



Raman tensor analysis of ultra-high molecular weight polyethylene and its application to study retrieved hip joint components

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ABSTRACT

The angular dependences of the polarized Raman intensity of A_g , B_{1g} , B_{2g} , and B_{3g} modes have been preliminary investigated on a model fiber sample of ultra-high molecular weight polyethylene (UHMWPE) in order to retrieve the Raman tensor elements, i.e. the intrinsic parameters governing the vibrational behavior of the orthorhombic structure of polyethylene. Based on this Raman analysis, a method is proposed for determining unknown crystallographic orientation patterns in UHMWPE biomedical components concurrently with the orientation distribution functions for orthorhombic lamellae. An application of the method is shown, in which we quantitatively examined the molecular orientation patterns developed on the surface of four *in vivo* exposed UHMWPE acetabular cups vs. an unused cup. Interesting findings were: (i) a clear bimodal distribution of orientation angles was observed on worn surfaces; and (ii) a definite and systematic increase in both molecular orientation and crystallinity in main wear zones vs. non-wear zones was found in all retrieved acetabular cups. The present crystallographic analysis is an extension of our previous Raman studies of UHMWPE acetabular cups related to assessments of oxidation and residual strain and suggests a viable path to track back wear-history information from the surface of UHMWPE, thus unfolding the *in vivo* kinematics of the bearing surfaces in hip joints on the microscopic scale.

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1. Introduction

The most widely used type of prosthesis in total hip arthroplasty (THA) consists of a system with a femoral head made of a metal alloy (e.g. CoCr) impinging against an ultra-high molecular weight polyethylene (UHMWPE) acetabular cup. In this hip joint system, the UHMWPE acetabular cup undertakes the multiple roles of body-weight bearing, low-friction sliding surface, and impact absorber. Accordingly, it is liable to experience extensive creep and wear damages with the concurrent formation of polyethylene debris, which eventually leads to joint loosening and osteolysis (i.e. to the need for further surgery) [1,2]. In other words, UHMWPE components unavoidably degrade both chemically and mechanically during *in vivo* implantation. In an attempt to both clarify the origin of implant degradation and propose methods for elongating their lifetime, a number of Raman studies have been carried out, focusing on phenomena of chemical and structural degradation (e.g. oxidation and degree of crystallinity) in the polyethylene structure [3–7]. On the other hand, Raman measurements of residual strain in UHMWPE acetabular cups have provided an effective

tool for the quantitative assessment of mechanical degradation in terms of residual strain [8,9]. In particular, this latter Raman spectroscopic method provided us with an experimental path to separate creep and wear contributions from the dimensional change experimentally observed in *in vivo* exposed acetabular cups. Although Raman studies of chemical, structural, and mechanical alterations have greatly contributed to advancing our knowledge of degradation processes in biomedical UHMWPE grades, there is still a long way to go before the development of a rigorous *in vivo* lifetime prediction of biomedical components becomes available. The reason for such a lack of information might partly reside in the fact that additional structural factors (i.e. besides crystallinity) are often not considered to be as important as the chemical and mechanical ones: the occurrence of local crystallographic alignment of the polyethylene lamellae. Polarized Raman spectroscopy possesses the potential to quantitatively unfold the missing crystallographic information by screening with a laser microprobe the molecular orientation patterns developed on the surface of acetabular components [10–15]; however, such an evaluation represents a formidable experimental and computational task. Crystalline (e.g. mainly orthorhombic) phases in UHMWPE might be randomly oriented within the amorphous matrix or be preferentially oriented as a consequence of the manufacturing pro-

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cess. However, the orientation of crystalline lamellae is sensitive to mechanical and frictional loading [16–18]. Therefore, the lamellae will unavoidably tend to preferentially orient themselves on the surface of UHMWPE acetabular cup during *in vivo* loading. This molecular re-arrangement reflects both primary and secondary motions generated at the contact surface in artificial hip joints, thus representing an important mechanism, precursor to the formation of wear debris throughout the loading history.

In this paper, we have focused on the determination of a spectroscopic method aimed at quantifying the degree of molecular orientation and the angular distributions of orthorhombic lamellae on the surface of UHMWPE. Preliminary to such assessments, we made efforts in explicitly describing the Raman selection rules and in experimentally calibrating the relevant Raman tensor elements intrinsic to the orthorhombic structure of polyethylene using a model sample (i.e. an UHMWPE fiber with almost totally aligned molecular structure). An additional step has then been that of introducing an orientation distribution function (i.e. formulated from Wigner functions in terms of Legendre polynomials [19–21]) into the mathematical algorithm of Raman crystallographic orientation analysis, with the ultimate goal of quantifying the local degree of alignment of the structure concurrently to the orientation in space of the *c*-axis of the orthorhombic cell. According to the knowledge of both intrinsic vibrational parameters and orientation distribution functions, we could quantitatively discuss the orientation of orthorhombic lamellae from relative changes in intensity of selected Raman bands in both parallel and cross polarization geometries. The structure of the paper is organized as follows. Section 2 briefly describes the UHMWPE material used for Raman calibrations, the unused and retrieved samples from hip joint surgeries, as well as the salient technical aspects of our confocal/polarized Raman equipment. Section 3, which also contains a brief description of the Raman bands of the orthorhombic UHMWPE structure, is mainly dedicated to theoretical analyses of the Raman intensity dependences on molecular orientation and to the explicit description of the role of orientation distribution functions in the Raman selection rules of an orthorhombic polyethylene structure. This section ends with establishing the working equations that describe the orientation distribution function and the Raman selection rules in terms of three Euler angles, thus locating the *c*-axes of orthorhombic lamellae in space with respect to the sample surface. In Section 4, we apply the polarized Raman scattering technique to quantitatively describe the orientation patterns generated in four acetabular cups retrieved after different periods of *in vivo* exposure (ranging between about 2 and 12 years of exposure time *in vivo*). Areas from main wear and non-wear zones are characterized in comparison to an unused acetabular cup, and a brief discussion is offered in comparison with crystallinity data collected at the same studied locations. In Section 5 we present our conclusions.

