On UHMWPE post-irradiation oxidation

Luigi Costal, Pierangiola Bracco, Valentina Brunella, Ilenia Carpentieri, Elena M. Brach del Prever

1IFM Chemistry Department and NIS Centre of Excellence, University of Torino, Torino, Italy; 2Orthopaedics and Traumatology Department, University of Torino, Torino, Italy

pierangiola.bracco@unito.it

Introduction: Ultra high molecular weight polyethylene (UHMWPE) has been the material of choice for bearing components of total joint arthroplasty for the past 30 years. According to the ASTM regulation, the UHMWPE for orthopaedics does not contain any stabiliser and therefore it can oxidise very easily. Sterilization with high energy radiation in the presence of air is well known to be the main cause of oxidative degradation of orthopaedic UHMWPE. The irradiation process with high energy radiation (gamma radiation or e-beam) produces, at the end of sterilization, an amount of macroradicals proportional to the absorbed dose and, in the presence of oxygen, the oxidation process start at low temperature. This process is called post-irradiation oxidation [1-2].

Aim of this work is to evaluate the radical reactions of formation of hydroperoxides, ketones and acids during the post irradiation process.

Materials and Methods: Commercially available grade GUR 1020 and 1050 UHMWPE slabs were microtomed to 180 μm thick films in air, at room temperature (PolyCuts Microtome, Reichert-Jung, Germany). The films were irradiated to 60 kGy with e-beam, at room temperature (Bioster, Seriate Italy) and stored at room temperature (RT) in the dark until analyses were performed.

The FTIR measurements were run on a Spectrum 100 spectrometer (PerkinElmer, Shelton, Connecticut, USA). All spectra were run in the transmission mode with a 4 cm⁻¹ resolution and 16 scans per spectrum. The peak at 2020 cm⁻¹, a combination band associated with the twisting of CH₂, was used as an internal standard, since it can be regarded as unaffected by minor changes in the polymer structure. At the peak at 2020 cm⁻¹, all the spectra were normalised at an absorption of 0.05, correlating to a film thickness of ca. 100 μm. All the absorbance values were corrected on spectral subtractions (irradiated - original).

Hydroperoxides were also detected after reaction with nitrogen monoxide (NO) for 15 hours in a dark reaction vessel. Under these conditions, hydroperoxides in polyethylene are converted into more easily detectable nitrates [2].

Results: Figure 1a shows the build-up of ketones and hydroperoxides as a function of the ageing time at RT for films irradiated in air at 60 kGy, while Figure 1b shows their rate of formation.

Discussion: The stability of alkyl macroradicals in the UHMWPE amorphous phase is around 10 hours, while the thermal stability of macro-hydroperoxides at 110°C is very high [3]. Two different kinds of hydroperoxides are formed: bounded hydroperoxides, decomposing in 30 hour, and free hydroperoxides, more stable. Irradiated UHMWPE was kept at room temperature in the dark, then the oxidation process was followed by FTIR for long time in the absence of hydroperoxides decomposition.

The behaviour of hydroperoxides is very similar to that of ketones. Ketones and ROOH are accumulated during the post-irradiation process. The rate of ketones formation is high when the concentration of ROOH is minimum and the macroradicals concentration is high.

Therefore, ketones and ROOH could form with a similar mechanism: a direct reaction between macroalkyl radicals and oxygen. Two different oxidation processes are evident. The first, occurring in the very first hours after irradiation, is due to the reaction between O₂ and the alkyl macroradicals produced by e-beam in the amorphous phase, while the macroradicals are decaying. The second process, which takes place when the rate of oxidation is very low, is due to the alkyl macroradicals present in the crystalline phase, which slowly move to the amorphous phase or to the crystalline-amorphous interphase and react with the oxygen present there.

It is evident that the formation of ketones does not arise from the thermal decomposition of hydroperoxides for two different reasons: first, hydroperoxides are stable at room temperature, then, at the beginning of the oxidation process, the concentration of hydroperoxides is very low and the rate of formation of ketones is maximum.

At the beginning of the oxidation process, the concentration of alkyl and peroxy macroradicals is very high, therefore a reaction in which ketones are formed straight from the peroxy radicals must be hypothesized:

\[
\text{CH}_2\text{C}=\text{CH}_2 + \cdot \text{OH} \rightarrow \text{CH}_2\text{C}-\text{CH}_2\cdot + \text{H}_2\text{O}
\]

The enthalpy of this reaction is about -47 kJ/mol (calculated using the peroxy radical of isopropane as a model compound), thus it is an exothermic reaction that takes place with increase of entropy and therefore it occurs spontaneously at room temperature.

At this stage, a new mechanism of oxidation, which justifies the formation of ketones at room temperature, can be suggested:

\[
\text{R}^+ + \text{O}_2 \rightarrow \text{ROO}^+
\]
\[
\text{ROO}^+ \rightarrow \text{RCOR} + \text{HO}^+
\]
\[
\text{HO}^+ + \text{PH} \rightarrow \text{H}_2\text{O} + \text{P}^+
\]

We have compared the relative amount of the oxidation products - ketones and acids - produced during the thermal decomposition of the UHMWPE at 90°C, with or without induction of the e-beam irradiation, and we have found the same products obtained at room temperature. Therefore, the same reaction occurs at room temperature and at high temperature, also in the presence of the auto-acceleration effect due to the thermal decomposition of hydroperoxides.

In conclusion, it must be pointed out that the post-irradiation process is always present when UHMWPE is sterilized with high energy radiation. The resulting oxidation level will be dependent on many factors, as dose rate and oxygen concentration in the packaging.


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