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Effect of cumulated dose on hydrogen emission from polyethylene irradiated under oxidative atmosphere using gamma rays and ion beams

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HIGHLIGHTS

- Polyethylene is radio-oxidized, using gamma rays and ions beams.
- H_2 emission rate is determined as function of dose and irradiation type.
- H_2 emission rate is observed to decrease when dose increases.
- H_2 decrease is attributed to energy and radical transfers to oxidized defects.

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ABSTRACT

This work reports the effect of very high doses, up to 10 MGy, on the H_2 emission from high density polyethylene (HDPE) irradiated with gamma rays and ion beams, in the presence of oxygen. This was obtained through a two-step procedure. First, HDPE films were pre-aged, at different doses, using either gamma rays or ion beams. In the second step, the pre-aged samples were irradiated in closed glass ampoules for gas quantification, using the same beam type as for pre-ageing.

The hydrogen emission rate decreases when dose increases for both gamma rays and ion beams. However, the decreasing rate appears higher under gamma rays than under ion beam irradiations and this is assigned to a lesser oxidation level under the latter. Herein, we show the effectiveness of the radiation-induced defects scavenging effect under oxidative atmosphere, under low and high excitation densities.

1. Introduction

Organic materials, among which polymers, are present in Intermediate Level Long-Lived Waste (IL-LLW) contaminated by actinides. These polymers are submitted to γ, β and α radiations and their behavior on long time periods, thus high doses, should be studied for safety purposes.

Under ionizing radiations, polymers are modified through the creation of new groups in their backbone and gas emission (Chapiro, 1962; Dole, 1972). In polyethylene, the main gas is H_2 and in-chain defects are function of both the environment and the irradiation type. Under gamma rays and electron beams, C=C double bonds and crosslinking are preponderant under inert atmosphere whereas ketones and hydroperoxides are preponderant in presence of oxygen. Little is known on the 5 MeV α irradiations of polymers. Nevertheless, irradiation with α particles can be simulated with Swift Heavy Ions (SHI) of well-chosen characteristics (Ngono-Ravache et al., 2015). Under SHI, almost the same defects as under gamma rays are created, but with different concentrations and ratios. Swift Heavy Ions differ from gamma rays in two main features. First, the energy is deposited along the ion path in a cylinder of a few nanometers named the track, which, as a consequence, induces heterogeneity in the energy deposition at the nanometric level. Second, they induce high stopping power (high excitation and ionization densities) that can trigger specific modifications (Ngono-Ravache et al., 2007).

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Most of the defects created in PE irradiated under inert atmosphere present a common trend: their creation rate decreases with increasing dose. This behavior is assigned to energy and radical transfers towards defects created at lower doses, acting as sinks and therefore inducing the polymer stabilization under further irradiation. This has been evidenced theoretically (Ceresoli et al., 2005; Serra et al., 2000) but also experimentally (Chapiro, 1962; Ferry et al., 2014; Mitsui and Shimizu, 1979; Seguchi, 2001). Using pulse radiolysis (Tabata, 1993), energy transfers in polymers are shown to be very efficient over long distances and in a short time scale (less than 1 ns): these results are interpreted on the basis of the exciton model proposed by Partridge (1970).

Except for the study of Seguchi (2001), who has used doses as high as 8 MGy, most of the studies dealing with radiation-induced stabilization by defects were performed at low doses, under vacuum or inert environment. To our knowledge, no study was performed under oxidative environment.

Therefore, the aim of the present work is to evaluate the effectiveness of the radiation protection effect of radiation-induced defects both in presence of oxygen and at doses as high as 10 MGy. For this purpose, we have irradiated high density polyethylene (HDPE) under oxidative atmosphere, using both gamma rays and SHI, and we have determined the instantaneous H_2 emission rate at various doses. Using SHI is intended in this study to simulate the effect on HDPE behavior of actinide-emitted α present in nuclear waste tank.

2. Experimental

2.1. Material

High density polyethylene (HDPE) was supplied by Sigma-Aldrich (ref. 181900) and used without further purification. To ensure a homogeneous oxidation through the sample thickness, thin films were prepared by high pressure molding using a laboratory press. Films thicknesses were comprised between 50 and 100 μm for gamma irradiations, and were about 25 μm for ion beam irradiations.

