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JOURNAL OF MATERIALS SCIENCE. MATERIALS IN MEDICINE
(2014)
DOI: 10.1007/s10856-014-5254-9

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Abstract:

The possibility of in vivo, stress-induced oxidation in orthopaedic UHMWPE has been investigated. EtO sterilised, uncrosslinked UHMWPE liners, explanted or shelf-aged, have been collected. Linear wear and wear rate were assessed and FTIR spectroscopy was employed to detect oxidation and to build up oxidation products spatial maps across the liners section. Oxidation profiles have been compared to stress distribution profiles, resulting from a FE analysis conducted on the same liners geometries and couplings. It was found that oxidised and stressed areas followed the same asymmetrical, localized distribution profile. It was therefore possible to establish a correlation between stressed areas and observed oxidation.

Keywords:

UHMWPE, acetabular liners, oxidation, mechanical stress, EtO sterilisation

Introduction:

UHMWPE is currently considered as the gold standard for orthopaedic devices [1, 2], and future demand for primary hip replacement procedures is projected to increase by 171% by 2030 [3, 4]. Despite the wide use of UHMWPE as bearing material for total joint arthroplasty, its components often showed a limited lifetime: wear and *in vivo* damage are the most limiting factors [5]. During the past decades, the research has been focused on reducing the production of debris and subsequently osteolysis [6], by the development of a wear-resistant UHMWPE, and on inhibiting oxidation in the material, by adding anti-oxidant additives [7].

The oxidation of UHMWPE components is affected by a number of processing parameters, e.g. sterilization with gamma radiation in air, a common practice until the late 1990s, induces severe oxidation in the polymer [8-11], while radiation crosslinking, despite reducing *in vitro* and *in vivo* wear, induces free radicals formation, which, if not properly eliminated, can cause oxidation [6, 12-17]. Oxidation in UHMWPE is due to the interaction between polyethylene macroradicals and oxygen [18], which leads to the formation a number of oxidized products, such as ketones, hydroperoxides, esters, carboxylic acids, and alcohols [19-21]. The development of oxidation depends on various factors as macroradical presence, oxygen concentration, temperature, material thickness and processing conditions. Oxidation causes a decrease in the UHMWPE molecular mass and, consequently, a reduction of mechanical properties, especially ultimate tensile strength, fatigue

and wear resistance [22-25], seriously affecting the *in vivo* behaviour of UHMWPE. This may cause implant failure and retrieval of the device. Although many improvements on the understanding of these phenomena have been achieved, oxidation continues to be observed in retrieved components, creating concerns on the in vivo stability of contemporary UHMWPE.

Besides high energy radiation, the hypothesis that mechanical stress can induce oxidation has also been advanced [1, 2, 22, 26, 27]. In fact, even if annealing of the raw material is widely used to avoid the presence of residual stresses in UHMWPE, it is not possible to protect the material from the *in vivo* stress forces acting in the joint. Literature studies reported that even oxidation of un-irradiated, EtO sterilised UHMWPE can occur, favoured by the presence of calcium stearate [24, 25]. More recently, unexpected oxidation phenomena were observed also in contemporary cross-linked and thermally stabilized, virtually radicals-free, polyethylenes [28], while, in another recent study [29], cyclic loading and/or body fluids absorption have been regarded as possible oxidation initiators.

The aim of this study is to investigate if the stress induced by the *in vivo* joint forces on UHMWPE components can be responsible for an increased oxidation of the material and to explore the correlation between these two phenomena, in terms of a qualitative analysis. For this purpose, only EtO sterilised retrieved components have been used, to ensure the initial absence of macroradicals in the polymer and to exclude the confounding factor of radiation-induced oxidation. FTIR analysis on virgin, shelf aged and retrieved acetabular UHMWPE components have been performed, in order to evaluate their oxidation profiles. The results have been compared with stress distribution maps obtained by a Finite Element Analysis (FEA) reproducing the mean loading conditions acting in the hip joint replacement.

Materials and methods:

The specimens at disposal for this study were four retrieved LTO acetabular liners (LimaCorporate, Villanova di San Daniele, Italy), produced from UHMWPE GUR 1120 calcium stearate-added sheets, uncrosslinked and EtO sterilised, with implantation times ranging from 4 to 16 years, one shelf aged GUR 1120, EtO sterilised, LTO acetabular liner, and one 50x50x60 mm virgin GUR1120 block, of the same type (Table I). The shelf aged liner and virgin UHMWPE block were taken as references. To avoid the presence of processing-induced macroradical (i.e. by radiation sterilization), EtO-sterilized components only were selected for this study. This procedure allowed to exclude any eventual oxidation induced prior to implantation. Only UHMWPE liners that matched in vivo with a Titanium Grade 2 acetabular cup and a ceramic head were selected, in order not to introduce any difference in the material behaviour due to components coupling. The only

differences were in terms of size and liner geometry: E0, E1 and E2 were non-flanged Ø28 mm liners, while E3 and E4 were flanged Ø32 mm liners.

An average linear wear rate has been considered for E1-E4 components [30], and calculated by dividing the linear femoral head penetration by the implantation time. Penetration was assessed directly from the retrieved liners, by measuring E1-E4 thickness in separate locations, positioned both on the worn and unworn regions using a calibrated digital micrometer (Mitutoyo, Kawasaki. Japan), for a total amount of 15 measurements per region. The average thickness of the worn region was then subtracted from the unworn region to obtain the femoral head linear penetration value used for the wear rate calculation.

