Effect of cross-linking ultrahigh molecular weight polyethylene: Surface molecular orientation and wear characteristics

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(Received 3 October 2006; accepted 12 March 2007; published 2 July 2007)

Molecular orientation at the surface layer of cross-linked ultrahigh molecular weight polyethylene (UHMWPE) has been examined. Molecular orientation has been shown to affect the wear resistance and surface mechanical properties of UHMWPE under biomechanical loading conditions. This study utilizes a nondestructive synchrotron based soft x-ray technique; near edge x-ray absorption fine structure at the carbon K-edge to examine the degree of surface molecular orientation of UHMWPE subjected to various cross-linking/sterilization techniques as a function of stress and wear. UHMWPE samples prepared under gamma irradiation, ethylene-oxide (EtO) treatment, and electron beam irradiation were worn in a wear tester systematically. Results suggest that the cross-linking resists surface orientation when the samples were under tensile and biomechanical stresses. The molecular orientation in the C–C chains in the polymer showed a monotonic decrease with an increase in gamma irradiation dosage levels. EtO sterilized samples showed more C–C chain orientation than the electron beam irradiated samples, but lower than the 30 kGy gamma irradiated samples. Ordered C–C chains in UHMWPE samples have been associated with more crystallinity or large strain plastic deformation of the polymer. Higher levels of gamma irradiation appear to induce cross-linking of C–C chains and render a polymer with more amorphous phase which resists orientation after wear and imparts wear resistance to the polymer. © 2007 American Vacuum Society. [DOI: 10.1116/1.2723767]

I. INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) is the most widely used material for orthopaedic bearings in hip and knee prostheses.1 The overall success of the UHMWPE as a bearing surface has been attributed to its good biocompatibility and high mechanical strength, resisting wear and abrasions. However, under biomechanical loading conditions, wear of the joint materials generates wear debris. Highly localized deformation2,3 and wear debris accumulations, wear of the joint materials generates wear debris. Cross-linking of the chains in the amorphous phase makes the material more rigid and hard, and oxidation generates free radicals which degrade the structure. Although the UHMWPE material is biologically inert, its mechanical properties are strongly influenced by the manufacturing and sterilization processes. UHMWPE is typically formed by sintering the fine powder at or above the melting point of the material via molding and annealing.4,5 The formed material also undergoes sterilization processes such as gamma radiation, electron beam irradiation, or peroxides treatment before use. These sterilization processes, however, have also shown to induce cross-linking in the amorphous region of the polymer.5,8–11 Cross-linking of the polymer has been shown to reduce wear significantly, especially in oxygen-free atmosphere followed by annealing. Jasty et al. found from retrieval samples that conventional uncross-linked polyethylene material underwent large-strain plastic deformation, which led to strain hardening in the sliding direction but weakening of the material in the transverse direction.9 Alignment of crystalline chains in UHMWPE may be an important indication of strain hardening9 as well as increasing hardness and brittleness. For this reason, surface molecular orientation of the carbon chains in orthopaedic joint application provides an insight into the material property as influenced by the wear processes.10–12 Because of the complexity of the material, the common technique of measuring molecular orientation of UHMWPE uses staining, cross sectioning the polymer material, and observing the microstructural features under high magnification electron microscopy, which lacks quantification of orientation.5,13

This study involves the resonant x-ray excitation of a K-shell electron to an unoccupied low-lying molecular orbital of $\sigma$ or $\pi$ symmetry. The initial-state K-shell excitation gives near edge x-ray absorption fine structure (NEXAFS) its element specificity, e.g., carbon, oxygen, and substrate copper,14,15 while the final-state unoccupied molecular orbitals give NEXAFS its bonding or chemical selectivity. Because of the fixed sample geometry (relative to the incident x-ray beam) and the fact that the $1s \rightarrow \sigma^*$ and $1s \rightarrow \pi^*$ excitations are governed by dipole selection rules, the resonance intensities vary as a function of the direction of the electric

