Study of the hydrolysis of an industrial radio-oxidized poly(ester urethane)

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DE LA RECHERCHE À L'INDUSTRIE

STUDY OF THE HYDROLYSIS OF AN INDUSTRIAL RADIO-OXIDIZED POLY(ESTER URETHANE)

IRaP 2016, 25-30th September

Porquerolles Island, source: the Internet

E. Fromentin*, J. Frey, S. Legand, J.J. Pielawski,
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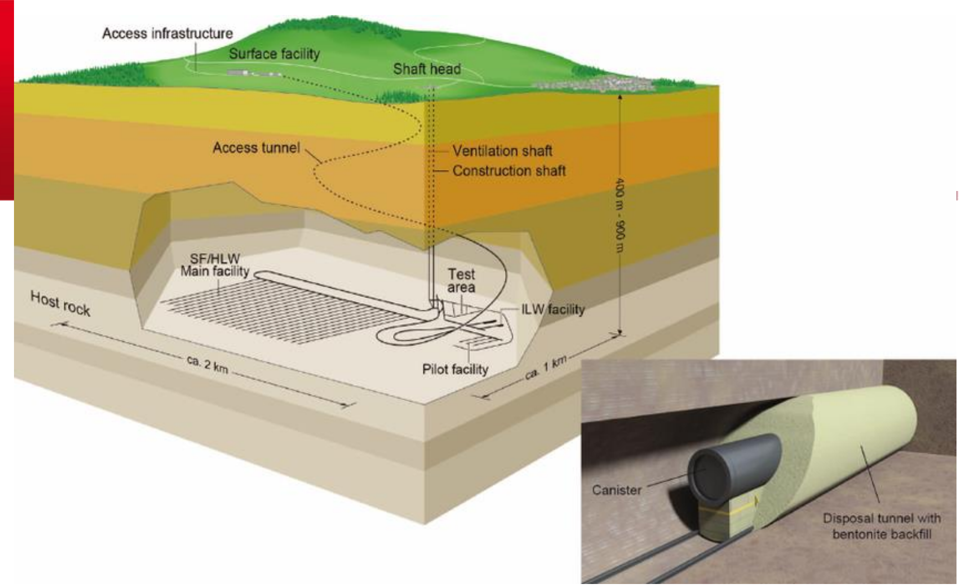
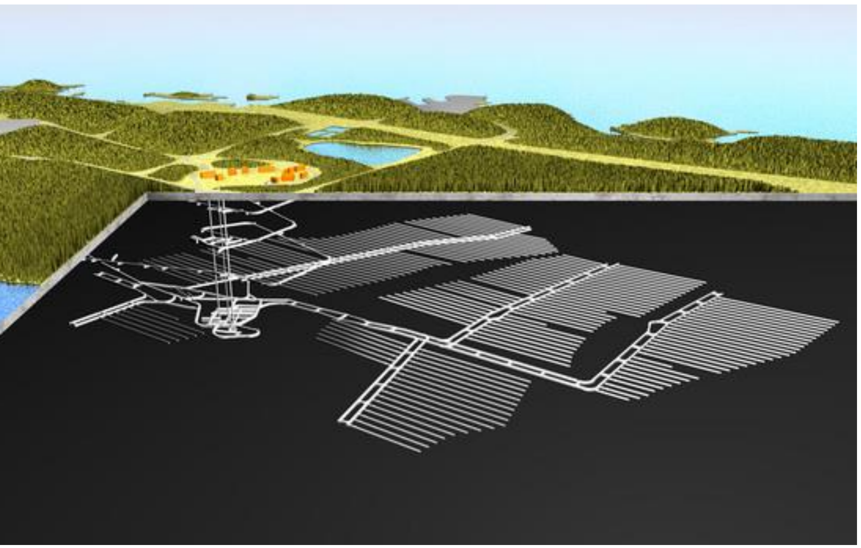
Nuclear waste management

