Electronic Supplementary Information

Effects of X-rays, Electron beam and Gamma irradiation on PE multilayer film properties

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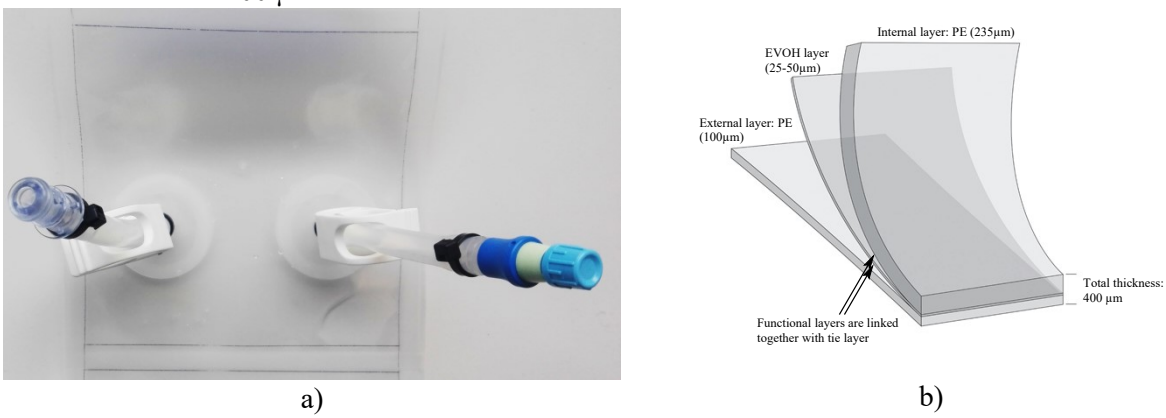
Experimental section

Sample bags

The PE single-use plastic bags investigated were made from a multilayer film composed of one layer of ethylene vinyl alcohol (EVOH) sandwiched between two layers of polyethylene (PE), with a total thickness of about 400 µm.



a) b)

Figure S1: PE single use plastic bag (a) and composition of the PE multilayer film (b).

Gamma irradiation

PE bags were packed, wrapped in multilayer (Polyethylene/Polyamide/polyethylene)packaging, thickness 100 ± 20 µm, and irradiated at room temperature with a ^{60}Co gamma source, at Ionisos, Dagneux, France. The dose rate provided was of 1-2 kGy/h. Alanine dosimeters were used on the

cardboard box to assess the radiation delivered to the single use bag samples (+/- 5%). The target dose average reached was 59 kGy. Irradiation was performed at room temperature under environmental atmosphere.

Electron beam irradiation

PE bags were individually wrapped in multilayer (Polyethylene/Polyamide/polyethylene) packaging and placed side by side in an 8 cm thin cardboard box so as to have the same and only thickness of plastic material.
Samples were irradiated in a 10 MeV Rhodotron (Ionisos, Chaumesnil, France), with a power source at 28 kW. The dose rate was 300 kGy/min. Alanine dosimeters were used on the cardboard box to assess the radiation delivered to the single use bag samples (+/- 5%). The average surface dose delivered was 51 kGy for double sided irradiation.

X-ray irradiation

PE bags were individually wrapped in multilayer (Polyethylene/Polyamide/polyethylene) packaging. They were irradiated in a 7 MeV Rhodotron (Steris, Däniken), with a power source at 360 kW . The average dose rate was 80 kGy/h. The average surface dose was 68 kGy for double sided irradiation, measured by alanine dosimeters.

High Performance Liquid Chromatography (HPLC)

Three months after irradiation, bags were filled with a 50 µM solution of methionine in buffer (10 mM NaH-2PO4, 10 mM Na2B4O7•10H2O, 5 mM NaN3, pH 8.2). Sampling was performed after 10 days of storage . The sample was analyzed with an Agilent 1260 HPLC equipped with a quaternary pump (G1311C), an autosampler (G1329B), and a fluorescence detector (G1321B).