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field vector $\mathbf{E}$ of the incident polarized x-ray relative to the axis of the $\sigma^*$ and $\pi^*$ orbitals. This variation in resonance intensity allows for the measurement of the average molecular orientation of the alkyl chain with respect to the surface of UHMWPE. Thus, NEXAFS is an ideal technique for probing the molecular bond chemistry and orientation in UHMWPE up to a depth of 5 nm.\cite{933Sambasivan, Fischer, and Hsu: Effect of cross-linking ultrahigh molecular weight polyethylene, 933}

The first group is labeled as C series (C0–C4), which had no irradiation. These samples were subjected to various extents of tensile elongation in one direction on an Instron machine. The second group is labeled as X series (X0–X2 and X5). These samples were subjected to 100 kGy gamma irradiation in air to induce cross-linking, but the top 3 mm surface layer had been removed by diamond cutting. The samples were then annealed at 145–245 °C for 10 h and then subjected to tensile elongation to different strains. So comparison between the C and X series will highlight the effect of cross-linking under the same mechanical tensile conditions.

The third group is labeled as E series (E1–E2). These samples were sterilized under ethylene oxide or electron (E) beam irradiation conditions in air. All the samples were then tested in an MTS knee simulator for $5 \times 10^6$ cycles of duration; details are described elsewhere.\cite{2} The fourth group is labeled as D series (D3, D5, D7, and D10). These samples were subjected to 30, 50, 75, and 100 kGy gamma irradiation in nitrogen to induce different degrees of cross-linking and then packed in nitrogen, heat treated at 50 °C for six days in the package. No surface layer was removed. This set of samples was treated in nitrogen atmosphere to avoid oxidation, which had shown deleterious effects on wear and fatigue properties. These samples were worn in the knee simulator under the same conditions. The control samples

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Material label & Processing & Load/wear history & % C–C orientation (±2%) \\
\hline
C0 & No irradiation & No deformation/wear (control) & 68.8 \\
C1 & No irradiation & 200% elongation in tension & 40.5 \\
C3 & No irradiation & 310% elongation in tension & 38.1 \\
C4 & No irradiation & 400% elongation in tension & 42 \\
X0 & 100 kGy gamma in air & No deformation (control) & 43.7 \\
X1 & 100 kGy gamma in air & 260% elongation in tension & 42.9 \\
X2 & 100 kGy gamma in air & 200% elongation in tension & 34.8 \\
X5 & 100 kGy gamma in air & 100% elongation in tension & 31.4 \\
E1 & 0 kGy/EtO sterilization & Knee simulator worn component & 25.6 \\
E2 & 100 kGy E-beam in air & Knee simulator worn component & 12.2 \\
D3 & 30 kgy gamma in N\textsubscript{2} (duration process) & Knee simulator worn component & 31.3 \\
D5 & 50 kGy gamma in N\textsubscript{2} & Knee simulator worn component & 22.4 \\
D7 & 75 kGy gamma in N\textsubscript{2} & Knee simulator worn component & 18.5 \\
D10 & 100 kGy gamma in N\textsubscript{2} & Knee simulator worn component & 18.4 \\
\hline
\end{tabular}
\caption{List of samples of UHMWPE (GUR 1050) studied using NEXAFS method. Various processing methods and wear/stress conditions with % C–C orientation from NEXAFS are also indicated.}
\end{table}
B. NEXAFS surface analysis