2.2. Irradiation procedure

Instantaneous hydrogen emission rates, at high doses, were determined during a two-step procedure. On the first step, polymers were irradiated at various doses, without gas analysis. During the second step, polymers are irradiated at low doses in a closed container and the emitted gases are analyzed. Between the two irradiation steps, samples are stored under inert atmosphere and in dark to prevent or at least reduce further ageing.

Using this two-step procedure presents great advantages. At a given dose, a single step irradiation in a closed container would have given the cumulated emission rate instead of the instantaneous emission rate. Moreover, irradiating in one single step up to so high doses should have led to the complete consumption of the oxygen present in the glass container, leading to the variation of the atmosphere composition through the irradiation. Finally, this excludes H_2 back reactions, in presence of high pressures of H_2 in the container, which can lead to a bias in gas quantification.

The oxygen pressure in the first step is sufficient to ensure a homogeneous oxidation process through the samples even at very high doses. For ion beams, the pre-ageing irradiations were performed under 1 bar of oxygen, in a large volume irradiation chamber. Gamma irradiations were performed in open pillboxes, covered to prevent dust deposition on the samples while allowing air to flow inside the container.

Table 1
Polymer pre-ageing using gamma rays under air at room temperature: irradiations dose and dose rates. * Samples pre-aged at LABRA.

Mean dose (MGy)	Mean dose rate (kGy h^{-1})
0.49 ± 0.03*	1.19
1.00 ± 0.06*	1.11
2.02 ± 0.12	0.96
4.02 ± 0.24	0.85
6.07 ± 0.36	0.84
10.14 ± 0.61	0.86

For both irradiation types and for the second-step irradiations, polymer samples were placed in glass ampoules equipped with a valve, under around 700 mbar of reconstituted air (20.0% O_2, 77.99% N_2, 2.01% Kr). Krypton is used as a tracer and enables to determine the final pressure. Sample masses were estimated to obtain, at the end of the irradiation, a final content in H_2 of about $1\%_{vol}$ and an oxygen consumption of about 50% of the initial concentration.

2.3. Irradiation conditions

2.3.1. Gamma irradiations

Gamma pre-ageing irradiations (Table 1) were performed at IONISOS (Dagneux, France) and LABRA (Saclay, France). Dosimetry was performed using regularly changed radiochromic dosimeters. The associated uncertainty is of about 6%. No correction was made to take into account the electronic density difference between water and polyethylene.

The second-step irradiations were performed using the Nordion Gammacell® (PCR, Saclay, France). Ampoules were inserted into the Gammacell® on a turntable. A Fricke dosimeter was used, without further electronic correction. The dose rate was estimated at 0.36 kGy h^{-1} and the deposited dose equal to 22 kGy.

2.3.2. Ion beam irradiations

Ion beam irradiations were performed at the Grand Accélérateur National d'Ions Lourds (GANIL, Caen, France). Ion energies were always high enough to ensure a relatively constant LET (Linear Energy Transfer) over the sample thicknesses. During both steps, samples were irradiated as a stack of films and the number of films superimposed was chosen to ensure a relative variation of the LET, below 25%, from the stack entrance to the exit.

Pre-ageing irradiations were performed on the Medium Energy Line facility (SME), using 11 MeV/A ^{20}Ne ion beam. The second-step irradiations were performed on the High Energy Line facility (HE) using 87.5 MeV/A ^{36}Ar ion beam. The ^{20}Ne beam is the one consistent to simulate actinide-emitted α irradiations (Ngono-Ravache et al., 2015). The use of high energy ^{36}Ar beam for the second step is justified by the need 1) to go through the ampoule glass walls without reducing drastically the energy of the beam reaching the samples placed in these ampoules and 2) to limit the LET variation below 25%, as explained just above.

Homogeneous irradiation was ensured by a x,y-scanned beam (typically 24 cm^2 for SME facility and 36 cm^2 for HE facility). The energy loss was calculated with SRIM, based on the TRIM code (Ziegler). Irradiation conditions are gathered in Table 2. Fluxes were chosen in order to limit the power deposition on the sample to 0.5 mW cm^{-2}, avoiding significant sample heating.

Statistical errors for a given sample and for a single beam are small, at most a few %. The systematic errors are higher and are mainly due to sample thickness and dose estimation, due to the material composition changes: they amount at the highest dose to be less than 10%. Total error on dose has been estimated at 10%.