On the radio-oxidation, at high doses, of an industrial polyesterurethane and its pure resin

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ARTICLE INFO

ABSTRACT

The polymers inside the technological waste packages degrade under radio-oxidation. In the context of the geological nuclear waste storage, the long-term behavior of these polymers must be better understood, especially at high doses. The general objective is to ensure the safety of the geological underground repository.

In this study, we focus on an industrial polyesterurethane, used as glovebox gloves, and its pure resin. These two materials were radio-oxidized at different high doses. The modifications induced by irradiation using low stopping power ionizing rays were assessed through the study of the gas release, the in-chain modifications, and the formation of oxidation products of low molecular mass.

Gas mass spectrometry was used to quantify the gas release with exposure doses up to 4000 kGy for the pure material and 10 000 kGy for the industrial polymer: the evolution with dose is weak and is increasing only in the case of carbon dioxide. The in-chain modifications were identified by infrared spectroscopy or X-ray photo-electron spectroscopy, and correspond probably mainly to the formation of hydroperoxides, hydroxyls and ke-tones, along with alkenes. By GC-MS or thermodesorption analyses, oxidation products trapped in the polymer matrixes are identified and are esters, carboxylic acids, alcohols, an aromatic molecule and oligomers.

1. Introduction

Organic materials, among which polymers, are present in Intermediate Level Long-Lived Waste (ILW-LL) contaminated with actinides. These polymers are submitted to α, β and γ radiations and their behavior on long time periods, i.e. high doses, should be studied for safety purposes. Under ionizing radiations, polymers are modified through the creation of new groups in their backbone, formation of oxidation products of lower molecular mass and gas emission [1,2].

In France, a deep geological repository is being designed, with galleries that will be filled with these waste packages [3]. Because gas released from the radio-oxidized polymers can be explosive and/or inflammable, their production rate must be estimated at least in order to size the forced ventilation used for the alveoli and the galleries. From a safety purpose, the maximal volume of hydrogen allowed to be emitted per year and per package is of 40 NL.[1] The gas release has to be estimated over years, so for doses from non-irradiated to radio-oxidized up to several MGy. The annual dose in a waste package will depend on the design of the waste package: in standard containers of compacted wastes now under study by AREVA, the absorbed dose is estimated to be about 34 MGy after 300 years [4]. This dose estimation is relatively high compared to other waste packages, such as CBF-C′2 (or F2-3-08), where the absorbed dose is estimated to be about 2 MGy after 300 years [5]. The aim of this article is to access to a better understanding of polyurethane polymers ageing in order to model properly the radiolysis gas release from this family of polymer.

In this study, an industrial aromatic polyesterurethane used as glovebox gloves, is investigated. Among polymers used in the nuclear industry, polyurethane polymers have gained in quantity due to the progressive replacement of poly(vinyl chloride).

Many articles are dealing with polyurethane radio-oxidation or photo-oxidation [6–13]. Polyurethanes are polymers composed of hard segments, which can be aliphatic or aromatic, and of soft segments (generally including the extenders), which can contain ester or ether groups. Walo et al. [14] have shown that the nature of these repetition units is of great importance in the degradation mechanisms encountered under radio-oxidation. For instance, polyurethane with aromatic hard segments is less sensitive to irradiation than polyurethane

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[1] NL: Normal Liter (volume at a pressure of 1 bar and a temperature of 20 °C).

with aliphatic hard segments, thanks to the radiation protection effect conferred by the aromatic structure of the hard segments repetition units [15–19]. This phenomenon has already been evidenced in aromatic polyetherurethane by Dannoux et al. [12].

It has also been shown that, whatever their chemical nature, rigid segments are less affected by radio-oxidation than soft segments [20,21]. The more important the length and the concentration of soft segments are, the more sensitive to radio-oxidation the polymer is, and the more modified the mechanical properties of the material are [22].

Only few articles are dealing with aromatic polyesterurethane, *i.e.* polyurethane with aromatic hard segments and ester soft segments. This kind of polymer has been studied under photo-oxidation by Wilhelm et al. [23]. Authors have evidenced the formation of mono- and di-quinone-imides, these molecules being formed from the aromatic hard segments and inducing the yellowing of the polymer. Moreover, they have also observed the homolytic rupture of the C-N bond, leading to the formation of two macroradicals PNH° and P'O-C°(=O), while a large part of these radicals are undergoing a photo-Fries rearrangement [23,24]. The PNH° macroradical can also pick up one hydrogen radical and thus form an aromatic amine. In addition, the oxidation of the aromatic hard segments catalyzes the oxidation of the polyester soft segments.

The methylene groups, present in the aromatic hard segments, can release one hydrogen atom, this reaction being followed by a reaction with an oxygen molecule to form peroxyl radicals. These lasts will then form hydroperoxides groups by hydrogen abstraction on another chain [4,23,25]. These hydroperoxides are not stable and will decompose to alkoxyl radicals after the O-O bond breakage, which will in turn react by chain scission to form an aldehyde and then a carboxylic acid by reaction with oxygen. Hydroperoxides could also be decomposed to form aromatic acids without intermediate steps.

In some cases, aromatic polyesterurethane have also been studied under radio-oxidation to follow scission to crosslinking ratio. Gel formation dose has been observed at doses as low as 50 kGy in acetone and dichloromethane at a temperature of 33 °C [26]. Moreover, crosslinking concentration increases with dose rate [27,28].