After wear evaluation, liners were cut in half so that their cross-section contained both worn and unworn areas, and microtomed into thin sections (~150 µm) for FTIR analysis, using a Reichert-Jung POLYCUT S microtome (cutting speed 4 cm/s, at room temperature). The same microtoming conditions were used to obtain thin films of the reference materials. Cutting scheme and FTIR analysis for all the considered liners are summarized in Figure 1. After a cyclohexane Soxhlet extraction, performed to remove in vivo absorbed lipids, FTIR analyses were conducted using a Perkin-Elmer SPOTLIGHT microscope, to assess the oxidation level and distribution in all samples. At first, FTIR line scans (100x100 µm spot size, 16 scans at $4cm^{-1}$ resolution) of E1-E4 samples were performed along the thickness of the worn cross section. The sections were scanned in 100µm deep increments from the articulating surface towards the backside (Figure 1a). E0 shelf-aged sample and the reference virgin block were also line-scanned for comparison. Then, FTIR spectral maps were collected (transmission mode, 16 scans at 4 cm^{-1} resolution for each point, autofocus every 10th scan). Maps allowed to gain information on the oxidation level of both worn and unworn liner areas (Figure 1b and c). The spot size for the IR maps varied from 100x100 µm to 25x25 µm, depending on the size of the scanned area (the whole area or the rim area by the worn side, respectively). This determined a more accurate data acquisition in the most worn areas of the samples. All spectra were normalized at 2020 cm^{-1}, a combination band associated with the twisting of CH_2, which can be regarded as unaffected by minor changes in the polymer structure [31]. A ketone index (KI) was calculated as the peak ratio between the deconvolved carbonyl peak centered at 1718 cm^{-1} and the reference band at 2020 cm^{-1}. Oxidation index (OI) calculation (following ASTM F2102 and F2381) was not performed, in order not to introduce measurement deviations in terms of esters presence introduced by microtoming [32].

Finite Element Analysis was performed using an ANSYS 10.0 environment; 3D models were created with IDEAS 12 NX Series M2 software. The same geometries of E1-E4 liners were modelled. Liners were fixed using a femoral head against the articular surface, and an acetabular

cup on the backside. Head and cup models corresponded to that used in vivo for each coupling. 3D meshes were automatically generated for all models, and were made up of appropriately dimensioned tetrahedral elements. Tetrahedron dimension was decreased towards the bearing and contact surfaces of the modelled system (head/liner and liner/cup), to obtain more precise results on those critical areas. Liner geometry consisted in a model of 341,261 nodes and 237,231 elements for the Ø28mm liner and in a model of 405,118 nodes and 281,816 elements for the Ø32mm liner, while cup and head were made of 4 mm and 1.5 mm elements, respectively. Contact areas were modelled using 1 mm tetrahedron elements. Considering the great variety of patient activity and physiology, working ambient and component positioning, it was not possible to represent in the FE model the exact loading conditions for each retrieved liner. Therefore, loading conditions were taken from literature data on biomechanical parameter measurements by telemetry [33]. Hip joint forces were obtained from previous similar FE studies [33-35]. A 2,000 N static load was applied along the symmetry axis of the femoral head, positioned with a 22° angle orientation in respect to the liner. Contacts between the three bodies (cup, liner and head) were set as frictional one, with a friction parameter of 0.1 and 0.02 for the liner/cup and the liner/head interface, respectively. The outer surface of the cup is fixed. Material properties of the three components were also introduced. ρ density values, as well as Young's modulus E and Poisson's ratio ν, representing the elastic deformation of a material under load, were set for each different body. The approximated values are listed in Table 2. The resulting stress distribution was examined along the liners cross sectional area, corresponding to the region investigated by FTIR analyses and linear wear assessment. Peak stresses were taken as the most critical parameter to assess for UHMWPE lifetime. [36].

Results:

Despite the differences between liners geometry and patient wear conditions, the average linear wear rate measurements showed a correlation between time *in vivo* and wear (Table 1). Linear wear increases with the *in vivo* lifetime of the liners. E0 sample, being shelf aged only, had no wear and therefore was not considered herein. Even if the time dependence of the linear wear was clearly assessed, it was not possible to define a correlation law between UHMWPE wear and *in vivo* time, due to the limited amount of samples.

Figure 2 reports the oxidation profile (in terms of KI) at the worn side of samples E1-E4 throughout the liners cross section (first 4mm from the bearing surface), along with that of the reference UHMWPE block, obtained from the line scan analyses. All the explanted samples show the same oxidation distribution across the liner thickness, having a maximum peak either at the inner bearing surface or in the first subsurface region. The strongest oxidation was observed in sample E1, with a

peak KI index of 3.92 at 0.5-0.6 mm depth. The amount of oxidation then decreases moving towards the bulk and the backside of the liner. The KI trend across the liner section seems not to follow any diffusive law, since the highest amount of oxidation was observed in the subsurface areas.

No correlation between linear wear data and oxidation could be detected. However, it is noticeable that for the highest in vivo time (E1 liner), the highest amount of oxidation products was observed. The reference UHMWPE block did not show any significant oxidation, while the shelf aged liner (E0) had a different oxidation profile, as reported in Figure 3 (note the difference in the KI trend, when compared to Figure 2). According to similar literature studies [24, 25], the oxidation profile throughout E0 cross section shows a symmetric path, with a maximum peak in the central region of the liner. When comparing the oxidation profiles of the explanted liners to that of the shelf aged one, no similarities can be found, neither in terms of KI trend, nor in terms of peak oxidation, as for the shelf aged liner the oxidation amount was lower than in the retrieved components.

Figure 4 shows the FTIR maps obtained from the whole area scan of E3 and E2 with the detail of the most worn area for each liner. Oxidation distribution is asymmetric and strongly localized, and significant presence of ketones was found in the worn areas only. No traces of oxidation were found at the opposite region of the liners cross section, indicating that oxidation occurred in correspondence of the loaded areas, that is where the contact between femoral head and liner occurred and, consequently, where the majority of wear concentrated.

Different geometries showed different IR maps, as documented by the data obtained from the lower rim detailed scans. In particular, oxidation distribution in the Ø32mm liner flanged area is different in respect to the non flanged Ø28mm liner geometry. As for the line scan analysis, the FTIR detailed map of sample E0 showed a different distribution of the oxidation products compared to E1-E4 retrieved liners (Figure 5).

