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ELSEVIER
Journal of the Mechanical Behavior of Biomedical Materials

Research Paper

In-vivo degradation of middle-term highly cross-linked and remelted polyethylene cups: Modification induced by creep, wear and oxidation

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ARTICLE INFO

Article history:
Received 24 April 2015
Received in revised form
22 June 2015
Accepted 23 June 2015
Available online 9 July 2015

Keywords:
UHMWPE
Total hip arthroplasty
Retrievals
Raman spectroscopy
FT-IR
Oxidation
Wear
Creep

ABSTRACT

In this study Raman (RS) and Fourier Transform Infrared (FT-IR) spectroscopic techniques were exploited to study 11 retrieved liners made of remelted highly cross-linked polyethylene (HXLPE), with the intent to elucidate their in-vivo mechanical and chemical degradation. The retrievals had different follow-ups, ranging from a few months to 7 years of implantation time and belong to the first generation of highly cross-linked and remelted polyethylene clinically introduced in 1999, but still currently implanted. Raman assessments enabled to discriminate contributes of wear and creep on the total reduction of thickness in different locations of the cup. According to our results, although the most of the viscoelastic deformation occurred during the first year (bedding-in period), it progressed during the steady wear state up to 7 years with much lower but not negligible rate. Overall, the wear rate of this remelted HXLPE liner was low. Preliminary analysis on microtomed sections of the liners after in-vivo and in-vitro accelerated aging (ASTM F2003-02) enabled to obtain a phenomenological correlation between the oxidation index (*OI*) and the amount of orthorhombic phase fraction (α_c), which can be easily non-destructively measured by RS. Profiles of α_c obtained from different locations of the cups were used to judge the oxidative degradation of the 11 retrievals, considering also the ex-vivo time elapsed from the revision surgery to the spectroscopic experiments. Low but measurable level of oxidation was detected in all the short-term retrievals, while in the middle-term samples peaks of *OI* were observed in the subsurface (up to $OI=4.5$), presumably induced by the combined effect of mechanical stress, lipid absorption and prolonged ex-vivo shelf-aging in air.

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http://dx.doi.org/10.1016/j.jmbbm.2015.06.028
1751-6161/

1. Introduction

Balance among wear, creep and oxidation resistance of UHMWPE exposed to biomechanical loads during implantation in the human body. After almost two decades from the development and launch of the first generation of highly cross-linked polyethylene for total hip arthroplasty (THA), this has become the primary issue to be addressed by scientists and engineers in order to achieve higher standards in long-term survivorship of hip joint replacements. The introduction of radiation cross-linking of ultra-high molecular polyethylene (UHMWPE) in the late 1990s indeed represents the major breakthrough in the research and development of orthopedic bearing materials with superior wear and creep resistance (Dumbleton et al., 2006; Gencur et al., 2006; Kurtz et al., 2011). In fact, by increasing the molecular weight through the formation of cross-links between adjacent molecular chains, the ability of the polymer to undergo large deformation is largely decreased. As a matter of fact, excessive deformation caused by the sliding of the harder femoral head on the surface of the polymer may induce molecular orientation along the direction of plastic flow (namely the direction of deformation). High molecular alignment along the primary sliding direction deteriorates the mechanical resistance of the polymer along the other directions and such a "strain-softening" phenomenon lead to the detachment from the surface of micrometric debris (Wang et al., 1997), which may eventually trigger an acute immune response that results in osteolysis and, ultimately, in joint loosening (James et al., 1993; Oparaugo et al., 2001; Zhu et al., 2001). If from one hand wear is a degradation of the material which occurs on the surface, on the other hand, when we deal with polymers, also the inevitable tendency of the bulk material to deform when subjected to load for prolonged time must carefully taken into consideration during the conception phase of bearings. The viscoelastic deformation (i.e., creep) might be deleterious for the correct function of the prosthesis, especially when it manifests in the form of pinch deformation, which changes the sphericity of the cup and induces equatorial contact and degradation of the fluid-film lubrication (Jin et al., 2006; Meding et al., 2013; Ong et al., 2009). In other words, excessive creep might adversely affect the wear resistance and the stability of the joint in the long term. Despite the different physical origin of wear and creep, from a phenomenological point of view, they both manifest themselves with a reduction of cup thickness, whose total extent is routinely measured both in vivo and on cup retrievals, and cumulatively recorded in clinical data. Moreover they are both exacerbated by oxidative degradation, which is progressing with long-term clinical use, leading to debris formation and, ultimately, to joint loosening, or, in the most unfortunate cases, to the premature mechanical failure of the component (Schmalzried and Callaghan, 1999). The first generation of HXLPEs was manufactured with including a melting or annealing step in order to quench the excess of free radicals generated during irradiation, which may eventually react with the oxygen dissolved in the polymer and lead to oxidative degradation (Yeom et al., 1998). However, the results of the first studies on retrievals made of first generation HXLPE showed the unexpected appearance of mechanical and chemical degradation (Currier et al., 2007, 2010). If from one hand a simple post-irradiation annealing step has proved to be insufficient to remove all the free radicals generated during cross-linking (Oral et al., 2011), on the other hand post-irradiation remelting reduces the crystallinity of the final microstructure, which conspicuously decreases the mechanical strength of the polymer (Baker et al., 2003; Gillis et al., 1999; Gomoll et al., 2001; Oral et al., 2011), and can not protect the material from possible generation of free-radicals during in-vivo service. In the attempt to enhance wear and oxidation resistance, a second generation of HXLPEs was engineered by introducing two alternative methods. The first one is based on a 3-step irradiation and annealing process, using a lower dose of γ-ray at each step (i.e., 30 kGy), which enables to optimize the efficiency of the cross-linking during each annealing, to

Table 1 – List of retrievals and their clinical data.

No.	In-vivo time (mo/yr)	Ex-vivo time (mo/yr)	Age (yr)	Sex	BMI (Kg/m^2)	Abd. Angle (°)	Thickness (mm)	Cause of revision	Femoral head
Short term									
No 1	0.5/0.04	137/11.4	71	F	29	45	10.3	Cup loosening	Zirconia
No 2	1.0/0.08	6.0/0.50	58	F	35	46	6.3	Infection	Delta
No 3	1.5/0.13	92/7.70	71	F	18	35	15.4	Infection	Zirconia
No 4	3.0/0.25	74/6.20	67	F	29	39	8.2	Dislocation	Zirconia
No 5	6.0/0.50	39/3.30	78	F	20	30	7.2	Cup loosening	CoCr
No 6	6.5/0.54	94/7.80	71	F	26	40	15.4	Stem loosening	Zirconia
No 7	8.0/0.67	89/7.40	32	M	26	47	12.4	Neuro-paralysis	CoCr
Middle term									
No 8	49/4.10	50/4.20	72	F	33	45	6.4	Dislocation	CoCr
No 9	73/6.10	76/6.30	68	F	30	40	8.2	Stem loosening	Zirconia
No 10	77/6.40	78/6.50	61	F	25	48	7.2	Stem loosening	Zirconia
No 11	86/7.20	15/1.30	75	F	20	45	6.3	Infection	CoCr