Development of a Successive Self-Nucleation and Annealing (SSA) protocol for the characterization of biomedical UHMWPE

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Introduction: Characterizing various UHMWPE formulations pre- and post-implantation is often crucial to understanding their clinical performance. The technique of Successive Self-Nucleation and Annealing (SSA), developed and introduced by Müller et al. in 1997 [1], is now a well-established thermal fractionation technique that exploits the molecular segregation capacity exhibited by semicrystalline polymeric systems when they are isothermally crystallized or annealed. SSA is conceptually based on the sequential application of self-nucleation and annealing steps to a polymer specimen. Numerous literature works highlight the excellent potential of SSA for characterizing ethylene-based homo- and co-polymers. SSA has shown excellent results in characterizing and differentiating various LDPE and LLDPE. On the contrary, UHMWPE, like HDPE, is a challenging material to fractionate, due to its high linearity and minimal presence of molecular defects [2]. To our knowledge, there are currently no studies of SSA on UHMWPE. However, we postulate that various treatments used on medical UHMWPE may induce differences in morphology detectable with SSA experiments and therefore that SSA could provide useful insights for characterizing different UHMWPE formulations.

Methods and Materials: Five UHMWPE materials were investigated: 1) as-received 2) aged, oxidized (OI=1.4) 3) 30kGy irradiated, 4) 100kGy irradiated and annealed 5) 100kGy irradiated and remelted. All samples came from the same batch of ram-extruded GUR 1050. Differential Scanning Calorimetry experiments have been performed using a DSC 250 equipped with an RCS40 Refrigerated Cooling System (TA Instruments).
Each sample was heated to 170°C and held in the melt for 3 min to erase thermal history, then it was cooled, at a constant rate of 20°C/min, to 40°C, in order to allow the crystallization of the material. An ideal T_s (the lowest T at which the sample is only self-nucleated and not annealed) of 139,5°C was determined through a Self-Nucleation (SN) experiment, as described in [2]; potential T_s value were explored within a range from 140°C down to 136°C, with decreasing steps of 1°C. Finally, an SSA thermal protocol was developed employing a total of 9 annealing steps, a 5°C fractionation window and a 5 minute isotherm at each T_s explored. The same SSA protocol was applied to all samples

Results and discussion: SSA thermal fractionation employs a temperature protocol (a series of heating and cooling cycles) design to produce a distribution of lamellar crystals whose sizes reflect the distribution of methyl sequence lengths (MSL) that are present within a specific polyethylene [1]. Fractionation occurs because defects are generally segregated to the amorphous regions of the sample, with most MSL being incorporated inside lamellar crystals.

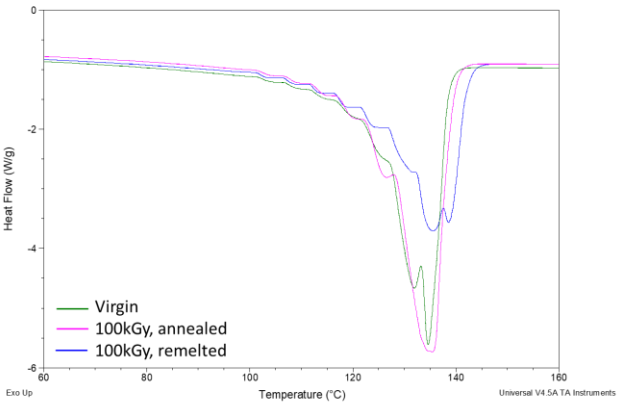

Figure 1 DSC final heating scan after applying SSA to sample #1, #4, and #5

The results of thermal fractionation for the 100kGy-annealed and 100kGy-remelted specimens are presented in Figure 1 as an example, along with pristine UHMWPE for comparison. The reference UHMWPE exhibits a total crystallinity of 54% with seven fractions, the principal of which is the highest melting, centered at 135°C. The irradiated and annealed sample demonstrates increased crystallinity (61%), but the broad fraction with the highest melting point corresponds to two thermal fractions that were not separated, confirming that, as expected, crosslinks do alter the lamellar size distribution. Conversely, the irradiated and remelted sample shows eight melting fractions with a completely different size distribution: although the total crystallinity has decreased (47%), there appears to be a fraction with a higher melting point (139°C), indicative of thicker lamellae, while the quantity of all other fractions decreases.
The SSA technique has preliminarily proven to effectively discriminate between different formulations of UHMWPE. As the next step, we will test its efficacy in characterizing other formulations, for instance those containing additives at various concentrations.

References

[1] Müller AJ et al European Polymer Journal 65 (2015) 132–154
[2] Rojas de Gáscue B et al J Therm Anal Calorim (2011) 103:669–678