Observation of free radicals on electron beam irradiated UHMWPE by electron spin resonance

Sungsik Kim * Phil Hyun Kang * Young Chang Nho * O-Bong Yang

School of Chemical Engineering, College of Engineering, Chonbuk National University, *Radioisotopes Radiation Application Team, Korea Atomic Energy Research Institute

Abstracts

Electron spin resonance (ESR) spectroscopic study was undertaken to investigate the remaining radicals in ultra-high molecular weight polyethylene (UHMWPE) after electron beam (EB) irradiation up to 500 kGy in $N_2$ or air environment. The free radical concentration (FRC) as a function of dose and the decay of radicals as a function of storage time were observed by the change of ESR spectra. The FRC gradually increases with irradiation dose and the FRC of irradiation in $N_2$ is a little higher than irradiation in air. It is accepted that irradiation of UHMWPE produces alkyl radicals ($\cdot$CH−CH$_2$−), which gradually transform to more stable ally radicals ($\cdot$CH−CH=CH−).

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is routinely used for the manufacture of the acetabular cup in total hip replacements, and patellar components in total knee replacements. However, occasional failures, within 6–8 years of implantation in case of active or heavy patients, have been reported. Most of failures are attributed to oxidative degradation of PE molecules initiated by the reaction of free radicals, generated by irradiation, with oxygen during shelf storage and implantation. The radiation chemistry of polymers has also disclosed that the polymer radicals generated by irradiation transform into oxidized moieties if oxygen is present in the
vicinity of formed radicals or remain trapped in the polymer matrix for a certain period of time after irradiation. These trapped radicals may further undergo some reactions during storage after irradiation, resulting in significant alteration of the physical properties of irradiation UHMWPE, if a large amount of polymer radicals remain trapped after irradiation. This study was undertaken to investigate the UHMWPE radicals remaining after irradiation as a function of dose and storage time at room temperature.

2. Experimental

2-1. Material and method

The samples in this experiment were prepared from 10 mm diameter ram extruded UHMWPE cylindrical bar stock (GUR 4150, average molecular weight of approximately 9.2 million and density of 0.93 g/ml). The UHMWPE samples were packed in a polyethylene bag, followed by charging with N₂ gas and sealing for the environment of N₂ gas during the EB irradiation. EB irradiation was carried out at a dose rate of 7500 kGy/h using ELV-4 accelerators (energy: 1 MeV, current: 2.5 mA) up to 500 kGy. The samples that had been irradiated were cooled to room temperature.

2-2. Electron spin resonance

The specimens for trapped free radical measurements were machined (3×5×1.5 mm³) after cutting off 0.8 mm from the surface of UHMWPE bar stock as shown in Fig. 1. An X-band ESR spectrometer (EPR EMX, Bruker), operating at 9.648GHz microwave and 100 kHz magnetic field modulation frequencies, was used. While the microwave power was maintained 20.12 mW, modulation amplitude was 1 G or 5 G as needed for a good signal-to-noise ratio. The double integration method was used to determine relative free radical concentration (FRC).

Fig. 1. The schematic preparation of specimens.

3. Results and discussion

ESR spectra of the UHMWPE irradiated by EB in N₂ are shown in Fig. 2. The relative FRC was calculated by integration of these ESR spectra assuming that the peak area of the UHMWPE irradiated to 50 kGy in N₂ was unity.

Fig. 2. The change of ESR spectra of UHMWPE irradiated in N₂.
Fig. 3. The relative FRC of irradiated UHMWPE as a function of dose.

While Fig. 2 shows the spectra of the specimens irradiated in N₂ only, the relative FRC of the specimens irradiated in N₂ and air are given in Fig. 3. Additionally, any expected significant difference between irradiation in N₂ and air was not shown in the ESR spectra. As seen, the FRC gradually increases with irradiation dose and the FRC of irradiation in N₂ is little higher than irradiation in air.

To examine the transformation of the polyethylene radical species, the g-factor was evaluated from the ESR spectra. ESR is a forum of microwave absorption spectroscopy for transitions induced between the Zeeman energy levels arising from the interaction of an assemblage of paramagnetic electrons with an externally applied magnetic field H. The energy difference E between the Zeeman levels is associated with a characteristic absorption frequency ν, given the Einstein Planck relation

\[ E = h \nu = g \beta H \]

Where h is Planck’s constant and β the Bohr magneton. Spectroscopic splitting factor g is defined by \( h \nu = g \beta H \). The position center of the spectrum gives the magnetic field H at which resonance occurs and can be used to calculate the g value. A free electron spin is expected to have a value of \( g = 2.0 \). In real materials, g may differ from this value, depending on variations in the coupling between spin and orbital angular momentum. The g values of some organic radicals are as follows:

\[ \text{CH}_3-\text{CH}_2-2.0027 \quad \text{CH}_3-\text{CH}=\cdot \text{CH}_2: 2.0026 \]

\[ \text{CH}_3-\cdot \text{CH}_2: 2.0041 \]

\[ \text{CH}_2=\text{CH}-\text{CH}=\cdot \text{CH}_2-\text{CH}_2: 2.0156 \]

Fig. 4. The g-factor as a function of dose.

It is accepted that irradiation of UHMWPE produces alkyl radicals (\( \cdot \text{CH} = \text{CH}_2 \)), which gradually transform to more stable ally radicals (\( \cdot \text{CH} = \text{CH} = \cdot \text{CH} \)) as an increase of dose in irradiation in N₂.

Fig. 5 shows ESR spectra of the UHMWPE which was irradiated to 300 kGy in N₂ by EB and then stored in air at 25°C. It is seen that the number of spectra peaks decreases with the storage time, approaching a single peak spectrum.
Fig. 5. The change of ESR spectra of 300 kGy-irradiated UHMWPE. Storage in the presence of oxygen at 25°C.

Fig. 6. The relative free radical concentration of UHMWPE irradiated to 300 kGy in N₂ as a function of storage time.

The relative FRC quickly decreases during storage until 20 days, although they did not disappear completely after a period of storage.

Fig. 7. The g-factor as a function of storage time in the presence of oxygen at 25°C.

If air is present in the irradiation system, the polyethylene radical will be oxidized to form oxygen containing radicals which have higher g-factors than the polyethylene radicals without any attached oxygen atom.

4. Reference