Recovery of Oxidative Damage in Irradiated UHMWPE

+[1]Sun, DC; [2]Lin, S; [2]Petty, RW; [3]Tsay R; [3]Chou GP
+[1]Taiwan Scientific Corporation, Taipei, Taiwan, [2]Exactech, Inc., Gainesville, FL, [3]Institute of Biomedical Engineering, National Yang-Ming University, Taipei, Taiwan

Statement of Purpose: Since the discovery of a subsurface white band in irradiated UHMWPE implants[1], oxidation and its prevention have received intensive research and development. Non-radiation sterilization (such as EtO) was first proposed to avoid free radical formation and thus oxidation, but wear resistance was found to be inferior. Gamma radiation has since remained the choice of crosslinking technology, while new methods were developed to eliminate residual free radicals (e.g. annealing or re-melting). Addition of vitamin E[2] was also proposed to scavenge free radicals. Oxidation can occur at various stages of fabrication process, including ram extrusion, compression molding, gamma radiation, post-radiation treatment, and storage. In this study, we sought a remedy for previously oxidized UHMWPE with the objective to restore its original material properties.

Methods: A tibial insert made of GUR1050 UHMWPE was gamma irradiated at 150 kGy in air and shelf aged for 7 years. The tibial insert was cut into two halves to reveal interior. One of the sections went through a high temperature treatment under nitrogen at 250*C for 2 hours. Before and after treatment, a photo was taken to show any appearance change. DSC was employed to investigate crystallinity and melting characteristics. FTIR oxidation index (OI) at the surface of the insert was measured following ASTM 2102. A compression molded slab made of GUR 1020 UHMWPE was gamma irradiated at about 50 kGy in air and shelf aged for 13 months. A section of this slab was taken for tensile tests. Another section was heat treated under vacuum at 270^{o}C for 2 hours followed by tensile tests per ASTM D638.

Results: Figure 1(a) shows the photo of the tibial insert before heat treatment. A sub-surface white band around the profile was observed. The photo taken after heat treatment (Fig 1(b)) shows an uniform surface without a white band. DSC melting curves are shown in Figures 2(a) and 2(b). The untreated insert showed a major melting peak at 139^{o} C with a secondary peak (shoulder) at 123^{o}C. After treatment, the insert showed a sharp single peak at 133^{o}C. Crystallinity was decreased from 68% before treatment to 54% after treatment. Oxidation index at the skin of the insert was decreased from 0.40 before treatment to 0.07 after treatment. Figures 3(a) and 3(b) show load-extension curves for the slab before and after treatment. Before treatment, a flat portion right after the yielding point due to specimen necking was observed. No necking was observed after heat treatment. Tensile data are presented in Table 1.

Discussion and Conclusion: UHMWPE consists of C-C and C-H bonds only. Oxidation adds C-O bonds to the chemical composition. Bond energies of C-O, C-C, and C-H are 78, 80, and 98 kcal, respectively. At sufficiently high temperatures (such as 250-270^{o}C used in the study), C-O bonds are expected to break, liberating oxygen-containing species while re-producing alkyl free radicals. C-C bonds would also break at similar temperature ranges creating new alkyl free radicals. C-H bonds might remain intact due to much higher bond energy. Upon cooling, free radicals could then react with each other to form crosslinks. Oxidation would then be eliminated as a result. Preliminary results obtained in this and other[3] studies seem to support the above hypothesis. Crystallinity was high at 68% in the oxidized tibial insert (due to radiation and oxidation damages) but returned to 54% by the 250^{o}C treatment, which is close to that of the virgin polymer. Short chain fractions in the oxidized insert, responsible for the 2nd (shoulder) melting peak, were largely gone after heat treatment. OI analysis confirmed that oxidation in the treated material was greatly reduced. Tensile properties were restored significantly in the molded slab as well, as indicated by disappearance of necking and increased elongation, ultimate strength, and toughness (Table 1). Future studies will focus on the details of the reaction mechanism.

Figure 1: Tibial insert photos at cut surface

(a) before treatment (b) after treatment

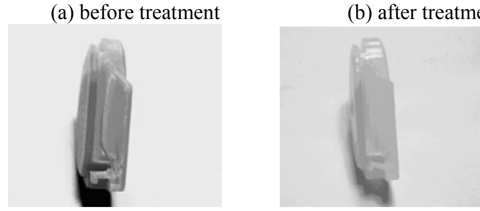


Figure 2: DSC melting curves of tibial insert

(a) before treatment (b) after treatment

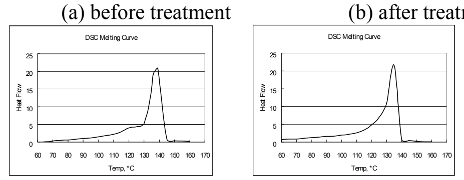
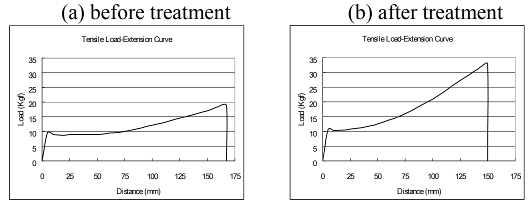


Table 1: Tensile data for compression molded slab

Sample	Yield Strength (MPa)	Ultimate Strength (MPa)	Elongation (%)	Fracture Toughness (MPa)
Bef. treat.	21 ± 2	35 ± 2	460 ± 20	122 ± 14
Aft. treat.	20 ± 1	55 ± 6	585 ± 40	180 ± 10

Figure 3: Load-extension curves for molded slab

(a) before treatment (b) after treatment



References: (1) D.C. Sun, C. Stark, and J.H. Dumbleton, 40th ORS Annual Meeting, New Orleans, LA, 1994, P173 (2) US patent 6,448,315, also see S. Kurtz, et al., 3rd UHMWPE International Meeting, Madrid, Spain, September 14-15, 2007 (3) US patent applications 11/463,423 and 12/076,969. **Acknowledgement:** Special thanks are given to Meditech Inc for providing UHMWPE material.