FE analyses revealed that the load distribution is located in the same liner cross section regions affected by oxidation (Figure 6). As for the IR maps, different geometries led to different stress fields. In fact, as expected, the flanged area affects the stress distribution in the Ø32mm liner, creating a different profile in respect to the Ø28mm non-flanged geometry. Moreover, it is observed that also the stress field range varies accordingly to the liner thickness, as for the Ø32mm liner it is more spread towards the bulk of the cross section. This is in accordance to literature data concerning the rise of stresses and applied loads for thinner and larger UHMWPE liners [37]. Stress levels, in terms of von Mises criterion, are 10.3 MPa and 13.9 MPa for the Ø28mm and Ø32mm geometries respectively. Values are in accordance with the liner geometry and thickness. Stress

field range covers the same region of the observed oxidised area for Ø28mm and Ø32mm liners, and maximum values of both von Mises stress and KI are located in the same area.

Discussion:

The experimental data collected in this study indicate that linear wear, as expected, increases with implant time, regardless of the coupling geometry. We did not attempt to establish a correlation between yearly wear rate and implant time, due to the lack of information on several factors, that likely have affected the wear rate of the retrieved liners, as patient activity, anatomy, component positioning, body weight, etc. However, this has been broadly discussed in literature, and is not the main purpose of this work, indeed aimed to establish a correlation between mechanical stress and oxidation.

To facilitate comparisons with previously published studies, it must be said that, although it is difficult to compare levels of oxidation assessed with different methods (KI vs. OI), the maximum KI found in our samples correspond approximately to OI in the range 0.4-0.8. The oxidation levels observed here are then substantially lower than those of most historical, gamma-air sterilized inserts, but comparable to those of some contemporary radiation sterilized polyethylenes [9].

The oxidation profiles across the liners section show a maximum KI in the first subsurface region, indicating therefore an *in vivo* material degradation mechanism not related to diffusion phenomena, as for example external contamination with lipids, oxygen or other molecules. Oxidation was observed also in the shelf aged liner (Figure 3 and 6), although to a lower level and with a completely different distribution profile. This confirms that calcium stearate added UHMWPE is prone to oxidation [24, 25]. The choice of a GUR 1120 UHMWPE, despite driven by the circumstances, is therefore considered to be extremely functional to our study.

Moreover, the oxidation throughout the explanted liners cross-section is limited to the surface and first subsurface region of the inner worn side of the liner (Figure 2 and 4). In all the other scanned areas, the oxidation level was equal or lower than that of the reference material. Therefore, oxidation seems to be strongly localized in the ball and socket coupling area, in which the sliding motion between femoral head and liner occurs and where physiological load is applied. As well as for the linear wear data, it can be hypothesized that differences in patient weight, activity and other external factors have influenced the results.

Comparing the IR maps to the FEA results (Figure 4 vs. 6), there is an evident correlation between the concentration of oxidation products and the stress distribution for both liners geometries. The asymmetric stress and oxidation maps reveal that these phenomena are related to the joint compliance, strongly depending upon the head and cup positioning. These data confirm that lifetime

of the components, as well as wear, is subjected to patient variability, and that a determination of the total stress amount acting on the liners during their *in vivo* permanence alone might not be enough to make a reliable prediction of the phenomena concurring to oxidation and, in general, to the material performance. Taking into account the differences in liners geometry and working conditions (i.e. artificial joint positioning), a direct and quantitative correlation between the amount of stresses acting on a joint and the amount of oxidation in its retrieved UHMWPE components cannot be established, as confirmed by the discrepancies in the observed E1-E4 oxidation levels.

However, our results indicate that: (1) FEA and IR maps showed a significant correspondence and (2) different geometries led to different stress and oxidation distributions, maintaining the similarities among these two parameters, thus suggesting a correlation between stress application and oxidation development. Further, (3) as a confirmation, oxidation in the retrieved components was observed only in the most loaded areas, and finally (4) the choice of EtO sterilized components allows to assume the absence of free radicals in the material at implantation, thus the absence of any kind of potential oxidation initiator, even if calcium stearate is believed to facilitate (but not to initiate) the development of oxidation. These factors leads to conclude that, on a qualitative scale, *in vivo* stress and oxidation can be correlated and that, as for the stresses distribution, geometric factors (for example, liner thickness) play a role also in the *in vivo* mechanisms of oxidation of UHMWPE.

A previous study [24, 25] showed that unexpected oxidation in the bulk of some never implanted, EtO-sterilised acetabular cups was due to a combination of bad consolidation of the material (likely favoured by calcium stearate) and internal stresses originated by processing. The oxidation profiles observed in those components were almost identical to that found in our E0, reference liner. We cannot exclude that the same phenomena are also involved in the degradation observed in the retrieved liners examined in the present study but, once again, it should be emphasized that they showed a different oxidation distribution and, in most cases, a much higher concentration of oxidized products, localized in the loaded area. Our hypothesis is that this originates from the mechanical stress caused by cyclic loading, possibly combined with the effect of bad consolidation and internal stresses due to processing.

Another recent study [38], investigated in-vivo oxidation in a larger collection of EtO sterilized tibial inserts. The authors did not mention the presence of calcium stearate in their retrievals, whose average implantation time (5 years) was much shorter than that of our samples. They found very low (~ 0.1) maximum oxidation indexes (OI), but still they noticed “subtle increases” of the oxidation indexes in the most loaded areas. This further corroborates our hypothesis that oxidation can be initiated by mechanical stress; only, in our samples the presence of calcium stearate and,

possibly, of some residual stress from processing might have exacerbated the whole process. It must be also emphasized that our reference, shelf-aged, calcium stearate containing GUR 1120 block did not show any significant oxidation, confirming that the presence of calcium stearate alone is not enough to develop oxidation.

