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

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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 \( \gamma \) and \( \beta \)
    - Energy deposition pattern
    - Dose distribution
- **Some results and applications**
  - Influence of LET on defects creation
  - How are SHI used to simulate \( \alpha \) 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)

**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**

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

**Polymers can be either amorphous or semi-crystalline**
Polymers under ionizing radiations

Polymers are sensitive to ionizing radiations

Bonds energy $\ll$ energy deposited by ionizing radiations

- Ionisations ($x, \text{PH}^+, e^-...$)
- Excitations ($\text{PH}^*$)

Recombination $h^+ - e^-$

Bond scission + reorganization

Radical formation

$\text{P}^\circ + \text{H}^\circ$

Macromolecular defects

Stable defects

Gas emission

Interactions with the electrons of the polymer

Radical chemistry

I.R
Radiation-induced defects under vacuum

**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

Polyethylene

Contains diagrams illustrating the processes of:
- Radiation-induced defects under vacuum
- Trans-vinylène \((TV)\)
- Trans-trans-diène
- Réticulation \((XL)\)
- Gas emission \((H_2, HCl, C_xH_y...\))

Ulanski 2009
Poly(vinyl alcohol)
Polyoxymethylene
Poly(ethylene oxide)
Polypropylene oxide
Polypropylene oxide
Poly(ethylene oxide)
Polyoxymethylene
Poly(vinyl acetate)
Polybutadiene
Polyisoprene
Polypropylene oxide
Poly(ethylene oxide)
Polyoxymethylene
Poly(vinyl acetate)
Polybutadiene
Polyisoprene
Polyethylene
Polypropylene
Polyisobutylene
Polyvinyl chloride
Polyvinylidene fluoride
Poly(vinyl alcohol)
Poly(methyl methacrylate)
Poly(methacrylic acid)
Poly(methyl acrylate)
Poly(acrylic acid)
Poly(vinyl acetate)
Poly(acrylic acid)
Poly(methyl acrylate)
Poly(vinyl acetate)
Poly(acrylic acid)
Poly(methyl acrylate)

R=H or CH₃
R’=OH or CH₃
R”=H or F

H₂
HCl or HF
CO or CO₂

G(gas) (10⁻⁷ mol.J⁻¹)

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

**Main Macromolecular Defects**

**Carbonyls**:
- Ketones: \( R_1R_2C=O \)
- 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)

Radiation-Induced defects in polymers

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 ($\gamma$-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

- Polyurethane (40.5%)
- Chlorinated polymers (18.1%)
- Polyolefins (11%)
- Polyamides (16.3%)
- Cellulose (11%)
- Fluorinated polymers (2.4%)
- Ion-exchange resin (0.3%)
- Other polymers (10.1%)

**MOx handling**
- Human protection
- Surface protection
- Liquid effluent storage

**Contamination by radionuclides** → α, β, γ radiations

**Medium Activity Long Life waste**
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 track = core + penumbra

Track: Heterogeneous
Track core: more or less homogeneous

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*-vinylene,
  vinyls, vinylidenes)
- Specific defects
METHODOLOGY

Ion beams of various energies  Basic science

Ion beams of specific characteristics  Simulation of $\alpha$ radiolysis
Ion beams to simulate α irradiations?

How to simulate α radiolysis by SHI irradiation?

- Equivalent LET
- Equivalent Dr$_{0.5}$

![Graph showing LET vs Energy for different ions and medium energy regions]

**Electronic interactions**
Ion beams to simulate α irradiations?

How to simulate α radiolysis by SHI irradiation?

- Equivalent LET
- Equivalent $D_{0.5}$

SHI irradiation Vs α radiolysis

- Equivalent LET and $D_{0.5}$
- 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 $O_2$ 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
Irradiation procedures

On-line analyses or two-step protocol

Advantages

✓ Instantaneous ≠ cumulated yields
✓ Limitation in secondary reactions

Chemical yield \((G)\)

\[ G = \text{number of moles of defects created per unit energy deposited} \]

Unit: \(\text{mol/J} \)

Dose \((D)\)

Energy deposited per unit mass

Unit: \(\text{Gy (Gray, 1Gy = 1J/kg)}\)
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**
  - $G(\text{defects})$ when LET
Specificity of SHI: Gas emission