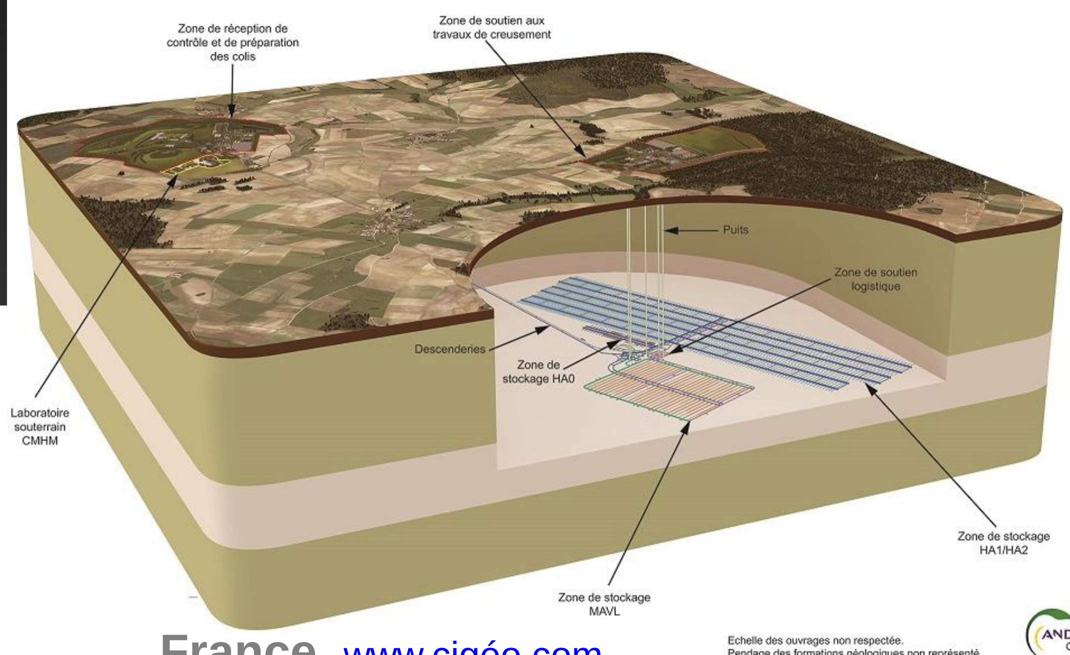
Several countries are considering a deep geological disposal.



Switzerland, www.nagra.ch
Opanilus clay, 300-900 meters depth



Finland, www.posiva.fi
Migmatic gneiss + bentonite clay, 400-450 meters depth



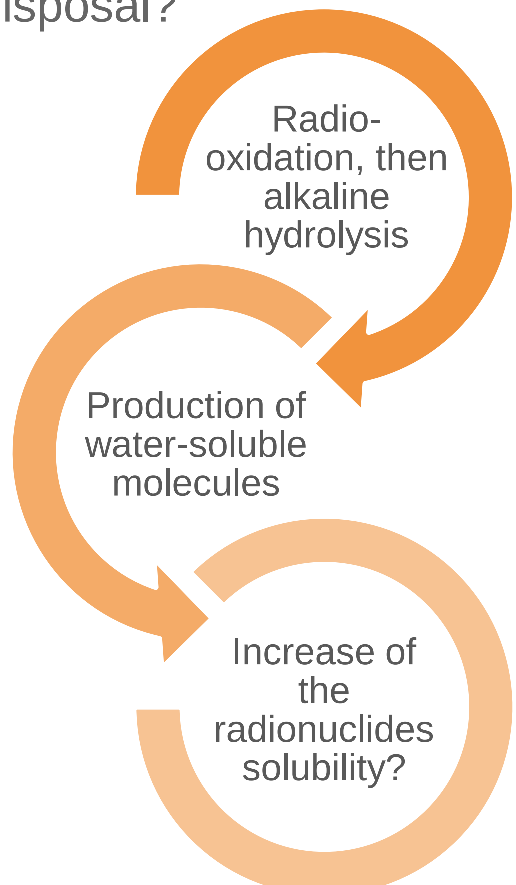
France, www.cigéo.com
Callovo-Oxfordian clay, 500 meters depth

INTRODUCTION

Polymers in nuclear waste packages

- Polyvinyl chloride, cellulose, ion-exchange resins, polyethylene…
- What will become polymers inside the geological disposal?