In our FE simulations, the applied load resulted in higher stress values for Ø32 mm liners with respect to Ø28mm geometry. On the contrary, the highest oxidation values were found in Ø28mm liners. This suggests that peak load should not be considered as the key factor for determining the amount of resulting oxidation, which may come instead from the total amount of cyclic stress applied during the *in vivo* lifetime of the component. In this sense, more comprehensive analyses are needed in order to quantitatively correlate stress and oxidation, as well as more details in patients and working conditions of the prostheses are mandatory to attain a better assessment of the total stress UHMWPE liners are subjected to.

Our study is subjected to some important limitations. First, our findings are based on a very limited amount of retrievals. Additionally, as discussed above, calcium stearate may have played a role in accelerating oxidation. Whether and in which time span the same extent of stress-induced oxidation might be developed in contemporary, calcium stearate free, EtO sterilized polyethylenes remains unknown.

Conclusion:

Keeping in mind that the UHMWPE components included in this study were EtO sterilized and therefore they were not expected to contain any free radical due to sterilization, the results obtained here allow to establish a clear correspondence between *in vivo* stress and *in vivo* UHMWPE oxidation in qualitative terms: the stress affected areas clearly showed to be oxidised as well. The great variety of patient conditions influences the correlation between linear wear, implant time and observed oxidation levels, as well as component positioning and patient activity play an important role on the total amount of load applied on the UHMWPE liners during their *in vivo* lifetime. For these reasons, discrepancies in oxidation levels and stress levels when comparing calculated KI and maximum stresses amounts were observed. It was clearly showed, however, that both phenomena are geometry dependent, and that oxidation seems to be correlated to the total amount of stress, rather than to the peak loads applied.

Further studies are needed in order to correctly determine the amount of total stresses the components underwent, and to correlate stress and oxidation at a quantitative scale.

References:

1. Kurtz SM, Muratoglu OK, Evans M, Edidin AA. Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty. Biomat 1999;20:1659-1688.
2. Kurtz SM. The UHMWPE biomaterials handbook. 2nd ed. Elsevier academic press; 2009.
3. Kurtz SM, Ong K, Lau E, Mowat F, Halpern M. Projections of primary and revision hip and knee arthroplasty in the United States from 2005 to 2030. J Bone Joint Surg Am 2007;89:780–785.
4. Kurtz SM, Lau E, Ong K, Zhao K, Kelly M, Bozic K. Future young patient demand for primary and revision joint replacement: national projections from 2010 to 2030. Clin Orthop Relat Res 2009;467:2606-2612.
5. Willert HG, Bertram H, Buchhorn HG. Osteolysis in alloarthroplasty of the hip. The role of ultra high molecular weight polyethylene wear particles. Clin Orthop 1990;258:95-107.
6. Costa L, Luda MP, Trossarelli L. Ultra-high molecular weight polyethylene: mechano-oxidative degradation. Polym Degrad Stab 1997;55:329-338.
7. Bracco P, Oral E. Vitamin E-stabilized UHMWPE for total joint implants. A review. Clin Orthop Relat Res 2011;469:2286-2293.
8. Mc Kellop H, Shen FW, Lu B. Effect of sterilization method and other modifications on the wear resistance of acetabular cups made of ultra high molecular weight polyethylene. A hip simulator study. J Bone Joint Surg Am 2000;82A:1708-1725.
9. Costa L, Bracco P, Brach del Prever EM, Kurtz SM, Gallinaro P. Oxidation and oxidation potential in contemporary packaging for UHMWPE total joint replacement components. J Biomed Mater Res B 2006;78:20-26.
10. Costa L, Luda MP, Trossarelli L, Brach del Prever EM, Crova M, Gllinaro P. Oxidation in orthopaedic UHMWPE sterilized by gamma and EtO. Biomat 1998;19:659-668.
11. Bohl JR, Bohl WR, Postak PD, Greenwald AS. The effects of shelf life on clinical outcome for gamma sterilized polyethylene tibial components. Clin Orthop Relat Res 1999;367:28-38.
12. Walsh HA, Furman BD, Naab S, Li S. Role of oxidation in the clinical fracture of acetabular cups. Trans ORS 1999;45:845.
13. Medel FJ, Kurtz SM, Parvizi J, Klein JR, Kraay MJ, Rimnac CM. In vivo oxidation contributes to delamination but not pitting in polyethylene components for total knee arthroplasty. J Arthtrop 2011;26:802-810.

14. Costa L, Luda MP, Trossarelli L, Brach del Prever EM, Crova M, Gallinaro P. In vivo UHMWPE biodegradation of retrieved prosthesis. Biomat 1998;19:1371-1385.
15. Brach del Prever EM, Bistolfi A, Bracco P, Costa L. UHMWPE for arthroplasy: past or future? J Orthop Traumatol 2009;10:1-8.
16. Baker DA, Bellare A, Pruitt L. The effects of degree of crosslinking on the fatigue crack initiation and propagation resistance of orthopedic-grade polyethylene. J Biomed Mater Res A 2003;66:146-154.
17. Avanzini A. Mechanical characterization and finite element modeling of cyclic stress–strain behaviour of ultra high molecular weight polyethylene. Mater Des 2008;29:330–343.
18. Lacoste J, Carlsson DJ. Gamma, photo and thermally-initiated oxidation of linear low-density polyethylene: a quantitative comparison of oxidation products. J Polym Sci A-Polym Chem 1992;30:493-500.
19. Igarashi M. Free radical identification by ESR in polyethylene and nylon. J Polym Sci Polym Chem 1983;21:2405-2425.
20. Arnaud R, Mosain JY, Lemarie J. Primary hydroperoxidation in low density polyethylene. Macromol 1984;17:332-336.
21. Costa L, Brach del Prever EM. UHMWPE for arthroplasty. 1st ed. Minerva Medica; 2000.
22. Oral E, Christensen SD, Malhi AS, Wannomae KK, Muratoglu OK. Wear resistance and mechanical properties of highly cross-linked, ultrahigh-molecular weight polyethylene doped with Vitamin E. J Arthrop 2006;21:580-591.
23. Brach Del Prever EM, Costa L, Crova M, Dallera A, Camino G, Gallinaro P. Unacceptable biodegradation of polyethylene in vivo. Biomat 1996;17:873-878.
24. Costa L, Jacobson K, Bracco P, Brach Del Prever EM. Oxidation of orthopaedic UHMWPE. Biomat 2002;23:1613-1624
25. Costa L, Jacobson K, Bracco P, Brach Del Prever EM. Erratum to “Oxidation of orthopaedic UHMWPE”[Biomaterials 23 (2002) 1613–1624]. Biomat 2005;26:347-348.
26. Costa L, Luda MP, Trossarelli L. Ultra-high molecular weight polyethylene: thermal and foto oxidation. Polym Degrad Stab 1997;58:41-54.
27. Costa L, Bracco P, Brach del Prever EM, Luda MP. Oxidation and stabilization of orthopedic UHMWPE. UHMWPE for arthroplasty: from synthesys to implant. 1st ed. Università degli studi di Torino; 2005.
28. Currier BH, Van Citters DW, Currier JH, Carlson EM, Tibbo ME, Collier JP. In vivo oxidation in retrieved highly crosslinked tibial inserts. J Biomed Mater Res B 2013;101B:441-448.

