Molecular weight characterization to assess aging in ultra-high molecular weight polyethylene

Cambridge Polymer Group

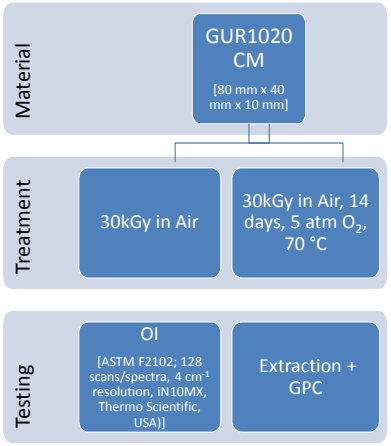
Turner, N.; Spiegelberg, S.; Le, K.-P., Song, L.

stryker

Objective

Ultra high molecular weight polyethylene (UHMWPE) is commonly used as a bearing surface in hip, knee, shoulder, and other total joint replacement arthroplasties. Aging of UHMWPE that has been irradiated without additional treatment to stabilize the residual free radicals can result in oxidation followed by chain scissioning. Researchers will usually measure oxidation index to characterize shelf-life, but this technique does not capture the actual degradation due to oxidation. In this study, gamma sterilized UHMWPE was accelerated aged, and the molecular weights of extractable material were characterized with gel permeation chromatography in attempt to see if this technique can be used to characterize shelf-life of the aged material.

Materials and Methods



Two sample sizes were investigated with three extraction times each; the larger mass was sampled at 2, 8 and 24 hours and the smaller mass was sampled at 1, 2 and 4 hours. The portion of the extraction solvent removed at each time point was tested by gel permeation chromatography (GPC) to determine the molecular weight of the extracted material (TCB at 135 °C against polyethylene standards).

Results

The oxidation index for the samples shows a measurable increase in oxidation after accelerated aging (Fig. 1). The aged samples lost as much as ten times more mass during the extraction than the unaged samples. The molecular weight of the extracted material from the aged samples decreased compared to the unaged samples at the lower molecular weight moments (Mn and Mw) (α=0.05, p<0.01 for Mn, p<0.04 for Mw), but increased for the higher molecular weight moment (Mz) (α=0.05, p<0.01 for Mz) (Fig. 2). This pattern is consistent with aging of the polyethylene material, as there is likely to be some chain scissioning as well as cross-linking during aging if free radicals are present. The Mz moment for the three time points in the unaged samples is statistically the same (α=0.05, *p*>0.05), whereas there is an increase in the Mz with increasing extraction time for the aged samples, suggesting that the higher molecular weight species take longer to diffuse out of the samples.

The UHMWPE mass to volume ratio during extraction influenced the outcome of the testing. With the larger sample mass for the aged sample, the extracted material appeared to have gelled after the 8 and 24 hour time points. The unaged sample did not show this same result. A comparison of the extracted material at the 2 hour time point for the two sample masses for both the unaged and aged samples shows a similar trend, where the Mz increases after aging and the Mn decreases (Fig. 3).

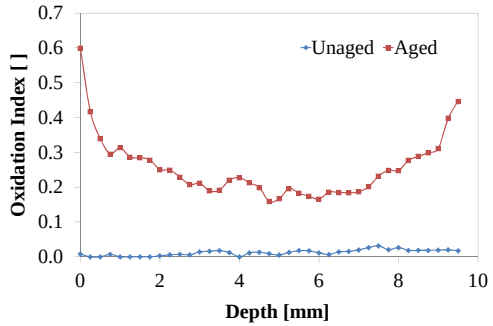


Figure 1: Oxidation index through the depth of each sample.

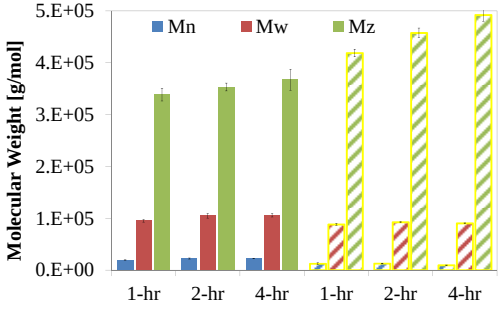


Figure 2: Comparison of the molecular weight moments for the extractable portions of the unaged (solid) and aged samples (stripe) at the three shorter extraction time points.

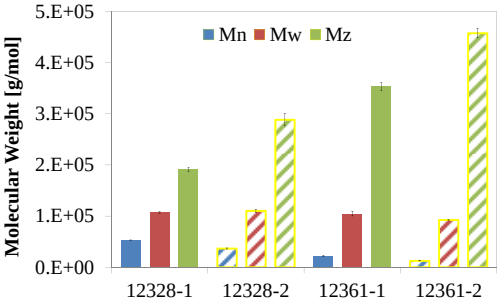


Figure 3: Differences between starting sample mass [12328: high; 12361: low] on extraction results for both unaged (solid) and aged (stripe) groups. Measurements are made on the two hour extraction time point.

Discussion

The extraction of the polyethylene material in this study shows that there is a molecular weight difference between the unaged and aged material, with the aged material showing broadening in the molecular weight distribution. This change can be explained by oxidative degradation, which is supported by the oxidation index. The test methodology shows that a larger ratio of solvent to sample is required to ensure extraction without gelation of the extracted material, and that 4 hours is sufficient to extract the larger molecular weight species. The impact of the molecular weight change on in vivo performance, however, cannot be discerned from this test.

Significance

This study demonstrates a method of characterizing the shelf-life of UHMWPE.

Acknowledgements

This study was funded in part by Stryker Orthopedics.