard et al., *Trans. 25th Soc. For Biomaterials*, 325(1999).
- (2) Hastings et al., *Trans. 25th Soc. For Biomaterials*, 328(1999).
- (3) Stöhr NEXAFS Spectroscopy, Springer, New York, 1992.
- (4) Fischer et al., *Trans. 25th Soc. For Biomaterials*, 351(1999).
- (5) Outka et al., *J. Chem. Phys.* **88** (1988) 4076.

[§] Materials and equipment are identified only for describing experimental procedure and do not imply recommendation or endorsement by NIST.