Before analysis, the flow rate was set to 3.0 mL/min using vacuum-degassed mobile phases [A, 10 mM NaH-2PO4, 10 mM Na2B4O7•10H2O buffer at pH=8.2; B, acetonitrile:methanol:water (45:45:10, v:v:v)]. Before use, solvent A was filtered through a 0.22 µm microporous cellulose acetate filtering membrane. As the methionine is non fluorescent, an automated derivatization process is performed to make it fluorescent. The reaction is detailed in the Figure S2. The automated online derivatization (in the autosampler) using an injection program is detailed in **Table 1**. The derivatization reagent used was the ortho-phthaldehyde (OPA).
The gradient program was as follows: 0–13.4 min, 2% B; 13.4 min, 57% B; 13.5-15.8 min, 100% B; 18 min, 2% B. Separation was carried out on an Agilent Poroshell HPH-C18 column (4.6 mm × 100 mm, 2.7 µm particles) used with a pre-column, UHPLC guard Poroshell HPH-C18, 4.6mm. The column was maintained at 40°C +/- 0.8°C in a thermostatted column compartment (G1316A) during the analyses. The fluorescence detector was set to an excitation wavelength of 340 nm and an emission wavelength of 450 nm. The total runtime of the method was 20 min. Chromatographic data were acquired (Figure S3) and evaluated with the HPLC 1260 openlab software. Internal calibration was done by spiking 20 µL of L-Norvaline in each sample and standard. For electron beam and gamma irradiated samples, results are displayed as the average of two batches and the statistical errors represented are calculated on these two batches. For X-ray irradiated samples, the result is displayed for one lot and the statistical error represented is calculated on the seven analyses of the 3.8 µM of methionine sulfoxide standard.

Table 1: automated online derivatization

1. Draw 2.5 µL from borate vial
2. Draw 1.0 µL from sample vial
3. Mix 3.5 µL in wash port five times
4. Wait 0.2 minutes
5. Draw 0.5 µL from OPA vial
6. Mix 4.0 µL in wash port 10 times default speed
7. Mix 4.4 µL in wash port 10 times default speed
8. Draw 32 µL from injection diluent vial (100 mL of mobile phase A and 0.4 mL concentrated H_3PO_4)
9. Mix 20 µL in wash port eight times
10. Inject
11. Wait 0.1 minutes
12. Valve bypass

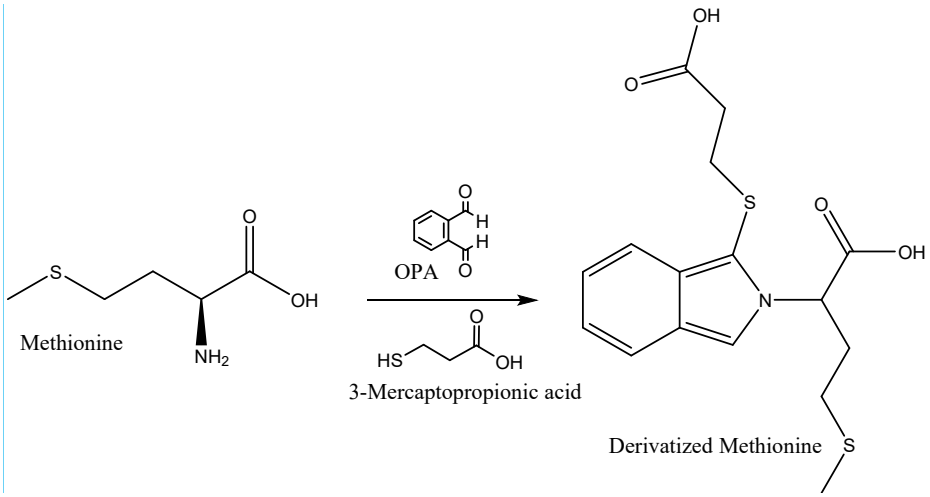


Figure S2: derivatization reaction of methionine

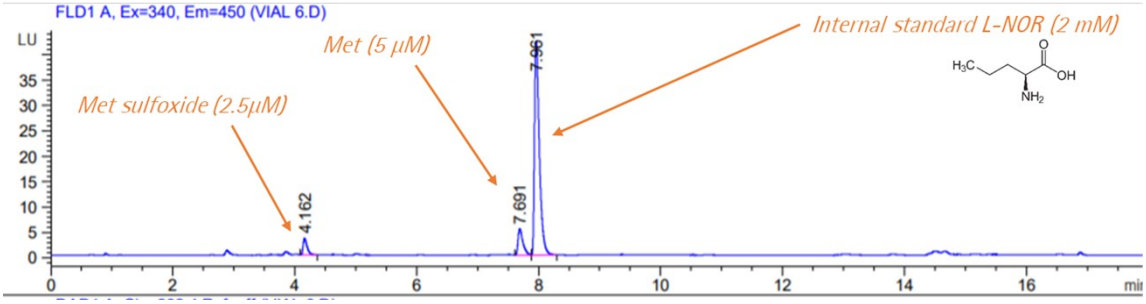


Figure S3: chromatogram of a standard vial

Differential Scanning Calorimetry (DSC)

