



Effect of swift heavy ions on an EPDM elastomer in the presence of oxygen: LET effect on the radiation-induced chemical ageing



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ABSTRACT

With the aim of understanding the radiation effects of alpha particles on polymers, this paper analyses the role of the heterogeneity of energy deposition, at the nanometric scale, on the radiation-induced oxidation of an ethylene-propylene-diene elastomer based on 1,4 hexadiene (EPDMh). This polymer was irradiated with ²⁰Ne, at various Linear Energy Transfer (LET), in the presence of oxygen. Macromolecular defects such as carbonyls, alkenes and alkynes were monitored *on-line*, using Fourier Transform Infrared Spectroscopy (FTIR), and their evolution as a function of both LET and irradiation dose were studied.

Carbonyl group consists of various chemical functions which absorption bands overlap one another in a limited spectral area. The different components were extracted by curve fitting, allowing monitoring the specific evolution of each of these chemical functions as a function of the irradiation conditions. Among carbonyl containing functions, the creation of ketone groups is the most important.

LET influences the alkene radiation chemical yield at initial dose and, apart from *trans*-vinylene, it also influences the dose evolution of their concentration. Conversely, LET has no significant influence on the total carbonyl concentration.

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1. Introduction

Polymers are widely used in the nuclear power industry. Consequently, their sensitivity to ionising radiations should be addressed. Various polymer-based materials are used in the nuclear power industry and they face various irradiation conditions [1,2]. They can be exposed to γ , β , and α irradiations. As an example for the latter, polymer materials being components of glove boxes, used for fuel pellet fabrication and analysis, are contaminated by actinides that are α emitters. Similarly, bitumen, used as immobilisation matrices for radioactive aqueous effluents and mud, also suffers α -irradiation.

In well-chosen conditions, presented hereafter in Section 2.2, α particle effects on polymers can be simulated by Swift Heavy Ions (SHI). Generally, the energy deposition pattern induced by SHI in polymers is very different from the one resulting from low-ionising

radiations (β , γ). Low-ionising radiations deposit their energy quite homogeneously, whereas SHI deposit their energy through electronic processes (ionisation/excitation) occurring close to the ion path, in a track-core of a few nanometres [3]. This induces an inhomogeneous energy deposition at the nanometric level. The huge amount of energy deposited locally by SHI within the track-core triggers specific damage processes, which involves complex molecular rearrangements and collective atomic motions. A great effort has been made for a better comprehension of the effect of this huge ionisation/excitation density in polymers, under vacuum or inert environment [4–11]. Defects created are of two types: defects created in the polymer chain, called hereafter macromolecular defects and gaseous molecules (gas release). Macromolecular defects created in polymers submitted to SHI can be classified in two groups: 1) defects common to low LET ionising radiations and SHI, and 2) defects specific to SHI.

Alkenes (*trans*-vinylene, *trans-trans*-diene, vinyl and vinylidene), chain scissions and crosslinkings are part of the first group of defects and the LET influence on their formation varies from one group to another. Triple bonds (alkynes, cyanates) and cumulenes

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(allenes, isocyanates) are part of the second group. SHI specific defects are created above a LET threshold and the influence of LET on their creation is tremendous [12–15].

Contrary to what has been done under inert environment for assessing the specificity of SHI on polymers, only few detailed studies on the combined effects of oxygen and SHI on the physico-chemical ageing of simple polymers have been undertaken. Under low-ionising radiations, in the presence of molecular oxygen, the P° radicals, stemming from C–H (or C–C) radiation-induced homolytic scissions, readily react with the oxygen molecule giving a peroxy radical (POO°). According to the generally accepted chain reaction involving alkyl and peroxy radicals, inactive products are created [16]. Inactive products are made of 1) oxygen containing defects such as carbonyl groups, hydroperoxides, alcohols or ethers and 2) non-oxidised groups such as alkenes and cross-links. The question of knowing how radiation-induced oxidation is modified by the non-homogeneous energy deposition, at the nanometric scale, and the related high ionisation/excitation densities induced by SHI is still open. The aim of the present study is to characterise and quantify defects created in an ethylene-propylene-diene monomer (EPDM), based on 1,4 hexadiene (EPDMh), irradiated under SHI in the presence of oxygen.

Detailed studies of the radiation-induced oxidation of different EPDM under γ -rays have been done [17–21]. Trials to define the influence of the diene monomer types and concentration have also been made [22]. Few studies of EPDM ageing under swift heavy ion irradiations, under oxidative conditions, exist [23–25]. It appears from the latter that: first, oxidation ageing is effective under ion beam irradiation and second, oxidised defects created under SHI are almost the same as those created under low-ionising irradiations. However, their radiation chemical yields are lower under SHI; as is the oxygen uptake.