The x-ray absorption experiments (NEXAFS) at the carbon \(K\)-edge were carried out at the National Synchrotron Light Source NIST/DOW U7A beamline.\(^{16}\) Multiple samples approximately 1 cm in diameter (or width) and about 3 mm thick were loaded on a stainless steel bar and introduced into the vacuum chamber through a sample load lock system. Samples were precisely aligned with the aid of a fully automated computerized sample manipulator stage.\(^{17}\) Energy resolution and photon energy calibration of the monochromator were performed by comparing gas-phase carbon monoxide with electron-energy-loss reference data.\(^{18}\) The partial-electron-yield NEXAFS measurements were made using a channel electron multiplier with a \(-100\) V bias on the entrance grid to enhance surface sensitivity. Under these bias conditions, the partial-electron-yield measurement is dominated by the Auger yield from the sample surface \(\sim 5\) nm sensitivity (probe depth of approximately \(3\,\text{–}5\) nm).\(^{16}\) The sample was charge compensated using a low energy electron flood gun, which added no noticeable background to the NEXAFS spectra. Electron-yield data are subject to incident beam intensity fluctuations and monochromator absorption features. The spectra were normalized to the incident beam intensity \(I_0\) by collecting the total electron-yield intensity from a gold-coated 90% transmitting grid placed in the incoming x-ray beam path.

The samples were first analyzed with the overall elongation (stress) direction parallel to the electric field polarization plane \((\phi=0^\circ)\) in an x-ray beamline, as shown in Fig. 1. Then the samples were rotated by 90\(^\circ\) such that the elongation direction was perpendicular to the electric field polarization plane \((\phi=90^\circ)\). In each of the parallel and perpendicular geometry, the NEXAFS spectra were obtained at normal incidence \((\theta=90^\circ\) incidence angle measured with respect to the surface), where the electric field vector \(E\) is parallel to the sample surface, and at glancing incidence \((\theta=20^\circ)\) when the \(E\) is nearly perpendicular to the sample surface, also shown in Fig. 1.

III. RESULTS AND DISCUSSION

NEXAFS partial-electron-yield spectrum of typical elongated UHMWPE at the carbon \(K\)-edge taken at normal incidence \(\theta=90^\circ\) (solid curve) and at glancing incidence \(\theta=20^\circ\) (dashed curve) is shown in Fig. 2. The C–H resonance Rydberg peak was observed at 287.3 eV, and the C–C \(\sigma^*\) resonance peak (292.7 eV), a weak peak at 285 eV, has been assigned to C=C \(\pi^*\) due to the small amount of unsaturation present in UHMWPE. All the NEXAFS spectra in this paper are pre-edge \((<275\) eV) subtracted to zero and post-edge \(>325\) eV) normalized to compare the degree of preferential molecular orientation as a result of wear or stress. In the first set of experiments, the UHMWPE samples were loaded such that the elongation direction was parallel to the electric field polarization plane \((\phi=0^\circ)\). It is observed that the C–H resonance peak is pronounced when \(\theta=20^\circ\) (glancing incidence) and C–C resonance peak is pronounced when \(\theta=90^\circ\) (normal incidence). This is indicative of a preferential molecular orientation of the polymeric C–C chains parallel to the sample surface. In order to highlight those bonds having preferred molecular orientation as a result of different deformation/elongation stress, the normalized spectrum \(I_{\phi=20^\circ}\) (dashed) was subtracted from \(I_{\phi=90^\circ}\) (solid) as shown with label (a) in Fig. 2. The spectral feature with no preferred orientation subtracts to zero.

It was observed that the elongation direction when parallel to \(E\) \((\phi=0^\circ)\) exhibits maximum \(\theta\) anisotropy (alkyl chain orientation) compared to perpendicular measurement \((\phi=90^\circ,\) data not shown). This implies that when the stress supplied provide a means by which to compare the mechanical properties of the samples and serve as a statistical baseline for measuring the effect of wear simulator procedure on surface molecular orientation.
Fig. 3. C–H % molecular orientation for the C and X series with different elongation stress conditions is plotted. A linear regression fit is also shown as a solid line for the C series and as a dashed line for the X series.

direction is perpendicular to the plane containing \( E \) vector, we observe a nearly isotropic behavior of the C–C and C–H peaks for the normal incidence and glancing incidence. This result for the perpendicular geometry indicates that majority of the C–C alkyl chains lie in the direction of elongation stress and very few in the perpendicular direction. This result is very similar to our previous work on rubbed UHMWPE (Refs. 10–13) and elongated polystyrene.20 In the present study, we will report the orientation calculations with elongation direction parallel (\( \phi = 0^\circ \)) to the \( E \).

