Lifetime of Macroradicals in UHMWPE Irradiated with Electron Beam

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Interaction of high energy radiation with UHMWPE leads to the scission of C-C and C-H bonds both in the amorphous and in the criystalline phase, giving H radicals, macroradicals and trans vinylene double bonds. If oxygen is present, alkyl macroradicals react immediately with it and the oxidation chain process begins. In this case the main products are hydroperoxides[1]. In our laboratory ultra high molecular weight polyethylene (medical grade GUR 1050) has been irradiated with electron beam in vacuum and in presence of oxygen at room temperature. Electron beam irradiation has been considered in order to neglect irradiation time, that is shorter (maximum 2 minutes) than gamma irradiation time and negligible compared to the following observation time. UHMWPE irradiated has been examined with two different techniques, FTIR and EPR spectroscopy. Micro FTIR Spectroscopy has been carried out on UHMWPE to evaluate hydroperoxide concentration in samples irradiated in presence of oxygen. Hydroperoxides and their distribution inside samples can be observed very well with FTIR microscopy after a derivatization process (with NO). The obtained hydroperoxide profile decreases when distance from the outer surface increases till it achieves a plateau. The first decrease can be attributed to macroradicals reaction with oxygen, that can diffuse only in the amorphous phase. Value obtained in the centre of block is correlated only with oxygen dissolved in UHMWPE before irradiation. If radicals live for some hours, oxygen can diffuse into UHMWPE during the macroradicals lifetime and the hydroperoxides profile is a curve similar to that obtained. Comparing the oxygen diffusion curve, calculated in the function of Fick's law, with the hydroperoxide profile, we have obtained a good agreement when oxygen diffusion is calculated over two hours. This means that the macroradicals must survive at least for two hours in the amorphous phase.

EPR Spectroscopy was undertaken to explore the nature of any radicals produced in UHMWPE and to study their decay as a function of time. Power saturation technique has been used to isolate alkyl from allyl radicals in polyethylene spectra. Alkyl macroradicals amount decreases with time. There are two different curves. At the beginning, some alkyl macroradicals died very rapidly (around 5 hours). These radicals are in the amorphous phase. The other radicals, which survive for long time are in the crystalline phase and they probably move over time into the amorphous phase. Amorphous macroradicals decay rapidly because of their high chain mobility. Crystalline macroradicals on the contrary cannot move quickly, so they stay for long time inside the material and are also present after long time in UHMWPE, as reported by others[2].

[1] Costa L., Bracco P. "Mechanism of Crosslinking and oxidative degradation of UHMWPE" Chap. 11 in "The UHMWPE Handbook: Ultra-high molecular weight Polyethylene in Total Joint Replacement" Ed S. Kurtz, Academic Press 2004: pp. 235-261.

[2] O'Neil P., Birkinshaw, Leahy J.J., Barklie R., Polymer Degradation and Stability 63 (1999) 31-39.