The EPDMh was irradiated at three different LET ranged from 4.3 to 11.5 MeV $\text{mg}^{-1} \text{cm}^2$, with Ne ion beams, in the presence of oxygen, at a constant dose rate and in a large domain of dose (D), up to 12 MGy. We focus on macromolecular defects, analysed *on-line* by Fourier Transform Infrared Spectroscopy (FTIR).

2. Experimental

2.1. Materials

The EPDMh was provided by Dupont De Nemours (ref. EPDM NORDEL 2722). The molar composition of this EPDMh obtained from ^{13}C solid-state NMR spectroscopy [22], is 84% ethylene, 13.8% propylene and 2.2% 1–4 hexadiene. The polymer shows a crystalline fraction of around 20%, as quantified by DSC using polyethylene as a reference. However, the very low melting point ($\approx 47^\circ\text{C}$) indicates very small crystallites.

The infrared spectrum of the virgin film is presented in Fig. 1. Bands of interest are labelled and the corresponding assignments presented in Table 1.

2.2. Irradiation conditions

2.2.1. Set-up

To record the in-film modifications, a specific device allowed us to irradiate and acquire the FTIR spectra without removing the sample from the cell. As a consequence, exactly the same area of the sample was irradiated and probed all along the experiment, thus excluding the inconvenience of possible local thickness variations.

Polymers were irradiated in the form of thin films, first to obtain a homogeneous oxidation profile, on a macroscopic level, and second to enable FTIR analysis, in the transmission mode, without band saturation. Polymer film thicknesses as well as irradiation

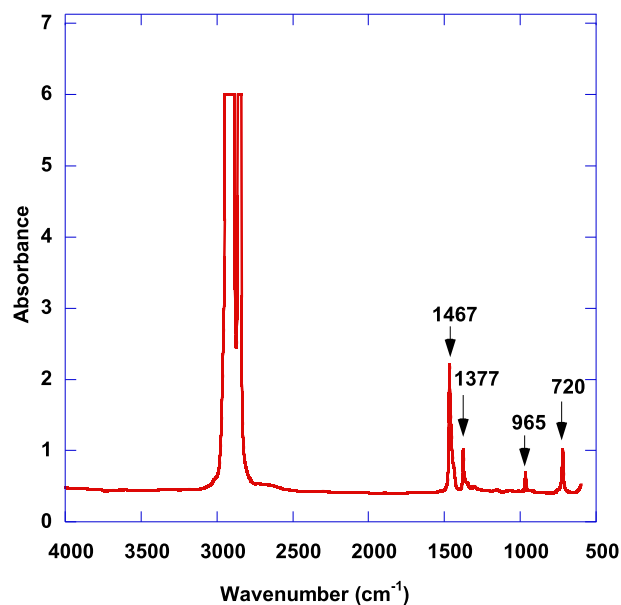


Fig. 1. Infrared spectrum of a virgin EPDMh film acquired at room temperature, at an angle of 55° using a polarized IR light.

conditions are gathered in Table 2. Interference fringes were avoided by recording the spectra with polarized light, at the Brewster angle (55°). The FTIR spectra were recorded at a resolution of 2 cm^{-1} and 256 scans were averaged for improving the signal to noise ratio. This is necessary for accurate defect quantification even at very low irradiation doses.

2.2.2. Beam and sample characteristics

Experiments were performed at the Grand Accélérateur National d'Ions Lourds (GANIL Caen, France), on the Medium Energy Line facility (SME), under a 1000 mbar oxygen pressure. A x, y -scanned beam was used to ensure a homogeneous irradiation field (typically 24 cm^2). This large field allows irradiating simultaneously different samples. The target temperature was not monitored during irradiation, but fluxes (Table 2) were chosen in order to limit the power deposition on the samples to 0.5 mW cm^{-2} , thus avoiding any significant sample heating. The energy loss was calculated with SRIM, based on the TRIM code [26].

The aim of this work is to analyse LET effects on radiation-induced oxidation, within the context of actinide-emitted α radiation, without insisting on exactly matching the real case. EPDMh films were irradiated with ^{20}Ne ion beams, at three different energies, and consequently LET (Table 2). Actinides emit α particles at a typical energy of 5 MeV. The range of these He ions is around $35 \mu\text{m}$. The LET significantly varies along the He ion path; going

Table 1

Infrared band attributions for non-irradiated EPDMh. ν , δ , γ , ω , R represent respectively stretching, scissoring, twisting, wagging and rocking vibration modes.

Wavenumber (cm^{-1})	Assignment
3000–2800	ν_{CH} – CHR_1R_2 , – CH_2R , – CH_3
1470–1460	δ_{CH_2}
1456	δ_{CH_3} antisymmetric
1377	δ_{CH_3} symmetric
1305	γ_{CH_2}
1150	ν_{CC} skeleton
965	ω_{CH} (<i>trans</i> -vinylene)
720	R_{CH_2} ($(\text{CH}_2)_n$, $n \geq 5$)

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