Tian et al. [27] showed by Small-Angle Neutron Scattering (SANS) that the radio-oxidation of an aromatic polyesterurethane decreases the segregation between soft and hard segments. The authors indicate a competition between, on one hand, of the crosslinking formation between segments, bringing together two segments of different nature, and on the other hand, of the increase in the mobility of the segments in the polymer caused by chain scissions. Results obtained on scission to crosslinking ratio are different considering the kind of polyurethanes.

Each kind of polyurethane has a particular behavior under irradiation. The objective of this article is to understand, as much as possible, the radio-oxidation mechanisms that are leading to the ageing of PURm, to be finally able to model the waste package behavior for periods as long as the reversibility period of the French deep geological repository. To obtain information on the fillers and additives effect of this industrial polymer, a pure resin with a chemical composition very close to the industrial polymer but with no fillers nor additives, has also been extensively studied.

2. Experimental

2.1. Materials

2.1.1. Industrial polyesterurethane

The chosen industrial polyesterurethane (named hereafter PURm) is a material used as glovebox gloves, shaped like a film of 0.5 mm thick. The characterization of this polymer has been realized and already presented in a previous article [29].

The resin of PURm is composed of three units that are presented in Fig. 1: 4,4′-methylene diphenyl diisocyanate (MDI), 1,4-butanediol (BDO) and poly(1,4-butylene adipate) (PBA). Hard segments represent

25.5 %$_{wt}$ of the polymer formulation, whereas extenders and soft segments represent 63.4 %$_{wt}$. Contrary to what is written in the previous article [29], the polymer formula in the industrial material can be written as $(MDI)_{0.20}(PBA)_{0.57}(BDO)_{0.23}$. As we will see in section 2.1.2, the PURm formula previously given in the last article is the one of the pure resin PURe chosen to evaluate the effect of the presence of fillers and additives on the degradation of PURm.

The manufacturer indicates that inorganic additives (probably mainly composed of SiO_2) represent 8.9%$_{wt}$ of the formulation. The remained 1.8 %$_{wt}$ are crosslinking agents and 0.4 %$_{wt}$ corresponds to white and green pigments. The identification of the fillers and additives present in the industrial polyesterurethane was, at least partially, realized by methanol extraction followed by mass spectrometry analyses (GC-MS and ESI-MS). Molecules identified and their role are given in Table 1.

The weight average molecular weight M_w is of 200 000 g.mol^{-1} in equivalent polystyrene and the polydispersity index I_p is of 2.8 with a 10% uncertainty value. Finally, the glass transition temperature T_g is equal to -32 ± 5 °C and this polymer is totally amorphous because of the absence of melting peak on the differential scanning calorimetry spectra in the scanned temperature range.

2.1.2. Choice of the corresponding resin and comparison with the industrial material

To evaluate the effect of the presence of fillers and additives on the degradation of the industrial polymer, a model resin, PUR Estane® 5703 (noted hereafter PURe), was identified and furnished by Lubrizol (Belgium).

The three repetition units are the same as the industrial one, and the resin formula can here be written as $(MDI)_{0.17}(PBA)_{0.63}(BDO)_{0.20}$. The weight average molecular weight M_w is 140 000 g.mol^{-1} in equivalent polystyrene and the polydispersity index I_p is 2.5 with a 10% uncertainty value. Finally, PURe presents a glass transition temperature T_g equal to -33 ± 1 °C and is also totally amorphous.

Except for the fillers and additives, the resins of PURe and of PURm, although non-identical, are really similar because they present the same extender, soft and hard segments in close ratios. Thus, it can be considered in the following that PURe is a good model polymer of PURm.

2.2. Irradiation

2.2.1. Polyesterurethanes oxidation critical thickness and shaping

To obtain representative irradiations, radio-oxidations have to be performed homogeneously. The radiation-induced oxidation distribution in the depth profile is known to be limited by oxygen availability through diffusion. This oxygen availability is the result of a competition between its permeation through the polymer, and its consumption under irradiation.

The critical thickness, L_c, is the thickness within which the oxidation profile is almost flat (thickness below which the integrated oxidation across the sample will be greater than 90% of the homogeneously oxidized result), and can be estimated following [30]:

$$L_c = \sqrt{8 \cdot \frac{P(O_2) \cdot p}{G_{-O_2} \cdot d}}$$

In this equation, $P(O_2)$ is the oxygen pressure, *i.e.* 0.207 atm. d is the dose rate in Gy.s^{-1}, G_{-O_2} is the oxygen consumption radiation chemical yield in mol.J^{-1}, and p is the oxygen permeation coefficient in mol.cm^2.g^{-1}.atm^{-1}.s^{-1}. p has been experimentally measured on the industrial polymer at the European Institute of Membranes and is equal to 6.32·10^{-13} mol.cm^2.g^{-1}.atm^{-1}.s^{-1}. G_{-O_2} has been determined in the laboratory and is equal to 5.6·10^{-7} mol.J^{-1}, at a dose rate of 1 kGy.h^{-1}.

In these conditions, the critical thickness calculated is of 0.8 mm: PURm films having a thickness of 0.5 mm, the radio-oxidation is