A. Effect of elongation on orientation

The first of these series is the C series, in which the samples were not subjected to any gamma irradiation and were elongated to 200%, 310%, and 400% of the original length. Along with the C series, experiments were done on the X series, which were irradiated with 100 kGy gamma rays prior to elongation stress of 100%, 200%, and 260%. Elongation stress of 310% and 400% on the X series were not available to complete our present study. From the subtracted NEXAFS spectrum (\( I_{\theta=90^\circ} - I_{\theta=20^\circ} \)) using the methodology illustrated by Outka et al.,21 the C–C and C–H tilt angles and percent molecular orientation can be extracted. Percent molecular orientation represents the degree of anisotropy or alignment of C–H or C–C chains with respect to a highly oriented UHMWPE reference. The C–H percent molecular orientation for the C and X series with different elongation stress conditions is plotted in Fig. 3. It was observed that the control materials C0 and X0 (0% elongation) had a very high degree of initial anisotropy (C–H and C–C orientation), which is attributed to the machining methods by which the control materials were prepared (See Table I). In the case of samples that are undergoing a large degree of strain hardening, which is attributed to increased alignment of amorphous C–C chains in the direction of stress,5 thereby, higher percent C–C molecular orientation in NEXAFS. In the X series, gamma irradiation leads to conglomeration of loosely bound chains to form a cross-linked amorphous material which resists strain deformation and has lesser alkyl chain orientation.

B. Effect of wear on orientation

From the comparison of the percent C–H orientation of C (no irradiation) and X series (100 kGy) (Fig. 3), The X series has overall lower orientation in parallel and perpendicular cases (not shown) and this trend remains the same in lower elongation cases. As the elongation is increased beyond 200%, the orientation of X series and C series tends to become similar within the limits of experimental errors. Irradiation of UHMWPE with gamma rays has definitely resulted in samples that resist orientation when an elongation stress of 200% or less is applied to them. The C–C percent molecular orientation (not shown in figure) for the C and X series followed a similar trend. Elongation stress in UHMWPE causes large-strain deformation and results in strain hardening in the direction of applied stress.22 From our observations, we can conclude that in the C series without gamma irradiation, uniaxial elongation stress causes greater strain hardening, which is attributed to increased alignment of amorphous C–C chains in the direction of stress,5 thereby, higher percent C–C molecular orientation in NEXAFS. In the X series, gamma irradiation leads to conglomeration of loosely bound chains to form a cross-linked amorphous material which resists strain deformation and has lesser alkyl chain orientation.
monotonic decrease for both $\phi=90^\circ$ and $\phi=0^\circ$ cases, with the exception of the 75 kGy sample. The out of trend result was attributed to extremely low anisotropy observed in the control material. It is well established for UHMWPE that the dosage of gamma irradiation levels similar to amounts in the present study causes various degrees of cross-linking to the chains of UHMWPE.\textsuperscript{2–4} In general, when the $E$ was parallel to the wear direction, more anisotropy or alkyl chain orientation was observed as compared to the perpendicular case. This result is very similar to the C and X series and our previous studies on GUR4150.\textsuperscript{10} Within the limits of 5\% experimental error, which arises due to NEXAFS peak intensity measurements, it was observed that the degree of orientation at C–C shows a linear response to the radiation dose for the range of dosage examined.

The difference in wear characteristics with varying amount of cross-linking may be explained by the different degrees of freedom of movement of the folded polymer chains as a function of the degrees of constraint imposed by cross-linking the chains. In the case of the 30 kGy irradiation level (D3), less cross-linking in the amorphous material makes the random C–C chains more susceptible to aggregation and realignment along the wear direction, with high percent C–C orientation. For the most highly cross-linked materials (100 kGy in our studies), more test (wear) time is necessary to break the cross-links and orient the folded chains, and hence, a smaller percent C–C orientation.