29. Oral E, Ghali B, Neils A, Muratoglu O. A new mechanism of oxidation in UHMWPE caused by squalene absorption. J Biomed Mater Res B 2012;100:742–751.
30. Livermore J, Ilstrup D, Morrey B. Effect of femoral head size on wear of the polyethylene acetabular component. J Bone Joint Surg Am 1990;72:518-28.
31. Costa L, Carpentieri I, Bracco P. Post electron beam irradiation oxidation of orthopaedic UHMWPE. Polym Degrad Stab 2008;93:1695-1703.
32. Costa L, Jacobson K, Brunella V, Bracco P. Effects of microtomy on the material properties of ultra-high molecular weight polyethylene. Polym Test 2001;20:649-659.
33. Bergmann G, Deuretzbacher G, Heller M, Graichen F, Rohlmann A, Strauss J, Duda GN. Hip contact forces and gait patterns from routine activities. J Biomech 2001;34:859-871.
34. Taylor M, Barrett DS. Explicit finite element simulation of eccentric loading in total knee replacement. Clin Orthop Relat Res 2003;414:162-171.
35. Bergstrom JS, Rimnac CM, Kurtz SM. An augmented hybrid constitutive model for simulation of unloading and cyclic loading behavior of conventional and highly crosslinked UHMWPE. Biomat 2004;25:2171-2178.
36. Furmanski J, Pruitt LA. Peak stress intensity dictates fatigue crack propagation in UHMWPE. Polym 2007;48:3512-3519.
37. Goebel P, Kluess D, Wieding J, Souffrant R, Heyer H, Sander M, Bader R. The influence of head diameter and wall thickness on deformations of metallic acetabular press-fit cups and UHMWPE liners: a finite element analysis. J Orthop Sci 2013;18:264-70.
38. Mac Donald D, Hanzlik J, Sharkey P, Parvizi J, Kurtz SM. In vivo oxidation and surface damage in retrieved ethylene-oxide sterilized total knee arthroplasties. Clin Orthop Relat Res 2012;470:1826-1833.

Sample name	*Implant time [y]*	*Size [mm]*	*Linear wear [mm]*	*Wear rate [mm/y]*	*KI [abs]*
Ref. (block)	-	-	-	-	< 0.02
E0 (shelf aged)	-	Ø28	-	-	0.06
E1	16	Ø28	1.54	0.09	0.196
E2	4	Ø28	0.636	0.15	0.1
E3	12	Ø32	1.4	0.11	0.06
E4	9	Ø32	1.114	0.123	0.1

Table 1

Body	*Material type*	*Density ρ [g/cm^3]*	*Young's modulus E [GPa]*	*Poisson's ratio ν*
Liner	UHMWPE	0.93	0.78	0.4
Cup	Ti cp Gr2	4.51	106	0.34
Head	Al_2O_3	4.37	380	0.23

Table 2

Figure legends:

Figure 1. Thin slices preparation of E1-E4 liners for FTIR analysis and investigated areas. From a to c, line scan path and direction (points collected every 100 μm); global IR map (surface scanned at 100x100 μm spot size); worn side detailed IR map (surface scanned at 25x25 μm spot size). Red dotted line indicates the most worn region.

Figure 2. Ketone index profiles across the most worn section of E1-E4 and Reference profile. The 0 depth value is located at the inner rim of the liner.

Figure 3. Ketone index profiles across the cut section of shelf aged E0 liner, and Reference profile. The 0 depth value is located at the inner rim of the liner.

Figure 4. FTIR maps of the ketones absorption (1718 cm^{-1}) in the retrieved liners (left sample E3, right sample E2). The distribution of the oxidation products is asymmetric, with the highest concentrations in correspondence of the worn area. On the opposite side of the section, no relevant oxidation was retrieved.

Figure 5. FTIR map of the ketones absorption (1718 cm^{-1}) in the shelf aged liner (E0). The maximum oxidation is located in the bulk of the liner.

Figure 6. FE analysis of the stress distribution in the cross-section of the liners (left Ø32 mm and right Ø28 mm).