Primary effect = C-H scission \implies H_2 emission common in organic molecules

\begin{align*}
-(\text{CH}_2-\text{CH}_2)_n- & \quad \text{Polyethylene} \\
-(\text{CH}_2-\text{CH})_n- & \quad \text{Polypropylene} \\
-(\text{CH}_2-\text{CH})_n- & \quad \text{Polystyrene} \\
\text{[CH}_2-\text{C}]_n- & \quad \text{PMMA}
\end{align*}

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

Specificity of SHI : Gas emission

**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 \( \Rightarrow \) with \( \Rightarrow \) LET = Protection efficiency lost

LET influence on \( G(H_2) \) depends on the polymer structure
High LET

Loss of the polymer chemical structure signature

\[ G_{\text{total}} \approx 4 \times 10^{-7} \text{ mol/J} \]

Highly unsaturated gases

**LET influence on hydrocarbon gases \((C_xH_y)\)**

Low LET

Polymer chemical structure signature

**Low LET**

Side group departure \(G_{\text{side}}\)

\[ (dE/dx)_e \text{ (MeV mg}^{-1} \text{ cm}^2) \]

\[
\begin{align*}
\text{CH}_2 &-\text{CH} - \\
&\text{H}_2\text{C} \quad \text{CH}_2
\end{align*}
\]

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

R-CH$_2$-CH=CH$_2$

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

![Graph showing LET vs G(x)](image)
Application of SHI in the nuclear industry context: influence of SHI under $O_2$

Gas emission

Macromolecular defects

$G(H_2)$ and $G$(oxidized groups) = f( dose)

✓ Various LET
✓ Under $O_2$
Specificity of SHI: oxidation

- Same oxidized defects as under gamma rays but with lower yields
  \[ G(-O_2)_{11 \text{MeV/A} 13C} \approx 0.2 \times G(-O_2)_{1\text{MeV/}} \]
- Almost no LET effect on carbonyl containing functions
- Creation of unsaturated bonds under SHI

- Ketones accumulate more rapidly
- Ratio ketone/acids \( \gtrapprox \) with \( \Rightarrow \) D

\[ G(\text{acids}) + G(\text{Esters}) \gtrapprox \text{ with } \Rightarrow \text{D} \]

EPDM 1,4 hexadiene
Almost no LET effect on any of the carbonyl containing functions

**EPDMn γ rays** (D< 500 kGy)*

G(ketone)/G(acids) ≈ 3

**Ion beam** (D<1500 kGy)

G(ketone)/G(acids) = 4-5


* Rivaton et al NIMB 227 (2005)
Almost no LET effect on any of the carbonyl containing functions.

**EPDMn** γ rays (D < 500 kGy)*

\[ \frac{G(\text{ketone})}{G(\text{acids})} \approx 3 \]

**Ion beam** (D < 1500 kGy)

\[ \frac{G(\text{ketone})}{G(\text{acids})} = 4-5 \]

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**Specificity of SHI**: oxidation

\[ \text{Ketones} \quad R_1R_2C=O \]

\[ \text{Acids} \quad R_1C(=O)QH \]

\[ \text{Esters} \quad R_1C(=O)OR_2 \]

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**Chemical Reactions**

\[ (\text{POOH})_\text{II} \rightarrow \text{P(O)OH} \quad \text{HP} \]

\[ \text{POO}^\circ + \text{POO}^\circ \rightarrow \text{P}=\text{O} \quad \text{BMR} \]
Almost no LET effect on any of the carbonyl containing functions

**EPDMn γ rays** (D< 500 kGy)*

G(ketone)/G(acids) \(\approx 3\)

**Ion beam** (D<1500 kGy)

G(ketone)/G(acids) = 4-5

\[ \text{POO}^\circ + \text{POO}^\circ \rightarrow \text{P}=\text{O} \] BMR

\(\text{Ratio BMR/HP} \uparrow \text{when LET} \uparrow\)
Specificity of SHI : oxidation

**Unsaturated bonds : vinyl**

-HC=CH₂

Unsaturated bonds created under SHI but not under gamma

**Low Doses**

\[ G₀ \uparrow \text{when LET } \uparrow \]

**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
**Conclusion**

**Simulation of high dose deposition over long time periods**

**Technological issues**: Simulation of $\alpha$ particles with SHI

- Evolution of gas emission and carbonyls with the dose
  - $\text{H}_2$ emission
  - Oxidized defects
    - Almost no effect on carbonyls but important dose effect
      in $\text{H}_2$ acids and esters with $\text{H}_2$ dose
      potential increase in hydrosoluble molecules
    - Presence of C=C: great acceleration of oxidation at high doses