An example of an Intermediate Level Long-Lived waste package

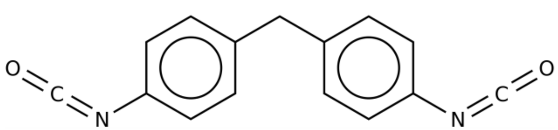


Considered polymer

- Poly(ester urethane) (PUR)
  - Constituent of gloves for glove boxes

  - Composed of 3 segments synthesized from these precursors:

hard segment

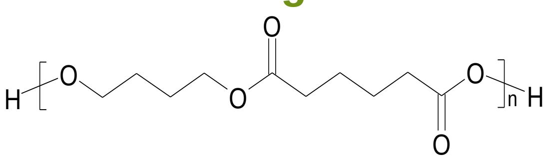


4,4'-methylene diphenyl diisocyanate

extender

1,4-butandiol

soft segment



poly(1,4-butylene adipate)

25.5%$_w$

63.4%$_w$

+ 8.9% inorganic fillers
+ 1,8% cross linking agents
+ 0,4% pigments

INTRODUCTION

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 the radionuclides

- Being able to model the complexant release kinetics

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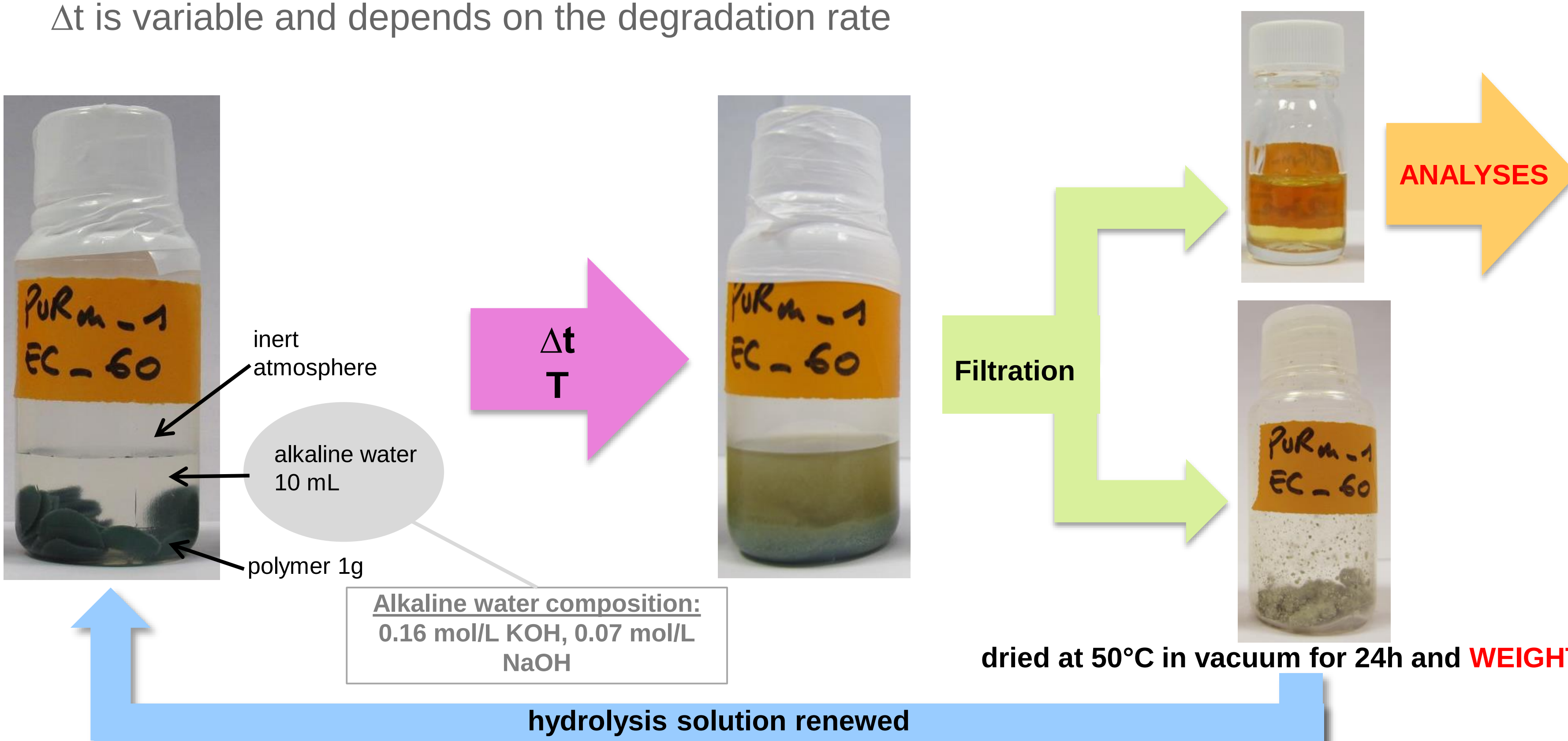
➡ **Being able to model the complexant release kinetics**

