Polymers under Ionizing Radiations: the Specificity of Swift Heavy Ions

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Compared to materials such as steel or ceramics, organic synthetic polymers are very prone to radiolysis. When submitted to ionizing radiations, molecules composing them are ionized and excited. These initial species lead to the formation of radicals which subsequent recombinations or reorganizations give stable defects. Defects can be either macromolecular or in the form of small molecules evolving from the polymer as gas.

The defects formed under irradiation, and their concentrations, are function of 1) the chemical structure of the polymer repeating unit and 2) the irradiation conditions (temperature, atmosphere, dose, dose rate, and radiation type). Polymers can be submitted to various types of radiations: α , β , γ and ion beams. Detailed studies on the effect of β and γ on polymer ageing do exist, even if some aspects of this should be refined. Conversely, detailed studies on the effect of ion beams, especially Swift Heavy Ions (SHI), are less numerous. Besides, in particular conditions, SHI can be used to simulate the effect of α irradiations on polymers.

Unlike β and γ irradiations that lead to a quite homogeneous energy deposition feature, SHI induce a heterogeneous dose deposition at the nanoscale level. Due to their high LET and because SHI deposit their energy close to the ion path, in a track core of a few nanometers, the local dose nearby these track cores is huge; in between, the dose is very low [1], [Fig. 1].

Fig. 1: Energy deposition structure of accelerated ion beams: increase in the density of events, along the track, with increasing LET.

A great number of detailed studies were performed under inert environment to assess the influence of the high ionization and excitation densities induced by SHI on polymer ageing. It was shown that, the huge amount of energy deposited locally by SHI induces specific damage processes [2], which involve complex molecular rearrangements and collective atom motions. Contrary to what has been done under inert environment for assessing the specificity of SHI on polymers, only few detailed studies have been undertaken under oxidative environments. Thus, our studies were aimed to understand how high ionization/excitation densities induced by SHI impact the mechanisms underlying polymer degradation in presence of oxygen.

Polymers submitted to ionising radiations are modified by the creation of macromolecular defects such as unsaturated bonds, chain scissions and crosslinks, or oxidative defects in presence of oxygen. The counterpart of these macromolecular defects is gas emission. We have examined both processes. We have studied the influence of the LET, the dose and the dose rate on different polymers [3]. Additionally, we have considered the influence of the polymer chemical structure on its oxidative ageing, particularly as a function of the LET.

References

- [1] Bouffard S, Gervais B, and Leroy C. Basic phenomena induced by swift heavy ions in polymers *NIM B* 105 (1995) 1-4.
- [2] Ngono-Ravache Y. Spectroscopic study of the chemical modification induced by swift heavy ions on polymers: the contribution of the CIRIL platform and the CIMAP laboratory. *Journal of Physics: Conference Series*. Vol. 629 (2015), Art. number: 012006
- [3] Ngono-Ravache Y. *et al.* Effect of swift heavy ions on an EPDM elastomer in the presence of oxygen: LET effect on the radiation-induced chemical ageing. *Polymer Degradation and Stability*, Volume 111, January 2015, Pages 89-101

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Polymers under Swift Heavy Ions (SHI)

OUTLINE

- Introduction

- What is a polymer?
- Why is it necessary to study polymers under SHI?
- The specificity of SHI vs γ and β
 - Energy deposition pattern
 - Dose distribution

- Some results and applications

- Influence of LET on defects creation
- How are SHI used to simulate α particles

- Conclusion

What are polymers?

Polymers = long chains of atoms linked covalently and formed from a repeating unit (the monomer in the case of homopolymers).

Atoms currently present in repeating units : C, H, O, N, S

Polymers are multi-scales materials

Molecular scale: monomer

Macromolecular scale: chain

Supramacromolecular scale: chain network (physical or chemical links)

Defect creation at the molecular scale = potential modifications on higher scales

Polymers can be either amorphous or semi-crystalline

Polymers are permeable to gases

- Behavior under ionizing radiations function of the environment
- Gas emission possible under irradiation
- Behavior under storage function of the environment

Study of polymer behavior under Ionizing Radiations very complex

Polymers under ionizing radiations

Polymers are sensitive to ionizing radiations

Bonds energy $\ll$ energy deposited by ionizing radiations

Macromolecular defects

- ✓ Unsaturated bonds
- ✓ New groups
- ✓ Chain scissions // Crosslinking

Gas emission (H_2 , HCl , $C_xH_y...$)

Cross-linking Vs Chain scissions

Chain scissions in presence of

- ✓ Quaternary carbons ($R_1R_2CR_3R_4$; $R_i \neq H$)
- ✓ Esters linkages ($R_1C(O)OR_2$)

Cross-linking preponderant in polymers with :