Figure 1
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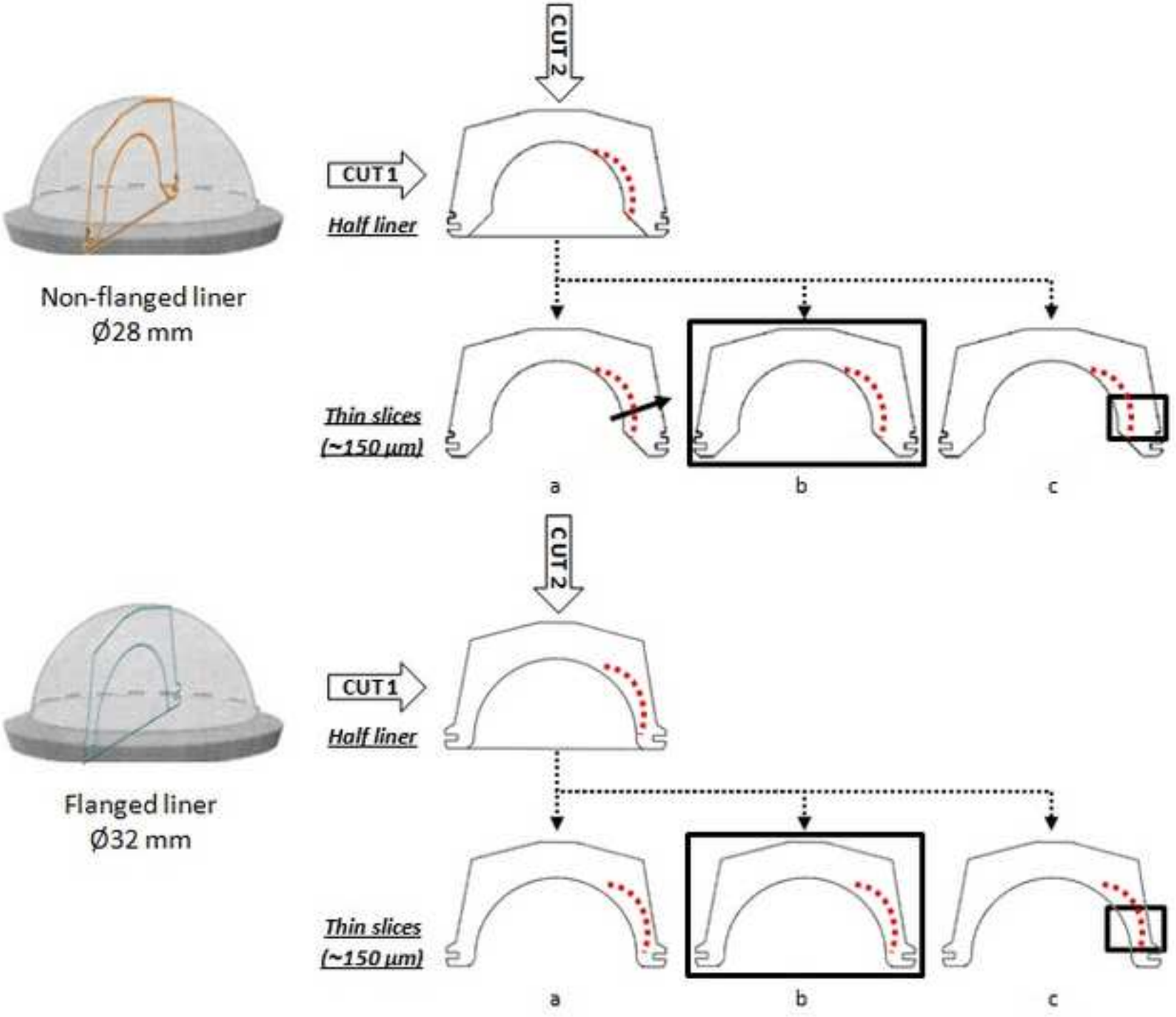

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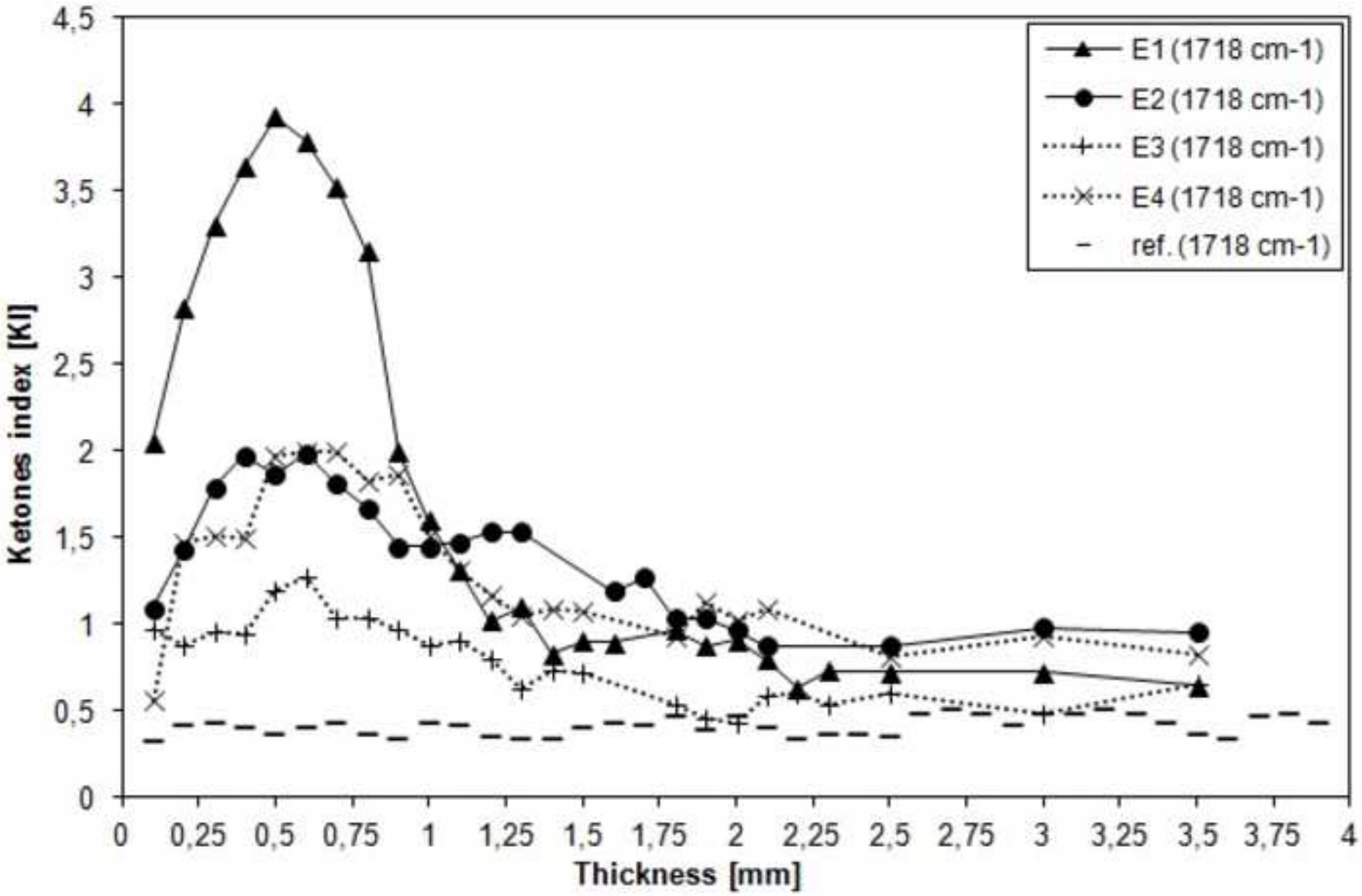