MATERIALS: A TWO-STEP PREPARATION

- **1st step:** PUR is irradiated under air using γ rays by LABRA (^{60}Co source), dose rate: ~ 0.9 $kGy.h^{-1}$, doses: 500 kGy and 1,000 kGy

- **2nd step:** non-irradiated and irradiated PUR are then hydrolyzed
3 temperature values: room temperature (≈23°C), 40 and 60°C
Δt is variable and depends on the degradation rate



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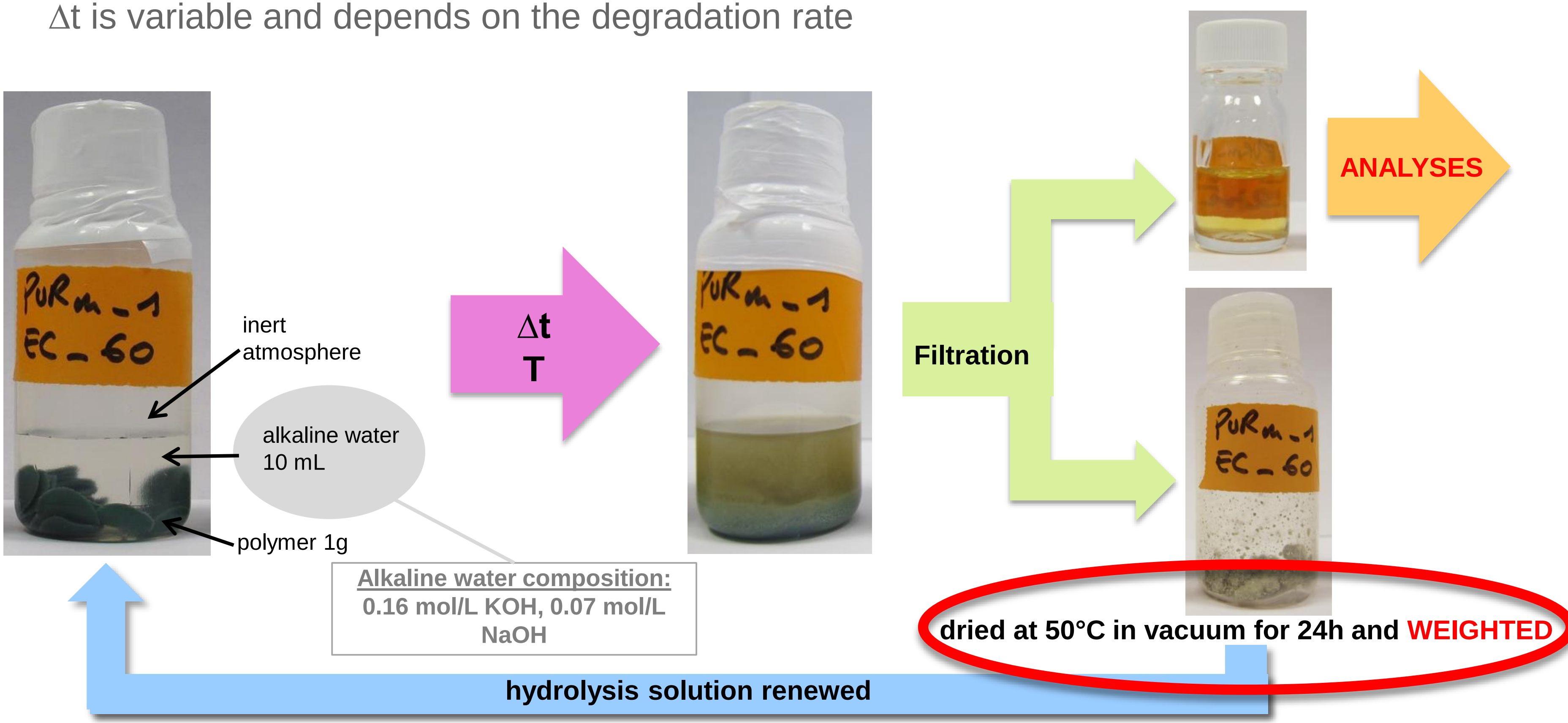
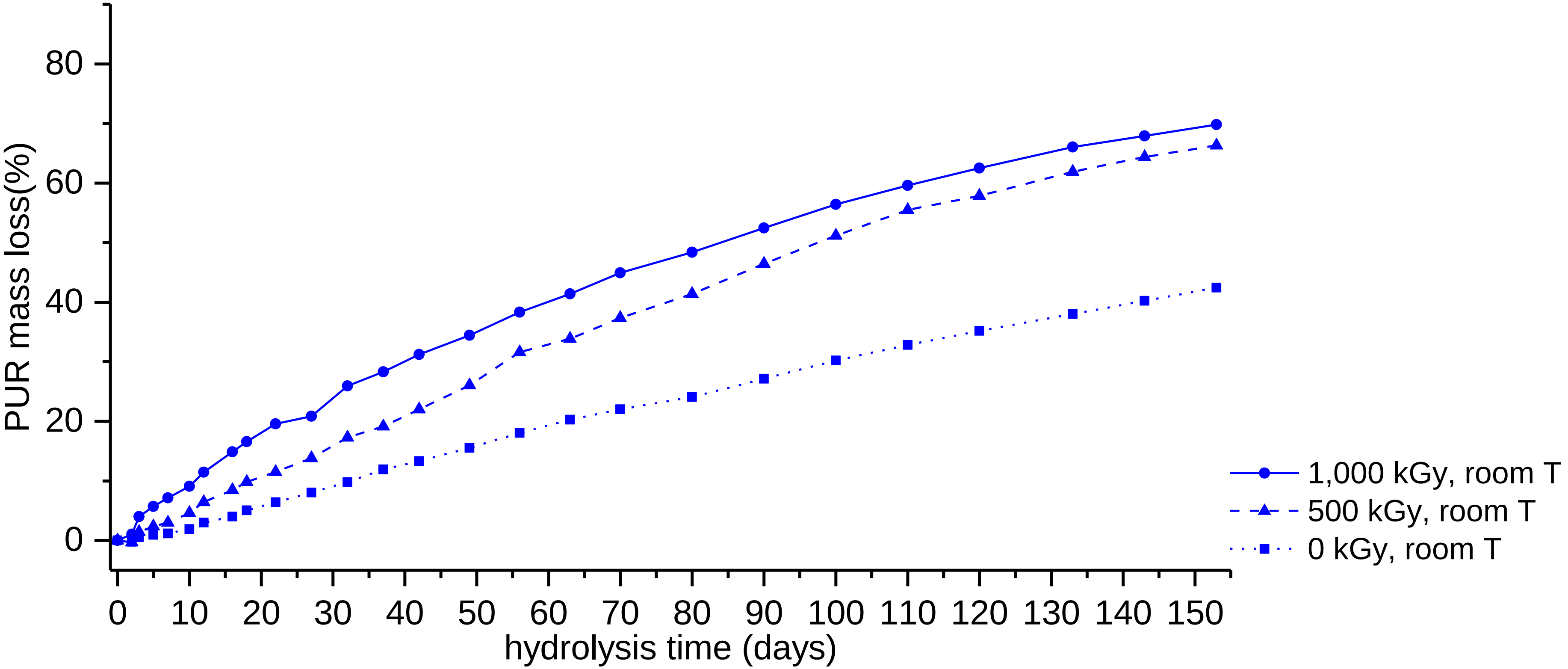