- CH_2CH_2 - suites
- CH_2-R_1CH - suites
- Alkene groups

Under vacuum and in presence of gamma rays and electron beams: gas emission is function of the polymer chemical structure

$G(\text{gas}) (10^{-7} \text{ mol} \cdot \text{J}^{-1})$

Carbonyls :

Carboxylic acids: $R_1C(O)OH$

Esters: $R_1C(O)OR_2$

■ ■ ■

Alcohols: $R_1R_2R_3COH$

Chain scissions (increase compared to irradiation under vacuum)

Under gamma ray and electron beam irradiations

Radiation-induced defects depend on :

- **The polymer structure**
 - Chemical structure of the repetition unit
 - Crystalline ratio
 - ...
- **Irradiation conditions**
 - Dose and dose rate
 - Surrounding atmosphere (inert or oxidative)
 - Irradiation temperature
 - ...

What happens under Swift Heavy Ions?

Linear Energy Transfer (γ -rays and electrons vs SHI)

Why study SHI effects on polymers?

Two fields of interest

Basic science :

- Study of mechanisms underlying polymer radiation-induced ageing by
 - ✓ Tuning the heterogeneous energy deposition pattern
 - ✓ Kinetics
 - ✓ Time scale of defects formation
 - ✓

Technological issues : Mainly radioactive waste storage

- Actinide-contaminated nuclear waste handling

Polymers widely used in nuclear industry

MOx handling

- Human protection
- Surface protection
- Liquid effluent storage

Contamination by radionuclides $\Rightarrow \alpha, \beta, \gamma$ radiations

Medium Activity Long Life waste

Medium Activity Long Life waste

Intended to Deep Repository

Deep repository = different phases

❑ Filling

- Emission of hazardous gases
 - ✓ Inflammability, corrosion...

❑ Post-closure

- Macromolecular defects
 - ✓ Polymer leaching
 - ✓ Radionuclides complexation

Safe management = What is the fate of polymers in conditions of long time periods and high doses?

Well-chosen conditions ⇒ Effects of α particles simulated by SHI

Ion beam characteristics :

- ✓ Energy deposited along the path in a reduced space
- ✓ High LET

Ion track = core + penumbra

Track: Heterogeneous

Track core: more or less homogeneous

- Energy deposited through interactions between :
- ✓ the ions and target electrons
 - ✓ the secondary electrons and the target electrons

Velocity effect

Gervais&Bouffard
NIMB 88 (1994)

Radial distribution of dose

- ✓ Radius ↗ when E ↗
- ✓ $Dr_{0.5}$ ↗ when E ↘

SHI = 2 Parameters (LET + $Dr_{0.5}$)

Aim

Swift Heavy Ions = High ionization/excitation densities

**How does high ionization/excitation densities
modify the polymers ageing?**

Objectives

Influence of dose and LET under inert and oxidative environments on:

- ✓ Gas emission
- ✓ Creation of new chemical groups (carbonyl groups, *trans*-vinylenes, vinyls, vinylidenes)
- ✓ Specific defects

METHODOLOGY

Ion beams of various energies

Basic science

Ion beams of specific characteristics

Simulation of α radiolysis

Ion beams to simulate α irradiations ?

How to simulate α radiolysis by SHI irradiation?

- Equivalent LET
- Equivalent $Dr_{0.5}$

Electronic interactions

Ion beams to simulate α irradiations ?

How to simulate α radiolysis by SHI irradiation?

- Equivalent LET
- Equivalent $Dr_{0.5}$

SHI irradiation Vs α radiolysis

Equivalent LET and $Dr_{0.5}$

- Higher ranges for SHI
 - ❖ Homogeneous LET
 - ✓ Homogeneous irradiation under large thicknesses

Irradiation procedures

Irradiation of thin films

On-line analyses (specific devices)

- Macromolecular defects
Infrared spectroscopy
- Gas emission or O₂ consumption
Mass spectroscopy (RGA mode)

Off-line analyses : Two-step protocol

- Pre-ageing
Up to high doses
- Determination of gas yields
Reduced dose
Ultra high-resolution gas mass spectrometry

On-line analyses or two-step protocol

Advantages

- ✓ Instantaneous $\neq$ cumulated yields
- ✓ Limitation in secondary reactions

$$G(X) = f(\text{polymer ageing level})$$

Chemical yield (G)

G = number of moles of defects created per unit energy deposited

Unit: mol/J

Dose (D)

Energy deposited per unit mass

Unit: Gy (Gray, 1Gy = 1J/kg)

RESULTS & APPLICATIONS

Specificity of SHI on defects creation

Two groups of defects created under SHI

➤ Defects common to other ionizing radiations

✓ Influence on the relative radiation chemical yields

➤ Defects Specific to SHI

✓ $\nearrow G(\text{defects})$ when $LET \nearrow$

Specificity of SHI : Gas emission

Primary effect = C-H scission $\Rightarrow$ H₂ emission common in organic molecules