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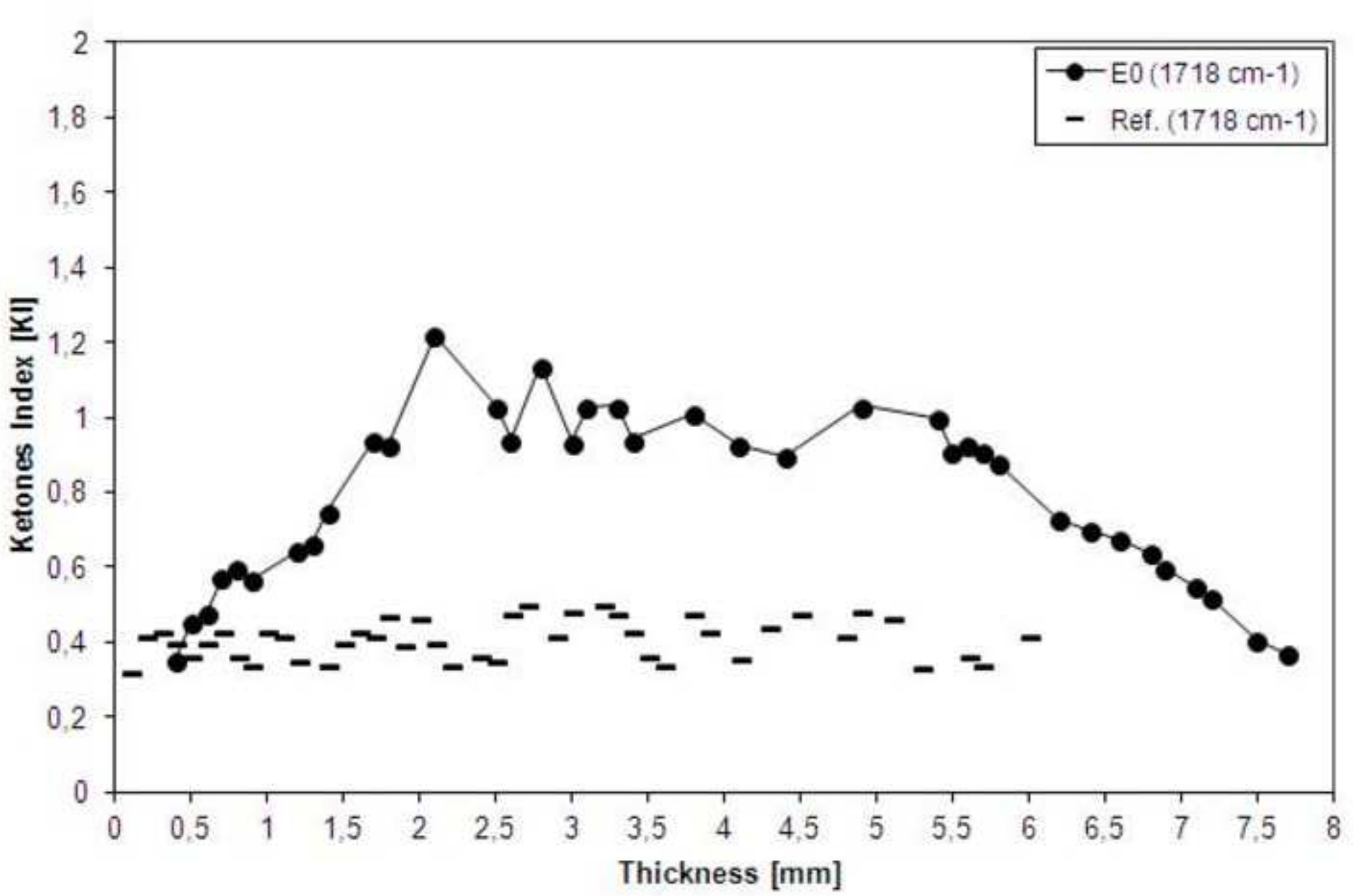

