Degradation of electron-irradiated polyethylene studied by positron annihilation lifetime spectroscopy

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Abstract. Degradation of electron beam irradiated high-density polyethylene was studied by positron annihilation lifetime spectroscopy (PALS), micro-FT-IR, and gel fraction measurements. The obtained results indicated that ortho-positronium intensity is influenced not only by the irradiation but also the post-oxidation, which illustrates that PALS may be a promising tool to monitor/evaluate the degradation of polyethylene induced by irradiation and long-term storage.

1. Introduction
Polyethylene (PE) is widely used for insulators and packaging materials in various radiation environments such as nuclear power plants and accelerator facilities [1]. During long-term usage, PE which is subjected to a severe radiation environment is degraded mainly through oxidation, cross-linking, and scission. The degradation by radiation has been studied because it has to be properly evaluated for ensuring the safety of the relevant facilities. In this work, we investigated the structural change of electron beam irradiated PE during irradiation and after long-term storage, and discuss the usability of positron annihilation lifetime spectroscopy (PALS) for the degradation assessment.

2. Experimental
Additive free high-density polyethylene (HDPE), having a density of 0.951 g cm\(^{-3}\) and a thickness of 2 mm, were examined. The samples were irradiated by an electron beam with up to 1000 kGy under vacuum at room temperature at Takasaki Advanced Radiation Research Institute, National Institutes for Quantum and Radiological Science and Technology (QST). The dose rate, the acceleration voltage, and the beam current were 10 kGy pass\(^{-1}\) (2.23 m min\(^{-1}\)), 2 MV, and 2 mA, respectively. The irradiated samples were stored under vacuum at room temperature, followed by exposure to air just before the first measurement.

The irradiated samples were immersed in \(p\)-xylene at \(\sim 140 \, ^\circ\)C for 24 h and were dried in air so that the sol fraction in the samples is removed. The gel fraction was calculated by the equation,

\[
gel\,\text{fraction}\, (\%) = \left( \frac{W}{W_0} \right) \times 100,
\]

where \(W\) and \(W_0\) are the sample weights after and before the above treatment, respectively.

The amount of carbonyl groups induced by the irradiation was evaluated by micro-FT-IR spectroscopy. The details of measurement are described elsewhere [2].
Positron lifetime spectra were recorded with a digital storage oscilloscope by determining the time interval between the detection of the 1.27-MeV $\gamma$-ray from the $\beta^+$ decay of the $^{22}$Na positron source and one of the 0.511-MeV annihilation $\gamma$-rays [3]. In the measurements, the positron source, sealed with 7.5-μm-thick Kapton foils, was sandwiched between two samples taken from identical preparation lots. The obtained spectra were analyzed assuming three exponential components to deduce the lifetime $\tau_3$ and relative intensity $I_3$ of the longest-lived ortho-positronium ($o$-Ps) component by the PALSfit program [4]. The time resolution of the system was $\sim$200 ps full width at a half maximum [3]. Correction was made for the positrons annihilating in the source material. The validity of our system was confirmed with certified reference materials NMIJ CRM 5601-a and NMIJ CRM 5602-a provided by National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology (AIST) [5, 6].

3. Results and discussion
The variations of the gel fraction for the HDPE samples taken just after the irradiation and stored for 1 year as a function of dose are shown in Figure 1. For both the samples the gel fraction increases with increasing dose, possibly ascribed to the increased amount of the produced radicals along with dose. As for the sample after 1-year storage, the gel fraction with a dose lower than 500 kGy significantly reduced from each value for the sample taken just after the irradiation. This implies that the subsequent chain-scission process in those samples with doses lower than 500 kGy has a considerable effect on the resultant molecular weight as compared to the samples with higher doses. Irradiation of HDPE produces two types of radicals, that is, alkyl and allyl radicals [7]. The alkyl radicals are unstable at room temperature, therefore most of them instantly disappear, followed by the production of cross-linking or carbonyl groups with oxygen remaining in the polymer matrix during the irradiation. On the other hand, the allyl radicals are relatively stable under vacuum at room temperature. Hence, they are expected to survive until the samples were exposed to air so that they induce to form hydroperoxides, otherwise they also induce to form carbonyl groups during the irradiation [7, 8].

Figure 2 shows the depth distribution of the carbonyl absorbance at 1716 cm$^{-1}$ for 500-kGy-irradiated HDPE. After storage beyond half a year, the absorbance near both surfaces of the sample drastically increased, indicative of an enhanced amount of carbonyl groups. With further storage over 1 year the absorbance around 1.0 mm in depth was further increased. Through thermolytic and/or photolytic

![Figure 1. Relationship between the gel fraction and dose for HDPE. The circle and square plots denote the gel fraction measured immediately after the irradiation and 1 year from the irradiation, respectively. Solid lines are drawn to guide the eyes.](image1)

![Figure 2. Depth distribution of the carbonyl groups for 500-kGy-irradiated HDPE. The dashed line denotes the absorbance of unirradiated HDPE. The circle, triangle, and square symbols denote the absorbance measured immediately after the irradiation, 0.5 year from the irradiation, and 1 year from the irradiation, respectively.](image2)
reactions hydroperoxide produces carbonyl groups as well as alternative radicals [7–9]. These radicals lead to a cyclic oxidation process during long-term storage, gradually increasing the amount of carbonyl groups. This cyclic oxidation process induces polymer-main-chains scission, resulting in reduced molecular weight, that is, a decrease in gel fraction as evident in Figure 1.