2. Materials and methods

2.1. UHMWPE fiber for Raman tensor calibration

The UHMWPE fiber used for spectroscopic calibrations was a commercially available sample manufactured by Ningbo Dancheng Advanced Materials Co. Ltd. (Zhejiang, China). This fiber, typically ≈ 25 μm in diameter, possessed a high molecular weight (approx. three million), interlinking, high degree of uniaxial orientation and high crystallinity. According to the X-ray diffraction measurements provided by the manufacturer, the orthorhombic cell is prevalent in the structure with its *c*-axis being strongly oriented along the long axis of the fiber. This point will be further clarified in the quantitative Raman analysis of the degree of molecular orientation

shown in the remainder of this paper. A draft of the orthorhombic cell and its average orientation with respect to the fiber structure is shown in Fig. 1a. Our Raman analysis also clarified that, as far as the rotation angle around the long axis of the fiber is concerned, the investigated UHMWPE fiber experienced a domain-like structure in the *c*-plane, each domain experiencing constant in-plane angle. The size of the domains was typically in the order of few cubic μm , namely of a size comparable with our confocal Raman probe (cf. Section 2.3 below). Such a peculiar microstructure of the fiber sample, already reported by other authors [22], was the key factor in locating the intrinsic vibrational characteristics of an UHMWPE orthorhombic crystal cell.

2.2. Unused and retrieved UHMWPE acetabular cups

Four different acetabular cups were investigated, which were all retrieved from left-side hip joints in the respective patient bodies at Tokyo Medical University. These acetabular cups will also be referred to as short-term (2.4- and 2.8-year) and long-term (10.3- and 12.2-year) retrievals, respectively. The short-term retrieved acetabular components were both made of highly cross-linked polyethylene, manufactured from 1900H bar stock by isostatic compression molding (with no addition of calcium stearate) (ArCom[®], Biomet Japan Inc., Tokyo, Japan) and sterilized by γ -ray irradiation with a dose of 33 kGy. One cup belonged to a 61 year old male patient for which the cause of revision was infection with a follow-up period of 2.4 years, while the other cup belonged to a 53 year old female patient for which the cause of revision was infection dislocation with a follow-up period of 2.8 years. On the other hand, two long-term retrievals were made from GUR4150 bar stock by Ram extraction molding (calcium stearate was added in these case) and sterilized with a dose of γ -ray radiation ranging between 25 and 37 kGy. One cup (manufactured by Zimmer Inc., Tokyo, Japan) belonged to a 47 year old male patient, while the other cup (ArCom[®], Biomet Japan Inc., Tokyo, Japan) belonged to a 60 year old female patient. Both cups were retrieved due to aseptic loosening and the follow-up period was 10.4 and 12.2 years, respectively.

For comparison, an unused acetabular cup was investigated, which was also from the Biomet manufacturer and possessed the same manufacturing characteristics of the short-term retrieval described above. Locating the main wear zone on both short-term and long-term retrievals could be pursued in a relatively easy way by the naked eye, owing to a slight difference in surface roughness (and thus in sample translucency) as compared to the non-wear zone. On the other hand, an exception was the short-term retrievals exposed *in vivo* for 2.8 years, for which such an observation was difficult. In this latter case, we assumed the main wear zone to be located within the angular interval 30–40° from the location of cup dome, in analogy with the other retrievals studied.

2.3. Polarized Raman spectroscopy

Raman spectra were collected at room temperature with a triple-monochromator (T-64000, HORIBA/Jobin-Yvon, Kyoto, Japan) equipped with a charge-coupled device (CCD) detector. Spectral analyses were performed by means of commercially available software (Labspec, HORIBA/Jobin-Yvon, Kyoto, Japan). The laser excitation source was a monochromatic blue line emitted by an Ar-ion laser at a wavelength of 488 nm (Stabilite 2017, Spectra Physics, Mountain View, CA) with a power of 100 mW. The integration time for acquiring a spectrum (namely at each pixel of the collected Raman maps) was typically 15 s. Preliminary experiments were made for checking about the possibility of heating effects on the sample by laser irradiation. The outcome of such experiments

ID	Title	Pages
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