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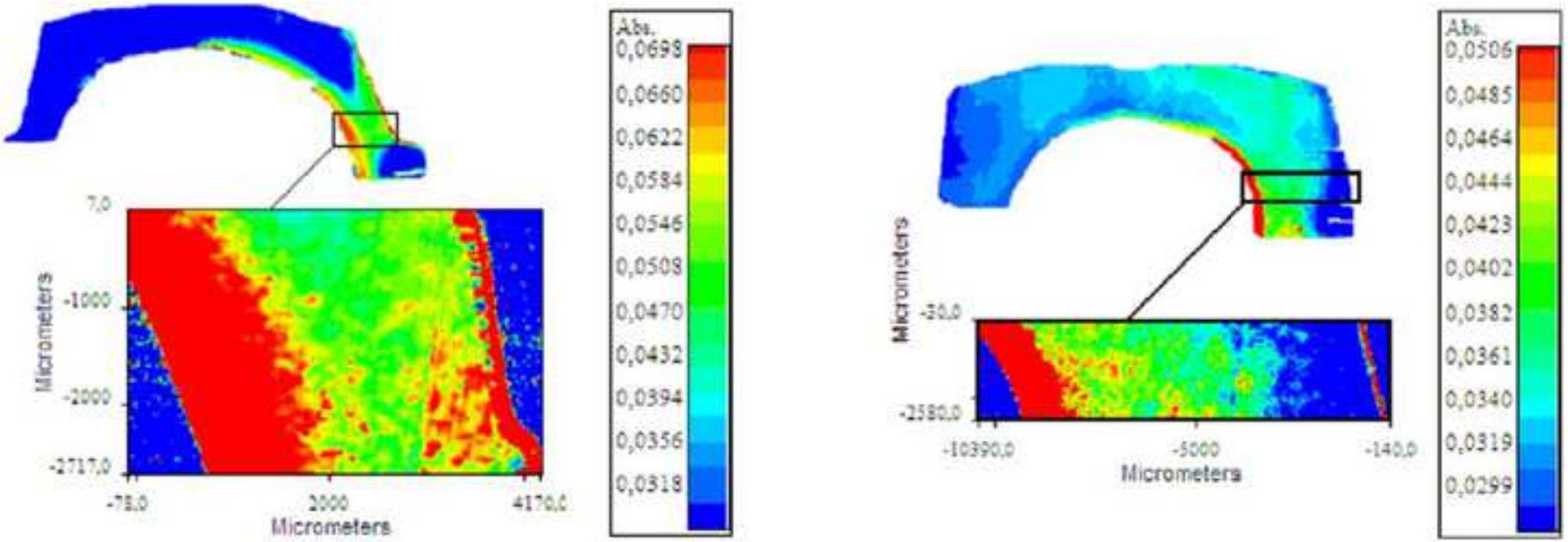

Figure 5
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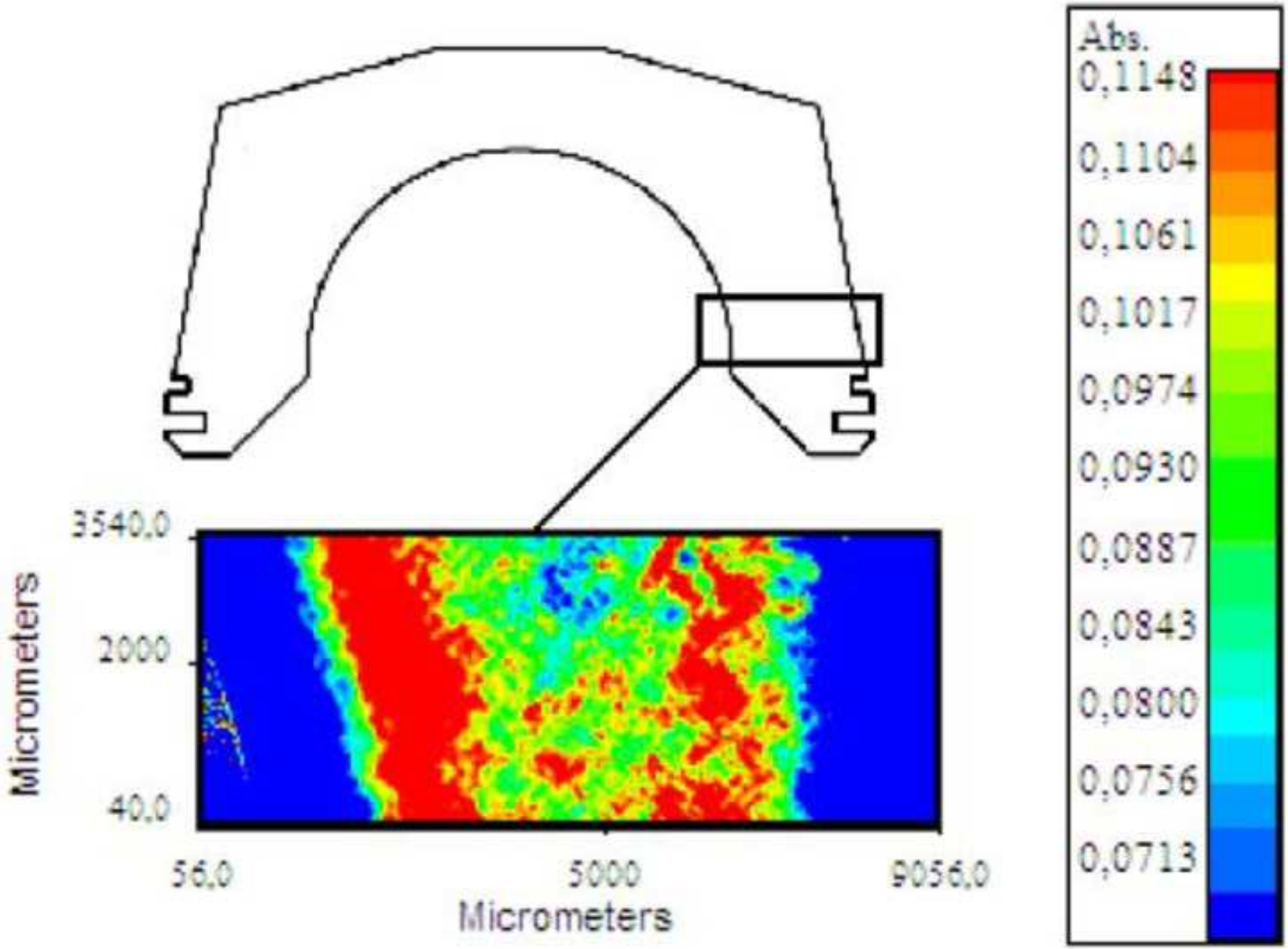

Figure 6
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