JOURNAL OF THE MECHANICAL BEHAVIOR OF BIOMEDICAL MATERIALS 59 (2016) 418–429

Available online at www.sciencedirect.com

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www.elsevier.com/locate/jmbbm

Research Paper

Does cyclic stress and accelerated ageing influence the wear behavior of highly crosslinked polyethylene?

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ARTICLE INFO

Article history:
Received 7 January 2016
Received in revised form
22 February 2016
Accepted 23 February 2016
Available online 2 March 2016

Keywords:
Accelerated ageing
Vitamin E
Crosslinked PE
Hip simulator
Raman spectroscopy

ABSTRACT

First-generation (irradiated and remelted or annealed) and second-generation (irradiated and vitamin E blended or doped) highly crosslinked polyethylenes were introduced in the last decade to solve the problems of wear and osteolysis.

In this study, the influence of the Vitamin-E addition on crosslinked polyethylene (XLPE_VE) was evaluated by comparing the *in vitro* wear behavior of crosslinked polyethylene (XLPE) *versus* Vitamin-E blended polyethylene XLPE and conventional ultra-high molecular weight polyethylene (STD_PE) acetabular cups, after accelerated ageing according to ASTM F2003-02 ($70.0 \pm 0.1\,^{\circ}C$, pure oxygen at 5 bar for 14 days). The test was performed using a hip joint simulator run for two millions cycles, under bovine calf serum as lubricant.

Mass loss was found to decrease along the series XLPE_VE > STD_PE > XLPE, although no statistically significant differences were found between the mass losses of the three sets of cups. Micro-Raman spectroscopy was used to investigate at a molecular level the morphology changes induced by wear. The spectroscopic analyses showed that the accelerated ageing determined different wear mechanisms and molecular rearrangements during testing with regards to the changes in both the chain orientation and the distribution of the all-trans sequences within the orthorhombic, amorphous and third phases. The results of the present study showed that the addition of vitamin E was not effective to improve the gravimetric wear of PE after accelerated ageing. However, from a molecular point of view, the XLPE_VE acetabular cups tested after accelerated ageing appeared definitely less damaged than the STD_PE ones and comparable to XLPE samples.

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http://dx.doi.org/10.1016/j.jmbbm.2016.02.029
1751-6161/

1. Introduction

It is well established that the oxidative degradation of ultra-high molecular weight polyethylene (UHMWPE) decreases its mechanical properties and represents one of the main causes of its failure (Brach del Prever et al., 2009; Bracco and Oral, 2011; James et al., 2009). Efforts were faithful to improve UHMWPE and to extend the lifetime of orthopedic implants (Affatato et al., 2016). Currently, highly crosslinked polyethylene (XLPE) used in total hip arthroplasty (THA), is clinically accepted as the material for acetabular liners articulated with metallic or ceramic femoral heads (Brach del Prever et al., 2009; Kurtz et al., 2008). Annealed or remelted XLPE substantially reduces the residual free radicals, but also crystallinity and mechanical properties of the polymer (Brach del Prever et al., 2009; Banche et al., 2014; Kurtz et al., 2006). Other strategies were approached to reduce or retard oxidation by adding suitable additives capable of interrupting the oxidation cycle, by decreasing the reactivity of the radical species; thus, stabilizers are compounds added to the polymer in order to slow the oxidation processes and to preserve its chemical, physical and mechanical properties, i.e. to prolong its lifetime (Zweifel, 1998; Kurtz et al., 1999). Vitamin E seems to be the ideal candidate, being already employed as a natural antioxidant in the physiological processes of the human body (Bracco et al., 2007).

The evolution of *in vivo* oxidation is complex, depending not only on the type of UHMWPE material, but also on the duration of implantation and the local availability of oxygen in body fluids and/or tissues (Kurtz et al., 2009). To this regard, it is important not only to characterize the actual orthopedic components from a tribological point of view, but also to expose these components to an accelerated ageing in order to compare their behavior with that observed following long-term exposure to natural ageing during shelf storage and/or *in vivo* exposure in human patients (Kurtz et al., 2009). Hopefully, a procedure of accelerated ageing should simultaneously reproduce the chemical changes in materials, as well as the depth profiles of these changes, including oxidation (Rocha et al., 2009).

