High Temperature Melting of Radiation Cross-linked UHMWPE

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Statement of Purpose: High temperature melting (HTM) of ultrahigh molecular weight polyethylene (UHMWPE) can improve elongation and toughness, presumably due to increased intergranular diffusion and chain scissioning, at elevated temperatures (280 - 330°C) [1].

Radiation cross-linking of UHMWPE is used to lower its wear rate and wear-induced osteolysis [2]. Post-irradiation melting to reduce the free radicals (caused by irradiation) to undetectable levels or stabilizing against their oxidative reactions by an antioxidant (vitamin E) are currently used to improve oxidative stability.

But, post-irradiation melting decreases the fatigue strength of cross-linked UHMWPE [3], and hence, the impact toughness [4]. Thus, we hypothesized that HTM will not only maintain but also improve the strength and toughness of radiation cross-linked UHMWPEs.

Methods: Sample Preparation Virgin (without additives) and 0.1wt% vitamin E/UHMWPE blends (GUR 1050) were consolidated, then e-beam irradiated to 150 kGy. After irradiation, they were HTMed in a N_2 convection oven at 280, 300 or 320°C for 5 hours. One set of irradiated virgin and vitamin E blended pucks was used as a control without HTM.

Characterization: Thin sections (150 um) were microtomed and a terminal vinyl index was calculated using Fourier Transform Infrared Spectroscopy (FTIR) by normalizing the absorbance at 880-920 cm^{-1} to 1850-1985 cm^{-1}. Double-notched impact strength measurements were conducted on samples (63.5 x 12.7 x 6.35 mm^3) according to ASTM F648. Type V tensile specimens (n=5) according to ASTM-638 were stamped out of 3.2 mm thick sections. Cross-link density was measured by swelling 3 mm cubes in xylene at 130°C and determined gravimetrically according to ASTM F2214-02. Pin-on-disc (POD) wear testing was performed on cylindrical pins (dia. 9mm, height 13 mm) as previously described [5] at 2 Hz for 1.2 million cycles (MC). Statistical significance was assigned to $p < 0.05$.

Table 1. Cross-link density, UTS and YS values of all the irradiated and HTMed virgin and vitamin E blended UHMWPEs.

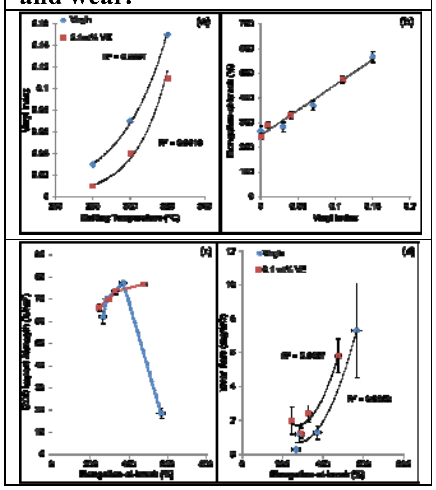
	Virgin				0.1 wt% Vitamin E			
	No HTM	280°C	300°C	320°C	No HTM	280°C	300°C	320°C
Cross-link Density (mol/m^3)	257 ± 4	215 ± 2	135 ± 3	25 ± 2	233 ± 7	220 ± 2	181 ± 4	67 ± 5
Ultimate Tensile Strength (UTS) (MPa)	48 ± 2	37 ± 7	45 ± 2	31 ± 1	45 ± 2	43 ± 4	43 ± 2	41 ± 2
Yield Strength (YS) (MPa)	21 ± 1	18 ± 2	19 ± 1	21 ± 0	21 ± 1	19 ± 1	18 ± 1	22 ± 0

Results: The vinyl index, a measure of the terminal vinyl groups in the material, increased significantly with increasing melting temperature for irradiated and HTMed virgin and vitamin E blended UHMWPEs (Fig 1a). The vinyl index for the irradiated and HTMed virgin materials was higher than the vitamin E blended UHMWPEs at the same melting temperatures (p=0.0023, 0.0026 and 0.000008 for 280°C, 300°C and 320°C respectively, Fig 1a). The elongation-at-break (EAB) increased linearly with increasing vinyl index (Fig 1b).

The impact strength increased with increasing EAB up to approximately 400% for the irradiated and HTMed virgin UHMWPEs and then rapidly decreased with a further increase in EAB beyond 400% (Fig 1c). In contrast, the impact strength increased with an increase in EAB for the irradiated and HTMed vitamin E blended UHMWPEs (Fig 1c).

The wear rate increased with increasing EAB (Fig 1d). The crosslink density decreased linearly with increasing vinyl index (Table 1; R^2=0.98). The ultimate tensile strength (UTS) and yield strength (YS) of vitamin E-blended UHMWPE did not change significantly with increasing melting temperature (Table 1).

Figure 1. Relationship between mechanical properties, vinyl index and wear.



Conclusions: Our hypothesis proved positive as the impact strength after HTM showed a significant increase, which was correlated to the marked increase in the EAB (Fig 1c). This was attributed to increased chain scissioning during HTM. For the virgin UHMWPEs, the impact strength rapidly decreased beyond an EAB of approximately 400%, thus showing an EAB threshold and hence a vinyl index threshold (Fig 1b), beyond which the toughness decreased as opposed to the vitamin E blended UHMWPEs. One possible explanation for this difference may be the interference in the terminal vinyl group formation after chain scissioning by vitamin E (Fig 1a), which is also an efficient free radical scavenger.

The steady increase in the wear rate of cross-linked UHMWPEs was presumably due to chain scissioning and degradation of the cross-linked network. The differences in the impact strength (Fig 1c) and wear rate (Fig 1d) of virgin and vitamin E-blended cross-linked UHMWPEs as a result of HTM suggest different responses in the network structure during HTM.

References: [1] Fu et al. Polymer 51 (2010) 2721-2731; [2] Kurtz et al. Clin Orthop Rel Res 469 (2011) 2262-2277; [3] Oral et al. Biomaterials 27 (2006) 917-925; [4] Doshi et al. ORS (2013) 1820; [5] Bragdon et al. J Arthroplasty 16 (2001) 658-665.