EXPERIMENTAL DATA

Mass loss

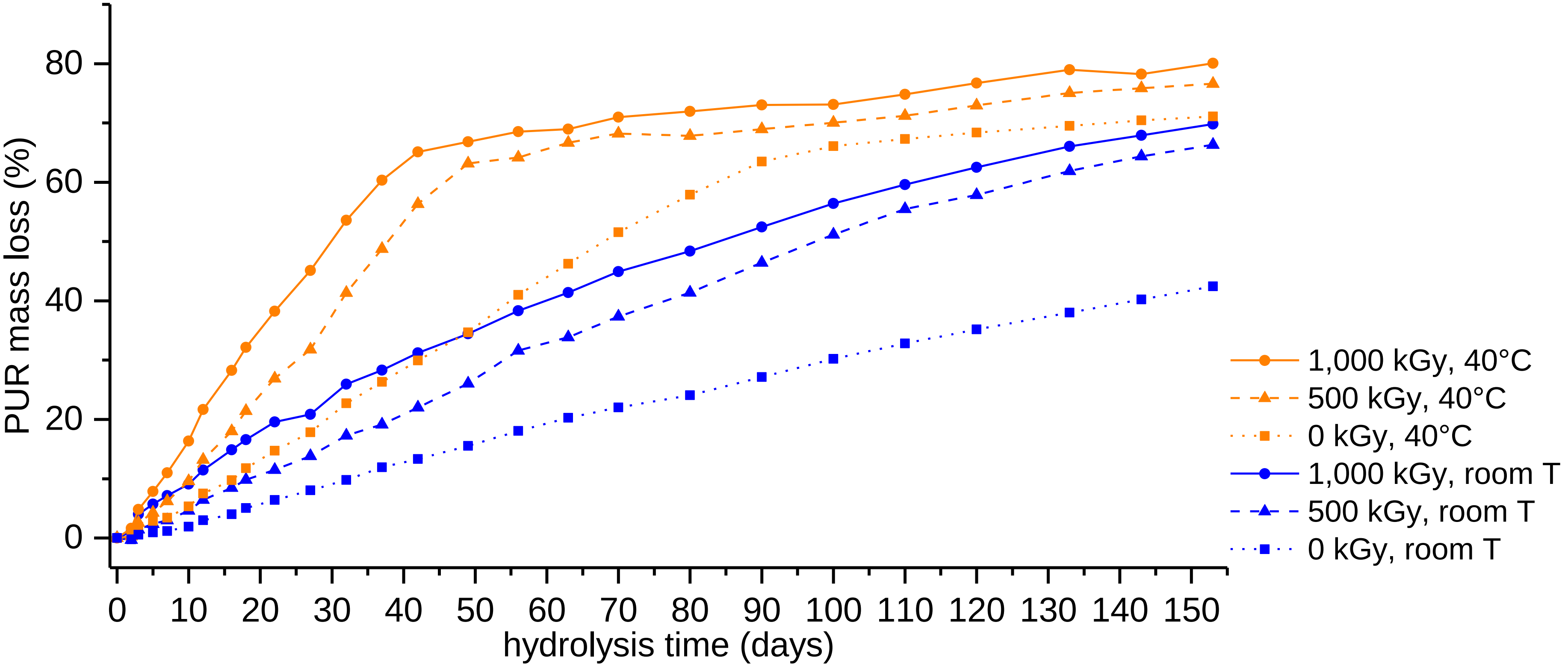
- 3 temperatures, 3 doses
  - Room temperature ≈ 23°C



