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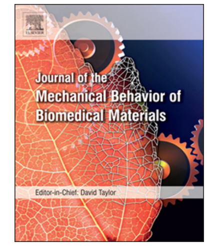

Research Paper

Wear performance of neat and vitamin E blended highly cross-linked PE under severe conditions: The combined effect of accelerated ageing and third body particles during wear test

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ABSTRACT

The objective of this study is to evaluate the effects of third-body particles on the *in vitro* wear behaviour of three different sets of polyethylene acetabular cups after prolonged testing in a hip simulator and accelerated ageing. Vitamin E-blended, cross-linked polyethylene (XLPE_VE), cross-linked polyethylene (XLPE) and conventional polyethylene (STD_PE) acetabular cups were simulator tested for two million cycles under severe conditions (i.e. by adding third-body particles to the bovine calf serum lubricant). Micro-Fourier Transform Infrared and micro-Raman spectroscopic analyses, differential scanning calorimetry, and crosslink density measurements were used to characterize the samples at a molecular level.

The STD_PE cups had twice mass loss than the XLPE_VE components and four times than the XLPE samples; statistically significant differences were found between the mass losses of the three sets of cups. The observed wear trend was justified on the basis of the differences in cross-link density among the samples (XLPE > XLPE_VE > STD_PE).

FTIR crystallinity profiles, bulk DSC crystallinity and surface micro-Raman crystallinity seemed to have a similar behaviour upon testing: all of them (as well as the all-trans and ortho-trans contents) revealed the most significant changes in XLPE and XLPE_VE samples. The more severe third-body wear testing conditions determined more noticeable changes in all spectroscopic markers with respect to previous tests. Unexpectedly, traces of bulk oxidation were found in both STD_PE (unirradiated) and XLPE (remelting-stabilized), which were expected to be stable to oxidation; on the contrary, XLPE_VE demonstrated a high oxidative stability in the present, highly demanding conditions.

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1. Introduction

Although ultra-high molecular weight polyethylene (UHMWPE) has been the material of choice for acetabular liners in total hip arthroplasty (THA) for more than 50 years (Brach del Prever et al., 2009; Kurtz et al., 2008), oxidative degradation of UHMWPE and biological response to debris particles, released by orthopaedic implants, are still key factors in periprosthetic osteolysis and subsequent implant loosening (Bracco and Oral, 2011; Brach del Prever et al., 2009; Grupp et al., 2014; Ingham and Fisher, 2000; James et al., 2009). Many efforts have been aimed at improving UHMWPE wear performances in order to reduce wear problems. In particular, highly cross-linked polyethylenes (XLPEs), developed in the last 15 years, have shown a markedly increased wear resistance (Bistolfi and Bellare, 2011; Muratoglu, 2009). In order to warrant the oxidation resistance, thermal treatments (annealing or remelting) were applied to the first and second generation of radiation cross-linked polyethylenes (Dumbleton et al., 2006; McKellop et al., 1999; Muratoglu et al., 2001). In recent years, a different approach to stabilization has been attempted and suitable additives (i.e. vitamin E), capable to interrupt the oxidation cycle by decreasing the reactivity of the radical species, are being added to UHMWPE, giving origin to a third generation of XLPEs (Bracco and Oral, 2011; Kurtz et al., 2009a; Lerf et al., 2010).

Currently, it is important to characterize the orthopaedic components from a tribological point of view under severe conditions: i.e. to expose these components to an accelerated ageing in order to compare their behaviour with that observed following long-term exposure to natural ageing during shelf storage and/or *in vivo* exposure in human patients (Kurtz et al., 2009b, 1999). For this purpose, a number of ageing protocols have been developed over time (Affatato et al., 2016; Kurtz et al., 2001; Rocha et al., 2009). A procedure of accelerated ageing would hopefully simultaneously reproduce the chemical changes in materials, as well as the depth profiles of these changes, including oxidation (Rocha et al., 2009).

The main aim of this work was to evaluate if the addition of vitamin E was effective in improving the oxidation resistance and the wear behaviour of polyethylene, under third-body wear conditions. Since it has been observed that abrasive wear, in the presence of third-body particles, can accelerate polyethylene wear (Bragdon et al., 2003), the adding of third-body particles on PE acetabular cups would recreate a *worst-case scenario*. In our experiment, third body particles were added to different polyethylene configurations, previously tested after accelerated ageing (Affatato et al., 2016), and our investigation was also aimed to establish a correlation, if any, between the observed wear behaviour and the chemical and morphological changes occurred in the PE as a result of the test under these severe conditions.

The three sets of acetabular cups were comparatively characterized by micro-Raman spectroscopy to gain insights into the wear mechanism, i.e. the possible changes in surface crystallinity, phases distribution and chain orientation upon wear. In addition, each component was analysed by Micro-FTIR spectroscopy to monitor the crystallinity profiles and oxidation level and by differential scanning calorimetry (DSC) to gain information on possible variations of the bulk crystallinity, following accelerated ageing and simulator testing. Gravimetric measurements of the cross-link density were also performed and compared to that of the original samples.

2. Materials and methods

In vitro wear simulation was performed using three different batches of polyethylene acetabular cups (28-mm inner × 44-mm outer dimensions; 4 specimens for each batch) coupled with 28-mm cobalt-chromium-molybdenum (CoCrMo) femoral heads. In particular, conventional UHMWPE acetabular cups (STD_PE) were machined from polymer bars made of GUR 1020 (Orthoplastics Ltd., Lancashire, UK). XLPE acetabular cups were obtained from a cylindrical bar, firstly electron beam-irradiated to 70 kGy, then thermally treated at 135 °C for 12 h, in order to remove free radicals formed during irradiation. After these treatments, the cups were machined to their final shape. Similarly, XLPE_VE acetabular cups 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).

2.1. *Wear test details*

Wear test was performed using a 12-station hip joint simulator (IORSynthe, Bologna, Italy). The lubricant used was 25% (v/v) new born calf serum balanced with distilled water, with 0.2% sodium azide in order to retard bacterial growth, 20 mM EDTA (ethylenediaminetetracetic acid) to minimize precipitation of calcium phosphate. The final protein mass concentration value of the lubricant was 28 mg/mL, which is in agreement with that recommended by international guidelines (Organization, 2012). In addition, in order to reproduce severe test conditions (a *worst-case scenario*) debris particles were added to the lubricant. The debris particles used were Polymethyl-methacrylate (PMMA) containing 90% of PMMA and 10% of barium sulphate ($BaSO_4$) as radiopaque material. The particles mean size was between 70 and 200 μm. These particles were added to the lubricant at each wear-stop (i.e. every 0.4 million cycles) with a concentration of 5 mg/L. In addition, a concentration of 1 mg/L was added at the head-cup coupling interface at each wear stop using a pipette. The components were rotated across the stations after each wear-stop to minimize the effect of inter-station kinematic variability. In this test, for each station an axial load up to 2600 N was applied, as recommended by the ISO 14242-3 international guideline, according to the rotation test frequency. Flexion/Extension and Adduction/Abduction translations are programmed using a biaxial rocking motion common to all channels. Typically, in an *in vivo* situation, the surgeon fixes the acetabular cup with an abduction of about 45° and this scenario is reproduced *in vitro* by considering an inclination of 23° with respect to a horizontal plane as observed in a previous study (Taddei et al., 2006). The acetabular cup orientation was set in up-side-down (inverted anatomical) position with the aim of reproducing worst-case scenarios,