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Leaching of radio-oxidized poly(ester urethane): water-soluble molecules characterization

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**INTRODUCTION**

Long-term degradation (≈ 1,000 years): radiolysis *and* alkaline hydrolysis

Question: what is the effect of water-soluble products on the radionuclides mobility?
Considered polymer

- Poly(ester urethane) (PUR)
- Used as glove for glove boxes

Composed of 3 segments issued from these molecules:

- **Hard segment**
  - 4,4’-methylene diphenyl diisocyanate
  - 25.5% \(w\)

- **Extender**
  - 1,4-butandiol
  - + 8.9% inorganic fillers
  - + 1.8% cross linking agents
  - + 0.4% pigments

- **Soft segment**
  - poly(1,4-butylene adipate)
  - 63.4% \(w\)
Objectives

- Characterizing and quantifying water-soluble molecules created by the alkaline hydrolysis of the non-irradiated and irradiated PUR at different doses

- Understanding the degradation mechanisms
  - PUR under radiolysis
  - Irradiated PUR under hydrolysis

- Identifying the products than can complex with the radionuclides

- Being able to model the complexant release kinetics
Objectives

Characterizing and quantifying water-soluble molecules created by the alkaline hydrolysis of the non-irradiated and irradiated PUR at different doses

Understanding the degradation mechanisms
- PUR under radiolysis
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Identifying the products that can complex with the radionuclides

Being able to model the complexant release kinetics
A two-step preparation

1\textsuperscript{st} step: PUR is irradiated under air using $\gamma$ rays by IONISOS ($^{60}$Co source), dose rate: $\sim 0.7\ \text{kGy.h}^{-1}$, doses: 4 MGy ($\sim 8$ months irradiation) and 10 MGy ($\sim 20$ months irradiation)

2\textsuperscript{nd} step: non-irradiated and irradiated PUR is then hydrolyzed and the pH is maintained constant = leaching

Filtrations

Cementitious water composition:
0.25 mol/L NaOH, $10^{-3}$ mol/L Ca(OH)$_2$ and 41.10$^{-3}$mol/L NaCl
RESULTS AND DISCUSSION

Analytical approach

<table>
<thead>
<tr>
<th><strong>Leachate</strong></th>
<th><strong>Total Organic Carbon analysis</strong></th>
<th><strong>TOC analyzer</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Targeted analyses of low molecular weight molecules</strong> (&lt; 2 000 Da)</td>
<td><strong>Targeted analyses of high molecular weight molecules</strong></td>
<td></td>
</tr>
</tbody>
</table>
| Organic acids **IC** | Volatile and semi-volatile organic molecules **GC-MS** | Other organic molecules **LC-MS MS-MS** | Weight average molecular **SEC**
RESULTS AND DISCUSSION

Analytical approach

Leachate

Total Organic Carbon analysis

TOC analyzer

Targeted analyses of **low** molecular weight molecules

(< 2000 Da)

Organic acids

IC

Volatile and semi-volatile organic molecules

GC-MS

Targeted analyses of **high** molecular weight molecules

Other organic molecules

LC-MS

MS-MS

Weight average molecular

SEC
Material balances obtained for leachates in **pure water**:

- **0 MGy**: 0.26 mol C/kg of PUR
- **4 MGy**: 8.53 mol C/kg of PUR
- **10 MGy**: 17.7 mol C/kg of PUR

Material balances obtained for leachates in **cementitious water**:

- **0 MGy**: 20.2 mol C/kg of PUR
- **4 MGy**: 26.1 mol C/kg of PUR
- **10 MGy**: 29.5 mol C/kg of PUR

There is a need to investigate the leachates by other analytical techniques.
Molecules detected in the 10 MGy irradiated PUR leachate in pure water

- Some molecules are directly identifiable in the polymer formula:
  - pentanoic acid
  - butanoic acid
  - propionic acid
  - 1,4-butanediol
  - 4,4′-diaminodiphenylmethane

- Other molecules are due to chain scission or chain ends radio-oxidation, or due to ester groups hydrolysis and rearrangements.

### Alcohols
- 1,3-propanediol
- 1,2-butanediol
- 2-hexanol
- 3-hydroxytetrahydrofuran
- 2-hydroxytetrahydrofuran

### Lactones
- gamma-butyrolactone
- gamma-valerolactone
- delta-valerolactone
- ethylene carbonate
- 1,6-dioxacyclododecan-7,12-dione
- 5-hydroxymethylidihydrofuran-2-one

### Linear Esters
- propyl propanoate
- propyl 3-methylbutanoate
- diisopropyl adipate
- 4-hydroxybutylacrylate
- dipropyl hexanedioate
- cyclobutyl hexanoate
- propyl butanoate
- 1,4-diacetoxybutane
Molecules detected in the 10 MGy irradiated PUR leachate in pure water

- Some molecules are directly identifiable in the polymer formula:
  - **pentanoic acid**
  - **butanoic acid**
  - **propionic acid**
  - **1,4-butanediol**
  - **4,4'-diaminodiphenylmethane**

- Other molecules are due to chain scission or chain ends radio-oxidation, or due to ester groups hydrolysis and rearrangements.

**Soft segment**
- **1,3-propanediol**
- **1,2-butanediol**
- **3-hydroxytetrahydrofuran**
- **2-hexanol**
- **1-hydroxypropan-2-one**
- **ethyleneglycol**
- **1,2-butanediol**

**Extender**
- **gamma-butyrolactone**
- **gamma-valerolactone**
- **delta-valerolactone**
- **ethylene carbonato**
- **1,6-dioxacyclododecan-7,12-dione**
- **5-hydroxymethylidihydrofuran-2-one**

**Hard segment**
- **4-hydroxybutylacrylate**
- **dipropyl hexanedioate**
- **1,4-diacetoxybutane**

**Alcohols**
- **propyl propanoate**
- **diisopropyl adipate**
- **cyclobutyl hexanoate**

**Linear esters**
- **propyl 3-methylbutanoate**
An example of a degradation mechanism:
Goals of the study:

- Characterizing and quantifying water-soluble molecules created by the alkaline hydrolysis of the non irradiated and irradiated PUR
- Understanding the degradation mechanisms
  - PUR under radiolysis
  - Irradiated PUR under hydrolysis

Ionic chromatography + TOC analyzer = material balance, but the material balances are not complete. **Solution** → developing other analytical techniques such as:

- Gas chromatography coupled with mass spectrometry
Results:

- New molecules detected: the knowledge of released molecules is improved
- Identification of the molecules origin
  - Fragments of the polymer formula
  - Compounds obtained by chain scission, chain ends oxidation, ester groups hydrolysis or/and rearrangements

=> Better understanding of the mechanisms of irradiation and of leaching

Perspectives:

- Quantifying the molecules detected by GC-MS
- Identifying the molecules that can complex with the radionuclides
- Following the complexant release kinetics

=> Irradiated PURm hydrolysis mechanisms to be proposed
Thank you for your attention.

ACKNOWLEDGMENT

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Do you have any questions?