A comparative study of surface percent C–C orientation of other forms of irradiation/sterilization techniques such as ethylene-oxide sterilization and electron beam irradiation examined is summarized in Table I. It can be seen that an ethylene-oxide (EtO) sterilized sample shows the highest degree of orientation, followed by the 100 kGy gamma irradiated sample and 100 kGy electron beam irradiated sample. By utilizing small angle x-ray scattering, differential scanning calorimetry and other methodologies, Goldman et al.\textsuperscript{25} concluded that both 25 kGy electron beam and gamma irradiation caused increased crystallinity as compared to EtO sterilization. Under these low levels of radiation (D3) in this present study, we observed a high degree of anisotropy after wear similar to the observation of Goldman et al. However, increasing the level of gamma (D5-D10) or electron beam (E2) irradiation, where cross-linking was the more dominant process, resulted in more amorphous phase which resisted orientation after wear. By using NEXAFS technique, it appears that electron beam irradiation methods are much more effective in cross-linking GUR 1050 to produce maximum wear resistance.

Highest anisotropy is observed in case C1, where as-received GUR 1050 was subjected to 200\% elongation stress, which was 40\% higher %C orientation in X2 (100 kGy gamma irradiated sample). An interesting comparison of different kinds of wear processes is provided, for example, by a GUR 1050 sample subjected to elongation stress or wear using a knee simulator. Comparing X2 (100 kGy gamma irradiated sample), which was subjected to 200\% elongation, and D10 (100 kGy gamma irradiated sample), which was worn in a knee simulator, shows that elongation stress is much effective in causing anisotropy or alignment of C–C chains. The ease with which the surface molecules can be oriented or aligned has several implications for the observed wear phenomenon. One hypothesis is that by subjecting the material to unidirectional sliding or elongation in one direction, the surface molecules align parallel to the wear or stress direction, forming a quasiglassy material. Wear, therefore, occurs by tensile cracking and brittle fracture of the hardened surface layer, producing a relatively low amount of wear. When the surface motion is multiaxial (as in knee-simulator instrument), the surface molecules are in a constant state of flux and all fracture modes (tensile, shear, and twist) come into play. The molecular orientation weakens interfiber strength and thus results in a much higher amount of wear than in the other cases.\textsuperscript{10–12,24}

IV. CONCLUSIONS

In this study, we utilized NEXAFS, a nondestructive synchrotron based soft x-ray technique, to examine the degree of surface molecular orientation of UHMWPE under various cross-linking/sterilization techniques as a function of stress and wear. Our studies reveal the effect of radiation on the wear characteristics from the top 5 nm surface perspective. We have concluded that gamma and electron beam irradiations render very high wear resistance by forming a more amorphous cross-linked surface molecular layer that resists surface orientation. This consequently makes cross-linked UHMWPE the most suitable candidate in orthopaedic bearings in hip and knee prostheses. The NEXAFS at the C edge showed that gamma irradiation of UHMWPPE has definitely resulted in samples (X series) which have a 30\% reduction in surface molecular orientation when elongation stress up to 200\% in length is applied. Increasing the amount of gamma radiation dose causes a linear decrease in molecular orientation of worn samples in a knee simulator. Below 50 kGy gamma irradiation, UHMWPE sample exhibited more anisotropy, indicating a greater fraction of crystalline phase, which has poor wear resistance. By increasing the radiation dose up to 100 kGy, UHMWPE appears to form a highly cross-linked rigid layer which has about 50\% reduced anisotropy in NEXAFS.

ACKNOWLEDGMENTS

The authors wish to acknowledge the support and collaboration from the members of the NIST Orthopaedic Wear Consortium. NEXAFS experiments carried out at the National Synchrotron Light Source, Brookhaven National Laboratory were supported by the U.S. Department of Energy under Contract No. DE-AC02-98CH10886. The authors would like to thank Ian Genzer at NCSU for his assistance with editing the sample geometry figure.

\textsuperscript{2}A. Wang et al., Wear 203, 230 (1997).


