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CORR Insights®: A Novel Technique for Assessing Antioxidant Concentration in Retrieved UHMWPE

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Where Are We Now?

Improving the wear resistance of load-bearing, articular implants with radiation crosslinked ultra-high-molecular-weight polyethylene (UHMWPE) has been one of the major advances in the field of total joint arthroplasty. Thermal treatments fol-

This CORR Insights® is a commentary on the article “A Novel Technique for Assessing Antioxidant Concentration in Retrieved UHMWPE” by Currier and colleagues available at: DOI: [10.1007/s11999-016-4939-4](https://doi.org/10.1007/s11999-016-4939-4).

The author certifies that he, or a member of his immediate family, has no funding or commercial associations (eg, consultancies, stock ownership, equity interest, patent/licensing arrangements, etc) that might pose a conflict of interest in connection with the submitted article.

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This *CORR Insights*® comment refers to the article available at DOI: [10.1007/s11999-016-4939-4](https://doi.org/10.1007/s11999-016-4939-4).

lowing irradiation are necessary to reduce the concentration of residual free radicals and improve the oxidation resistance of UHMWPE. While radiation crosslinking reduces the mechanical strength, postirradiation melting, the most-effective stabilization method, further decreases the strength of UHMWPE. Antioxidants such as vitamin E and pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)] propionate (PBHP) were introduced in the mid-2000s as an alternative for stabilizing the free radicals, eliminating the need for melting. This improved the mechanical properties of the polymer. Antioxidant stabilization is also expected to prevent the oxidation of highly crosslinked UHMWPE components in vivo in the long-term due to the more recently unveiled mechanisms triggered by the absorption of pro-oxidant lipids and cyclic stress

[3].

The long-term effectiveness of antioxidants would depend on their concentration and continued antioxidant properties. There is potential for elution of some fraction of the antioxidant out of the UHMWPE components, possibly compromising the long-term oxidative stability of the devices. Therefore, it is important to quantify the extent of elution and the amount of residual antioxidant in surgically explanted, antioxidant stabilized, and highly crosslinked UHMWPE components. In vitro studies have shown that vitamin E, the most commonly used antioxidant, will elute out of highly crosslinked UHMWPE in deionized water at body temperature when it is present in concentrations above its saturation limit [5]. This elution was shown to reach a plateau at a certain concentration, likely around the saturation limit of vitamin E in UHMWPE. We also know that radiation crosslinking or gamma sterilization after the incorporation of the vitamin E into UHMWPE components causes chemical grafting of the antioxidant molecules to the

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polymer backbone [4]. Grafting would also decrease the extent of elution of the antioxidant in the long-term.

Another potential concern is the local tissue reaction to the eluted antioxidant. Biocompatibility studies using animal models have shown no adverse effects to antioxidants, which may be present in the synovial fluid and the surrounding tissue because of elution out of UHMWPE components in vivo [2].

Where Do We Need To Go?

UHMWPE components absorb lipids during in vivo service. As a result, surgically explanted components, when analyzed using Fourier Transform Infrared Spectroscopy (FTIR), show carbonyl absorbance (mostly in the form of esters) as well as additional absorbances near where the antioxidant (vitamin E and PBHP) characteristic absorbances typically occur. Therefore, the absorbance of lipids complicate the quantification of oxidation and antioxidants in explanted UHMWPE components. Absorbed lipids typically contain esters and quantification of oxidation can either be performed by ketone absorbance height or by removal of the absorbed lipids using nonpolar solvents with a subsequent FTIR analysis [1].

The analysis for the antioxidant quantification is more challenging. While the solvent extraction of the

absorbed lipids helps in quantifying the PBHP, the same is not true for the analysis of vitamin E quantification as the nonpolar solvents also remove the vitamin E, as was elegantly shown by Currier and colleagues. The authors of the current study potentially devised an effective method to quantify the vitamin E concentration without the removal of the absorbed lipids. Their findings show that there is minimal elution of vitamin E and PBHP from these explanted antioxidant stabilized, radiation cross-linked UHMWPE components.

Their report is based on a small group of short-term explants. We need to perform more analyses of this type with larger numbers of explants and with longer in vivo service times in order to understand whether continued exposure to the in vivo environment could, at some time point, result in progressive elution of antioxidant molecules. An unlikely scenario is the loss of antioxidants during in vivo service in sufficient amount altering the stability of the polymer and adversely affecting the long-term performance of total hip and total knee devices. This would be important for tibial inserts in TKAs, which exhibit more-aggressive oxidation, primarily because of the higher stresses experienced by these components. As long as the antioxidants remain grafted to the host polymer backbone, the expectation is that the elution will be minimal.

How Do We Get There?

The work of Currier and colleagues has initiated efforts in effectively quantifying the concentration of residual antioxidants in retrievals, which is crucial to the long-term monitoring of antioxidant concentration and its relationship to oxidation behavior. We need to develop other methods to determine the concentration of chemically-grafted antioxidants and their antioxidant potency in explanted UHMWPE components containing absorbed lipids.

One indirect way of quantifying the changes in the oxidative stability of UHMWPE components following in vivo service is to subject the explanted components to accelerated aging [6]. The explants are preconditioned in vivo. By the time they are retrieved, they would have been subjected to cyclic loading and would have absorbed pro-oxidant lipids from the synovial fluid. Additionally, a fraction of the antioxidants would have eluted out. Findings from accelerated aging of explants would shed some light to overall changes in the oxidative stability that occurs in vivo in antioxidant stabilized, radiation crosslinked UHMWPE components in the long-term.

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