Polyethylene

Polypropylene

Polystyrene

PMMA

LET influence on $G(\text{H}_2)$ depends on the polymer structure

Chang & LaVerne, J. Polym. Sci.: Part A: Polym. Chem. 38 (2000), 1656

LET Effect on H_2 emission

- Almost inexistent on saturated polyolefines (PE, PP)
- Existent in presence of unsaturated bonds or more generally in presence of energy sinks
- PS: existence of a LET Threshold
 - ✓ Below the threshold
 $G(H_2)_{PS} < G(H_2)_{PE}$
 - ✓ Above the threshold
 $G(H_2)_{PS} \approx G(H_2)_{PE}$

Benzene ring destruction ↗ with
↗ LET = Protection efficiency lost

LET influence on $G(H_2)$ depends on the polymer structure

Specificity of SHI : Gas emission

LET influence on hydrocarbon gases (C_xH_y)

Low LET

Polymer chemical structure signature

High LET

Loss of the polymer chemical structure signature

❖ Low LET

Side group departure G_{side}

High LET

Chain fragmentation

→ Very efficient

PP, PB G_{total} ≈ 4 · 10⁻⁷ mol/J !

Highly unsaturated gases

V. Picq, J.M. Ramillon, E. Balanzat, NIMB 146 (1998) 496-503

V. Picq & E. Balanzat, NIMB 151(1999) 76-83

Specificity of SHI : Macromolecular defects

Under Inert environment

Unsaturated Bonds : LET influence
function of the defect type

➤ Vinyl groups

- ✓ Concentration ↗ with ↗ LET
 - ✓ High ionization densities mandatory

➤ Groups other than Vinyl

- ✓ At low doses : no LET effect
- ✓ At high doses : Concentration at saturation ↗ with ↗ LET

Evolution of Vinyl groups

Ngono-Ravache et al., Polym. Deg. Stab. 111 (2015), 89

Specificity of SHI : Defects specific to SHI

Under Inert environment

Specific defects

- Triple bonds (Alkyne, Cyanates...)
- Cumulated double bonds (Allene, Isocyanates...)

Energy deposition time scale crucial
“simultaneity of ionization events”

Existence of a LET Threshold

- $f(\text{defects, polymer structure})$
 - ➡ in presence of unsaturated bonds
- $\text{LET} < \text{LET Threshold}$
 - ✓ Creation after a dose threshold

Application of SHI in the nuclear industry context : influence of SHI under O₂

Gas emission

Macromolecular defects

$G(H_2)$ and $G(\text{oxidized groups}) = f(\text{dose})$

✓ Various LET
✓ Under O₂

Specificity of SHI: oxidation

➤ Same oxidized defects as under gamma rays but with lower yields

$$\checkmark G(-O_2)_{11 \text{ MeV/A } 13C} \approx 0.2 * G(-O_2)_{1 \text{ MeV } \beta}$$

➤ Almost no LET effect on carbonyl containing functions

➤ Creation of unsaturated bonds under SHI

✓ Ketones accumulate more rapidly

✓ Ratio ketone/acids ↘ with ↗ D

G (acids) + G(Esters) ↗ with ↗ D

EPDM 1,4 hexadiene

Specificity of SHI : oxidation

Almost no LET effect on any of the carbonyl containing functions

EPDMn γ rays ($D < 500$ kGy)*

$G(\text{ketone})/G(\text{acids}) \approx 3$

Ion beam ($D < 1500$ kGy)

$G(\text{ketone})/G(\text{acids}) = 4-5$

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Ratio BMR/HP $\nearrow$ when LET $\nearrow$

Specificity of SHI : oxidation

Unsaturated bonds : vinyl

Unsaturated bonds created under SHI but not under gamma

Low Doses

$G_0 \nearrow$ when $\text{LET} \nearrow$

High doses

- ✓ Creation preponderant at high LET
- ✓ Onset of destruction at the lowest LET

Same trend for vinylidenes and alkynes

Basic research : modifying the heterogeneity of energy deposition gives insight on defects creation mechanisms.

➤ LET Effect on C=C

- ✓ Under vacuum → on vinyl and defects specific to SHI
- ✓ Under oxidative environment → On all defects
Creation time scale < oxidation time scale

➤ LET effect on gas

- ✓ H₂ : Tremendous in presence of sinks after a threshold
- ✓ Hydrocarbon gases : tremendous

Simulation of high dose deposition over long time periods

Technological issues : Simulation of α particles with SHI

➤ Evolution of gas emission and carbonyls with the dose

✓ H_2 emission

✓ Oxidized defects

Almost no effect on carbonyls but important dose effect
in ↗ acids and esters with ↗ dose
potential increase in hydrosoluble molecules

Presence of C=C : great acceleration of oxidation at high doses