EXPERIMENTAL DATA

Mass loss

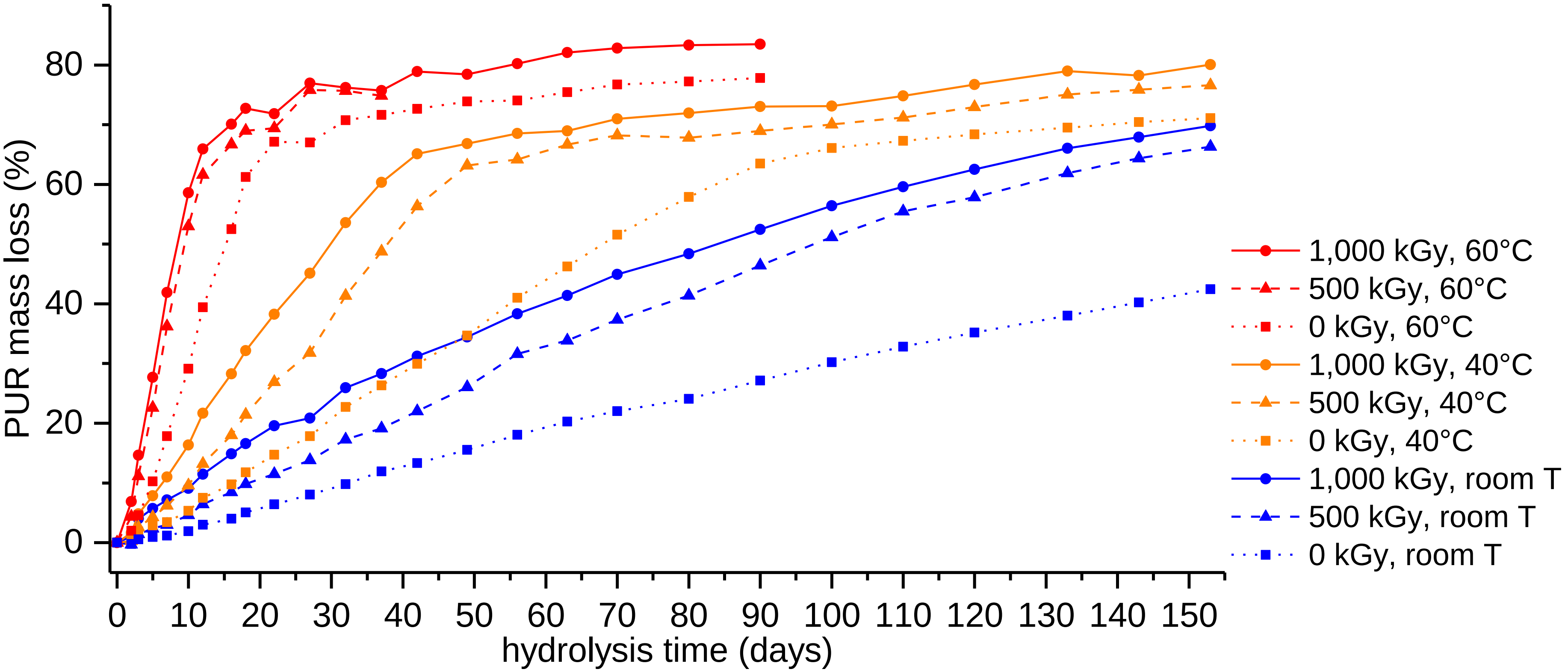
- 3 temperatures, 3 doses
  - Room temperature ≈ 23°C
  - 40°C