Protocols and standards for accelerated ageing of UHMWPE usually involve heating for 21 days at 80 °C in air or heating for 14 days at 70 °C under 5 bar oxygen (Rocha et al., 2009; Toohey et al., 2003; Lu et al., 2002; McKellop et al., 2000). However, there are no ageing protocols that have been adequately validated to replicate real-time shelf and *in vivo* ageing of XLPE or conventional UHMWPE (Willie et al., 2006; Wolf et al., 2006).

The present study was aimed at investigating the effects of the accelerated ageing on the wear behavior of vitamin E-stabilized XLPE acetabular cups in comparison to standard UHMWPE and remelted XLPE acetabular cups. To this purpose, in a first test, the wear behavior of the three sets of samples was investigated against CoCrMo femoral heads in a hip joint simulator for five million cycles (Affatato et al., 2012). After the test, the cups underwent an accelerated ageing treatment according to ASTM F2003-02 and subsequently were newly tested in the hip joint simulator for another two million cycles. The wear behavior of the three sets of acetabular cups was evaluated by gravimetric measurements. To gain more insights into the role of vitamin E in the wear mechanism of the aged acetabular cups, the samples were analyzed by micro-Raman spectroscopy before the second test (*i.e.* after accelerated ageing) and after it. This technique proved suitable to investigate at a molecular level the morphology changes (*i.e.* in crystallinity, phases distribution and chain orientation) induced by wear. Micro-Raman spectroscopy was chosen due to its non-destructive character, in view of continuing the tests under more severe conditions (*i.e.* in presence of third-body wear particles).

2. Materials and methods

The wear behavior of three different batches of polyethylene acetabular cups (28-mm inner × 44-mm outer dimensions; four specimens for each batch) coupled with 28-mm cobalt–chromium–molybdenum (CoCrMo) femoral heads was investigated using a hip joint simulator; three specimens of each test were tested, the fourth was used as control check (see below). All the components (acetabular cups and femoral heads) were produced through the same manufacturing procedures and supplied by the same manufacturer as finished-products. Standard UHMWPE acetabular cups (hereinafter called STD_PE) were machined from polymer bars made of GUR 1020 (Orthoplastics Ltd., Lancashire, UK). Cross-linked acetabular cups (hereinafter called XLPE) were obtained from a cylindrical bar, firstly electron beam-irradiated to 70 kGy, then thermally treated at 135 °C, in order to remove free radicals formed during irradiation. After these treatments, the cups were machined to their final shape. Similarly, Vitamin E-containing XLPE acetabular cups (hereinafter called XLPE_VE) were machined from a Vitamin E-blended UHMWPE bar (0.1% w/w; Orthoplastics Ltd., Lancashire, UK), after electron beam irradiation to 70 kGy followed by a thermal treatment at 160 °C under nitrogen for 12 h. All the cups were then subjected to Ethylene Oxide Sterilization (EtO). Further details are available in previous reports (Affatato et al., 2012). Following a standardized procedure, three control check acetabular cups (one for each type of material used) were stored (non-loaded) in bovine calf serum to compensate for weight changes due to fluid absorption. All polyethylene acetabular cups were pre-soaked for four weeks prior the wear tests (Affatato et al., 2012; Taddei et al., 2006).

2.1. Accelerated aging

In the first wear test the specimens were run for five million cycles (Affatato et al., 2012). Then, all the acetabular cups (worn specimens and soak controls) underwent an accelerated ageing treatment, which was performed in a stainless steel pressure vessel, under 503 ± 7 kPa of oxygen pressure at 70.0 ± 0.1 °C for 14 days, according to ASTM F2003-02. After accelerated ageing, the cups were newly mounted on the hip joint simulator and were run for two million cycles against the CoCrMo femoral heads (second wear test).