INTRODUCTION:
Currently, electron beam irradiation is a technique used by the majority of manufacturers to obtain highly crosslinked polyethylenes. Its current use in total joint replacement components may improve wear resistance, and decrease UHMWPE particle debris. However, the irradiation generates free radicals which are responsible for long-term oxidative embrittlement. Thus, a post-irradiation thermal step is usually conducted, under annealing or remelting conditions, to promote the recombination of remaining free radicals. Irradiation and both thermal processes introduce microstructural changes that may seriously affect UHMWPE mechanical properties, especially toughness and fatigue strength. This influence may be critical in total knee replacements, where fatigue-related damage limits the lifespan of the prosthesis. This study aims to evaluate the influence of annealing and remelting processes on fatigue and toughness behavior. In addition, the microstructure changes provoked by both stabilization methods were investigated.

METHODS:
Mechanical specimens were machined from GUR 1050 UHMWPE compression molded sheets (Perplas Medical Ltd.). These were electron beam irradiated in air (doses: 50, 100 and 150 kGy) using a 10-MeV Rhodotron TT 200 accelerator (Ionomed Esterilización S.A., Tarancón, Spain). After irradiation, specimens were maintained at -20 °C in a subzero freezer, prior to a remelting (150 °C) or an annealing (130 °C) process carried out in a vacuum oven for 2 hours.

To determine changes in crystallinity content due to irradiation and thermal processes, samples (n=3) were heated at 10 °C/min from 20 °C to 170 °C in a differential scanning calorimeter (Perkin-Elmer). Crystallinity was calculated by integrating heat flow from 80°C to 160°C, and normalizing it with the enthalpy of melting of a crystalline polyethylene (290 J/g). Besides, crystal size was measured from TEM images of irradiated samples before and after the stabilization processes.

Crosslink density measurements were performed per ASTM F2214 (Cambridge Polymer Group; Boston; MA) on the 50 kGy and 150 kGy-irradiated samples. To assess the effect of remelting, the more severe stabilization process, on the crosslink density, we measured it also on the 150 kGy-irradiated and remelted samples.

Cyclic stress-strain experiments were conducted on tensile specimens (ASTM D638 type M-1) up to 50 cycles at 15 mm/min and at two constant maximum nominal stress, σ\text{max} = 14 and 16 MPa, being the stress ratio R = 0. This test provided information about the total strain reached, ε(50), a measure of the material softening.

Long-term fatigue tests, S/N stress-life experiments, were performed per ASTM E606 specimens using a fatigue criterion based on 12% yield strain. They were performed under load control with R = 0 and frequency 1 Hz.

Fatigue crack propagation testing was done per ASTM E647. Compact tension specimens (n=3 for each material group) were pre-cracked and subjected to a stress ratio R = 0.1 in tension at a frequency of 5 Hz.

The tough response of highly crosslinked polyethylenes was assessed by means of three different experiments. Impact Izod tests were done on double-notched specimens following ASTM F648. Work of fracture values were calculated from engineering-stress-strain curves of tensile experiments (ASTM D638). Finally, J-R curves, toughness-crack growth resistance, were obtained following ASTM D6068-02 for all material groups. All the mechanical testing was conducted at T=24 ± 1 °C.

RESULTS:
Electron beam irradiation of UHMWPE increased its crosslinking density from 0.127 ± 0.010 mol/dm³ to 0.192 ± 0.009 mol/dm³ for 50 kGy and 150 kGy respectively. Samples irradiated at 150 kGy and subsequently remelted showed a slightly decreased crosslink density, 0.178 ± 0.003 mol/dm³.

DISCUSSION:
Regarding crystallinity, irradiation implied an increase in this property (55.5±2.2, 57.7±1.0 and 58.6±2.4 for 50, 100 and 150 kGy), whereas the thermal treatments studied were opposite effects: remelting caused a considerable drop in crystallinity (43.6±1.9, 46.8±1.1 and 49.7±3.3) and annealing produced an increase in it (59.5±0.3, 61.0±0.7 and 61.0±0.8). Coherently, irradiation produced a crystal thickening as observed in TEM images (from 35-40 nm to 40-45 for 50 and 150 kGy). Both thermal processes, remelting and annealing, caused a decrease in crystal size, being more accrued for the remelting process (20-25 nm and 30-40 nm for remelting and annealing respectively).

Cyclic stress-strain tests showed a small decrease with irradiation dose in softening (At 16 MPa: 5.9±0.5, 5.2±0.5 and 4.7±0.5 for 50, 100 and 150 kGy respectively). After remelting, irradiated materials had a doubled softening degree, ε(50)=12±1.6, which was independent of the dose. Annealing produced an increase in ε(50), but not so high than after remelting (7.1±0.5, 6.2±0.2, 5.2±0.8 for 50, 100 and 150 kGy respectively).

Long-term fatigue results clearly confirmed the trend found in cyclic stress-strain tests. A small increase of the fatigue life with irradiation dose was registered in S/N curves. Both thermal processes provoked a considerable loss on fatigue resistance, especially after remelting.

Fatigue crack propagation testing showed a monotonic decrease in stress intensity factor ranges at crack inception, ΔK, with irradiation dose (from 1.53±0.06 to 1.16±0.01 for 50 and 150 kGy). As for thermal treatments, annealing provided a better behavior for the fatigue resistance in notchched samples (from 1.64±0.05 to 1.29±0.04) and remelting maintained almost unchanged ΔK, except a decrease at the highest dose, ΔKε=1.03±0.07.

As impact Izod and to fracture results pointed out, toughness was clearly lower after irradiation. This trend was confirmed by J-R curves (see figure 1). Even though not noticed in impact and work to fracture data, J-R curves showed a clear drop in toughness after remelting (figure 1), and annealing produced a small toughness increase.

Figure 1. J-R curves of irradiated and irradiated and remelted UHMWPE

CONCLUSION:
In highly crosslinked polyethylenes, crosslink density dictates tough response and crack propagation properties, whereas crystal size controls fatigue life, as seen in this work. A suitable election of irradiation and stabilization conditions is needed in order to achieve optimal mechanical performances in different applications.