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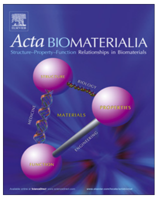

Full length article

Validation of a protocol based on Raman and infrared spectroscopies to nondestructively estimate the oxidative degradation of UHMWPE used in total joint arthroplasty

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ABSTRACT

As a matter of fact, the in vivo oxidative degradation of highly cross-linked polyethylene (HXLPE) still remains one of the limiting factors that affect the long term survivorship of joint replacements. Recent studies clearly pointed out that also the new generation of highly cross-linked and remelted polyethylene components in total hip and knee replacement underwent unexpected oxidation after 5–10 years of implantation. The standard methodology to investigate the oxidation of polyethylene (PE) relies on the use of infrared spectroscopy, which, if from one hand is a reliable technique for the detection of oxidized species containing carbonyl group, on the other hand it is not capable of discriminating the fraction of carboxyl acids that is responsible for chain scission and subsequent deterioration of the mechanical properties of the polymer. In the present study we validate a new protocol based on Raman spectroscopy, which is suitable on assessing the structural degradation of polyethylene induced by oxidation. Following in vitro accelerated aging experiments, the oxidation index (*OI*) of different commercially available HXLPEs, as calculated by infrared spectroscopy according to ASTM standard, has been univocally correlated to the most severe variation of crystalline phase (α_c), as calculated by Raman spectroscopy. In each material, locations with equal values of *OI* showed different degree of recrystallization induced by chain scission, confirming that infrared spectroscopy might overestimate the effective mechanical degradation of the polymer. In addition, as compared to the standards based on infrared spectroscopy, this new method of assessing oxidation enables to investigate the degradation occurring on the original surface of HXLPE components, due to the nondestructive nature of Raman spectroscopy and its high spatial resolution.

Statement of Significance

In the present study we validate a new protocol based on Raman spectroscopy, which is suitable on assessing the structural degradation of polyethylene induced by oxidation. In fact, the standard methodology to investigate the oxidation in polyethylene relies on the use of infrared spectroscopy, which is capable of detecting the presence of oxidized species containing carbonyl group, the main products of oxidation in polyolefins. If from one hand this technique enables quantitative analysis of oxidation, on the other hand it is not capable of discriminating the fraction of species with carbonyl groups responsible for the chain scission. In fact, esters, ketones and carboxyl acids are products of oxidation with carbonyl groups commonly formed on polyethylene at the end of the oxidative cascade initiated by the presence of free radicals, but only the latter are responsible for the chain scission and the subsequent deterioration of the mechanical properties. The oxidation index as obtained according to the ASTM standards is not univocally correlated to a certain degree of mechanical deterioration, but, in simple words, two retrievals with the same amount of carbonyl groups might have had different degradation of the mechanical properties. Recrystallization is a direct consequence of the reduction of molecular weight that occurs after

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chain scission. Raman spectroscopy (RS) is a viable non-destructive method to assess the fraction of crystalline phase in polyethylene and, due to its high spatial resolution, is perfectly suitable to analyze the microstructural modification at the mesoscopic scale, where the effects of oxidation manifest themselves. The aim of the present paper is twofold: i) to compare the microstructural modifications caused by in vitro oxidation on 5 different types of polyethylene currently available on the market of joint replacements; ii) to establish a protocol based on the comparative analysis of IR and RS results to obtain a phenomenological correlation capable to judge the mechanical deterioration of the material induced by the oxidative degradation.

