Modification of gas emission yields in polymers at high doses: influence of in-film defects creation

Yvette Ngono-Ravache: DSM/IRAMIS/CIMAP (Caen)
Adeline Dannoux: DEN/DPC/SECR/LSRM (Saclay)
Stéphane Esnouf: DSM/IRAMIS/SCM/LR (Saclay)

Polymers submitted to ionising radiations (I.Ra) are modified by the creation of defects such as unsaturated bonds, chain scissions and crosslinks. The counterpart of these modifications is the formation of small molecules released out of the polymer film as gases. This gas release is a problem in radioactive waste storage since, depending of the major gas, it can present risks of explosion, corrosion or toxicity. For this technological problem, it is essential to be able to predict the quantity of gas present in a radioactive waste repository as a function of the storage time and thus as a function of the absorbed dose, even at very high doses. This is somewhat difficult since polymers are continuously modified by irradiation and gas production yields G_{gas} vary with the dose: it is stable at low doses (< 1 MGy) but can be greatly reduced at high doses.

The decrease of G_{gas} as a function of the irradiation dose is a known but not really studied phenomenon. Recent studies on polyethylene[1], ethylene-propylene copolymers[2] and polyurethane[3] showed that the high decrease in $G(H_2)$ with dose could not be understood unless energy transfers through created defects are considered. Meanwhile, radiation-induced defects protect the polymer by acting as energy sinks. **The aim of this project is to isolate and quantify the impact of each radiation-induced defect type on the emission of H_2, CO, CO_2 and small hydrocarbon with the irradiation dose.**

To achieve this objective, tailor-made polymers containing one type of sink (C=C, C=O, hydroxyls) at the time, at controlled concentrations and positions (backbone or side chains), will be irradiated using ion beams, high energy electron beams or γ rays, at room temperature and low doses (10-100 kGy) in order to avoid competition between introduced sinks and radiation-induced defects. The modulation of side chain length will also permit to quantify the relative efficiency of in-main-chain transfers as compared to in-side-chain transfers and to determine the influence of crosslinking on energy transfers.

The design of the materials will be obtained through collaboration with the polymer synthesis specialists; M. Visseaux (ENSCL/UCCS, Lille) and C. Buisson (LCCP, Lyon). Polyethylene will be chosen as the reference material representative of saturated polyolefins. The first type of sink to be studied will be alkene groups. Polymers should contain sinks at molar ratio varying from 0,1% to 10%.

Evolved gas will be quantified either on-line using Infrared and mass spectroscopies (MS) during ion beam or high energy electron irradiations or off-line by Gas phase Chromatography and MS for polymers irradiated under γ rays in glass sealed vessels. Since transfers are intended to occur through sinks, the latter should be modified by irradiation. The evolution of the sinks will be characterised by FTIR spectroscopy. The effect of sinks on the radical production will be investigated using low temperature irradiation (77 K) and ESR spectroscopy.

Finally, swift heavy ion irradiations (simulation of α particles emitted by radionucleides) will be performed to analyse the influence of Linear Energy Transfer (LET) on the efficiency of energy transfers.

Up on completion of the study initiated by the present proposal, the effect of each type of sink will have been isolated and quantified. Therefore, it will be possible to model gas

emission either as a function of the polymer ageing level or as a function of the polymer chemical composition.

1. T. SEGUCHI. *Nuclear Instruments and Methods in Physics Research B* **2001**, *185*, 43-49.

2. Y.NGONO-RAVACHE, S.BOUFFARD, and E.BALANZAT "Simulation de la radiolyse alpha de polymères dans le cadre de CSD: émission de H_2. Evolution aux fortes doses et influence de la température d'irradiation," **2005**. CIRIL/2005/533

3. A.DANNOUX. thèse de doctorat "Extrapolation dans le temps des cinétiques de production des produits de dégradation radiolytique. Application à un Polyuréthane". Université d'Orsay, **2007**.

Demande : contrat post-doctoral

Candidat : contacts en cours avec 1 étudiant en fin de thèse (synthèse des polymères) à l'Institut Charles Sadron à strasbourg.