The sample bags were analyzed three months after irradiation. The melting temperatures of the polymers that composed the PE multilayer film were determined using differential scanning calorimetry (DSC). Samples (7-22mg) were introduced in the DCS device. Measurements were performed with a calorimeter Sensys Evo Setaram. More details regarding the analysis have been described in a previous article[1]. Results are displayed as the average of two heating rates for the

melting peak (when available) and of two batches. An example of a thermogram obtained is shown in Figure S4.

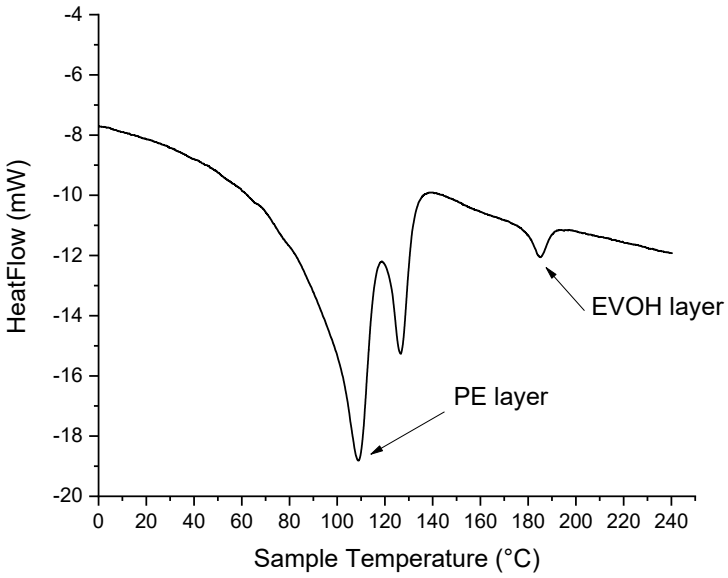


Figure S4: thermogram of electron beam irradiated sample at 50 kGy

Electron Spin Resonance (ESR)

ESR measurements were carried out on a Bruker EMX X-band spectrometer operating at 9.5 GHz and equipped with a highly sensitive rectangular microwave cavity. The spectroscopic parameters were modulation amplitude 2 G, magnetic field sweep 500 G, receiver gain 10^3, resolution 1024 points, power 20.12 mW and sweep time 20.972 s. Four scans were performed to record each ESR signal. Analyses were conducted over time after irradiation from 10 and 20 days for gamma irradiation and electron beam irradiation, respectively. For X-ray irradiation, the first ESR analysis were performed 80 days after irradiation. An example of a spectra for electron beam irradiated sample is shown in Figure S5.

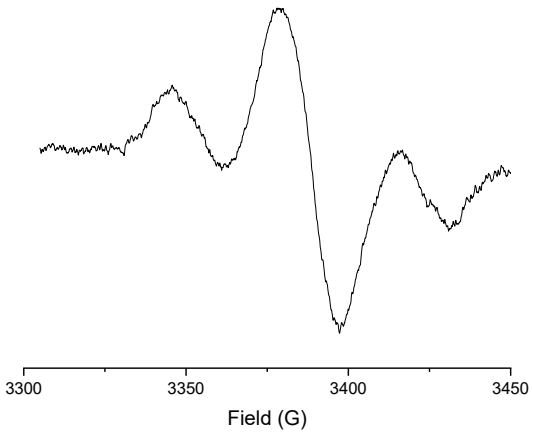


Figure S5 : ESR spectra of PE/EVOH/PE multilayer film 20 days after electron beam irradiation

Storage conditions

Before irradiation samples bags were placed in overpouches and a partial vacuum (not controlled) has been performed. The overpouches were placed in the cardbox and sent to irradiation. After irradiation and before analysis card boxes were stored in the dark, in an air-conditioned room at 20 ± 2°C