1. Introduction

Since the birth of the modern arthroplasty dated back to 1962 when Sir John Charnley introduced cemented metal-polyethylene components for the hip [1], the materials used for joint replacements have been subjected to continuous improvements with the aim to ameliorate the long-term survivorship of the orthopedic implants. Among the materials presently used to produce bearing components for joint replacements, highly cross-linked polyethylene (HXLPE) still represents the primary choice for patients necessitating total hip (THA) or knee (TKA) arthroplasty. The use of ionizing radiation to generate cross-links in the amorphous phase of the polymer combined with the refinement of post irradiation thermal treatments to quench residual free radicals, has proved to be quite effective in reducing the wear rate of the bearing surfaces. Several studies published in the recent past showed that HXLPE offers very satisfying performance during in vitro testing under physiologically relevant conditions and during the first decade of in vivo service [2–6]. 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. The low friction coefficient of polyethylene combined with the improved resistance to large deformation given by cross-linking confers to HXLPE an optimum resistance to wear in the multi-axial sliding condition experienced in the hip and knee joints. The excess of free radicals that did not react to form cross-links during irradiation must indisputably be removed in order to avoid the prompt formation of oxidized species and their recombination can be obtained through two different methods: annealing or remelting [7,8]. If from one hand a post-irradiation annealing step at temperature inferior to the melting point is less effective in completely removing the free radicals generated during cross-linking [8], on the other hand post-irradiation remelting reduces the crystallinity of the final microstructure, which decreases the mechanical strength of the polymer [8–10]. Several clinical studies on the in vivo oxidation of remelted or annealed HXLPEs have been published so far, but the knowledge that we can acquire from these investigations is merely limited to what might happen during the first decade of implantation [11–17]. Muratoglu et al. [11] did not detect high level of oxidation in retrievals made of remelted HXLPE after implantation, but, more surprisingly, it was noticed that the oxidation cascade was triggered after explantation during shelf aging in air, causing also severe damage. The authors postulated that the absorption of lipids, which can react with oxygen and then abstract hydrogen atoms from the surrounding polyethylene chains, induced the generation of free radicals and products of oxidation after explantation, when the oxygen consistently diffused inside the material. Conversely, Reinitz et al. [12,16] reported the onset of in vivo oxidative degradation in some cases of short and middle-term retrievals made of remelted and annealed HXLPEs, which had no measurable and very few free radicals before implantation, respectively. One of the most striking findings of this clinical study is certainly represented by the fast in vivo oxidation rates of post-irradiation thermally treated retrievals [17]. It has been hypothesized that during the post-irradiation thermal treatment the recombination of residual free radicals lead to the formation of cross-links and double bonds (trans-vinylenes) on the polyethylene chains, namely it induced higher degree of unsaturation and higher concentration of tertiary alkyl and allylic hydrogens, which are more susceptible to abstraction because of their low dissociation energy [18,19]. These reactive sites of the polyethylene chains might have initiated the unexpected oxidation and it may indicate that the oxidative degradation of the polymer during in vivo exposure can proceed even if the component has no detectable free radicals before implantation. In other words, alternative mechanisms of oxidation should be taken into consideration, which might follow different paths than those previously postulated for the well-known oxidation of polyolefins in the presence of free radicals. The assumption of a different in vivo oxidative cascade of events necessitates considering also the possibility of different effects on the microstructure of the oxidized polymer, namely it is mandatory to investigate if the formation of oxidized species in the new generation of HXLPEs without or with a low concentration of initial free radicals induces degradation of the mechanical properties. To counteract the limitations of remelted or annealed HXLPEs, Vitamin-E or, more precisely, α-tocopherol, which is a strong antioxidant agent, is currently incorporated into polyethylene during the manufacturing procedure through two different ways: blending before consolidation or infusing via a homogenizing heat treatment after consolidation and crosslinking. The improvement on wear and oxidative resistance of high molecular weight polyethylene (UHMWPE) with the addition of vitamin-E have been amply documented in the past decade by numerous studies [20–23], but still the performance of these new promising materials during in vivo exposure necessitates to be fully elucidated. The standard methodology to investigate the oxidation in polyethylene relies on the use of infrared spectroscopy (IR), which is capable of detecting the presence of oxidized species containing carbonyl group, the main products of oxidation in polyolefins [24]. This technique is potentially capable of detecting different species containing carbonyl groups, such as esters, ketones and carboxyl acids [25], which are products of oxidation commonly formed on polyethylene at the end of the oxidative cascade initiated in the presence of free radicals and oxygen [26,27]. Nonetheless, in the common practice, the use of IR to precisely discriminate and quantify the amount of these species in PE is quite cumbersome [28,29], due to the fact that their bands are broaden, overlapping and the main products of oxidation are ketones, whose band is predominant. The ASTM standards consider the entire integrated intensity of the carbonyl region as a parameter to calculate the *OI*. As a matter of fact, only carboxyl acids are responsible for the chain scission [27,30] and the subsequent microstructural modifications. This simple consideration suggests that the *OI* as obtained according to the ASTM standards is not univocally correlated to a certain degree of mechanical deterioration, but, in simple words, two retrievals with