Figure 3 shows the variation of the o-Ps lifetime $\tau_3$ and its relative intensity $I_3$ measured immediately after the irradiation as a function of dose. $\tau_3$ was $2.38 \pm 0.02$ ns and the free-volume hole size, estimated based on the Tao-Eldrup model [10–12], was $\sim 0.64$ nm in diameter. $I_3$ significantly decreases with increasing dose, whereas $\tau_3$ or the free-volume hole size does not. Figure 4 shows the time dependence of $I_3$ for 100-kGy- and 1000-kGy-irradiated HDPE samples. While no time dependence for $\tau_3$ was observed, $I_3$ for 100-kGy-irradiated HDPE levels off around 17% whereas $I_3$ for 1000-kGy-irradiated HDPE slightly decreases from 16% to 15% with increasing time.

According to the spur model, Ps forms in the terminal spur as a result of positron-electron recombination [13]. Ito et al. reported that the thermalized positron can diffuse over a distance of an order of $10^2$ nm in PE before it annihilates into $2\gamma$-rays [14]. This diffusion length is long enough for the positron to be trapped by a low concentration of oxygen-containing polar groups formed by thermal oxidation. Thus part of the positrons may not reach an electron to form Ps provided that a fraction of them are trapped by polar groups. For the present system, the produced radical could also be a positron trapping site [15, 16], in addition to the polar carbonyl groups involved with the cyclic oxidation process from the hydroperoxides. Thus these trapping sites of the polar groups and radicals possibly cause a reduction in the Ps formation probability, that is, $I_3$. 

**Figure 3.** Plots of the o-Ps lifetime $\tau_3$ (circle symbols, left-hand axis) and the o-Ps intensity $I_3$ (square symbols, right-hand axis) for HDPE vs dose. Data are taken immediately after the irradiation. Solid lines are drawn to guide the eyes.

**Figure 4.** Variations of $I_3$ during the long-term storage for HDPE. The circle and square symbols denote 100-kGy- and 1000-kGy-irradiated samples, respectively. Solid lines are drawn to guide the eyes.

**Figure 5.** Relationship between $I_3$ and the gel fraction measured immediately after the irradiation (filled symbols) and 1 year from the irradiation (open symbols). The circle and square symbols denote HDPE and LDPE, respectively. Solid and dotted lines are drawn to guide the eyes. The arrows represent the respective directions toward long-term storage for 1 year.
Finally, we discuss the relationship between Ps formation and the gel fraction. Figure 5 shows a plot of I₃ vs the gel fraction, obtained for the samples just after the irradiation and stored for 1 year from the irradiation, in which the result for low-density polyethylene (LDPE) with a density of 0.920 g cm⁻³ is also included. In LDPE alkyl and allyl radicals are produced by irradiation as in HDPE, but their lifetimes are much shorter than in HDPE [7, 8]. Hence almost of them are eliminated during the irradiation, so that the hydperoxides and subsequent carbonyl-group formation in LDPE should be much less than that in HDPE. Interestingly, I₃ for both LDPE and HDPE linearly decreased with increasing gel fraction. The reduction in I₃ for the samples taken just after irradiation is probably ascribed to radicals that survive until the measurement. After long-term storage, the relationship for HDPE deviates from the solid line to the dashed line. In light of the FT-IR and the gel fraction results, this shift is due to the reduction of I₃ and main chain scission along with long-term oxidation. On the other hand, no deviation was observed for LDPE because there is only a small increase in the carbonyl groups along with the chain scission. Note that I₃ may be influenced by both polar groups and radicals. It is necessary to consider these effects independently for better understanding of the irradiation effect and the long-term degradation of polyethylene.

4. Conclusion

Structural changes of electron beam irradiated HDPE during irradiation and long-term storage were investigated by micro-FT-IR, gel fraction measurement, and PALS. Significant changes of τ₃ were not observed whereas I₃ decreased not only with dose but also long-term storage. Carbonyl groups suppress the formation of Ps, therefore I₃ decreases with the formation of carbonyl groups. Furthermore, I₃ seems to correlate with the gel fraction for both HDPE and LDPE immediately after irradiation. Although further study is required to understand the relationship between I₃ and the gel fraction, the obtained results demonstrated that I₃ measured by PALS can be useful as an indicator of the structural change induced by irradiation and long-term storage in PE.

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