EXPERIMENTAL DATA

Mass loss

- 3 temperatures, 3 doses
  - Room temperature ≈ 23°C
  - 40°C
  - 60°C

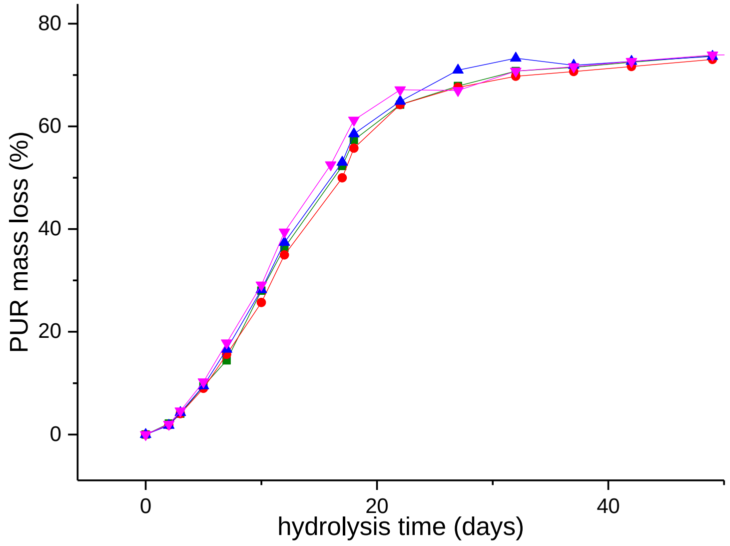


EXPERIMENTAL DATA

Additional data

- Error bar: σ_{max}= 4%

Measurements of the mass loss on the unirradiated PUR hydrolyzed at 60°C



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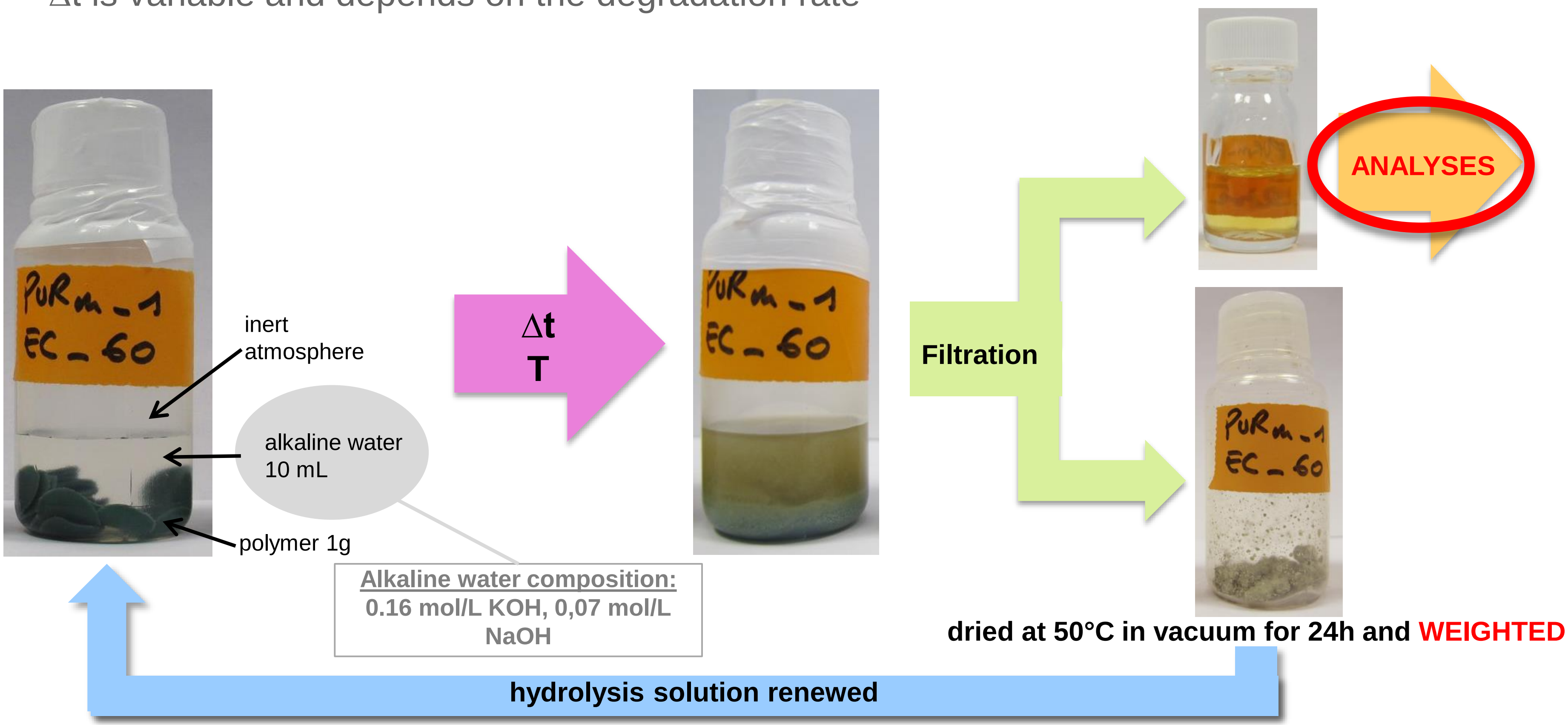

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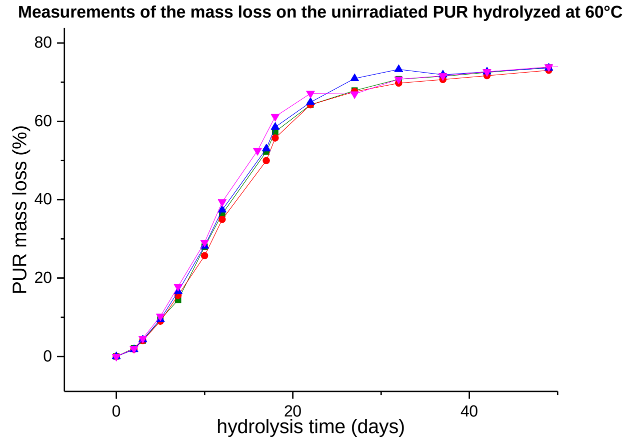
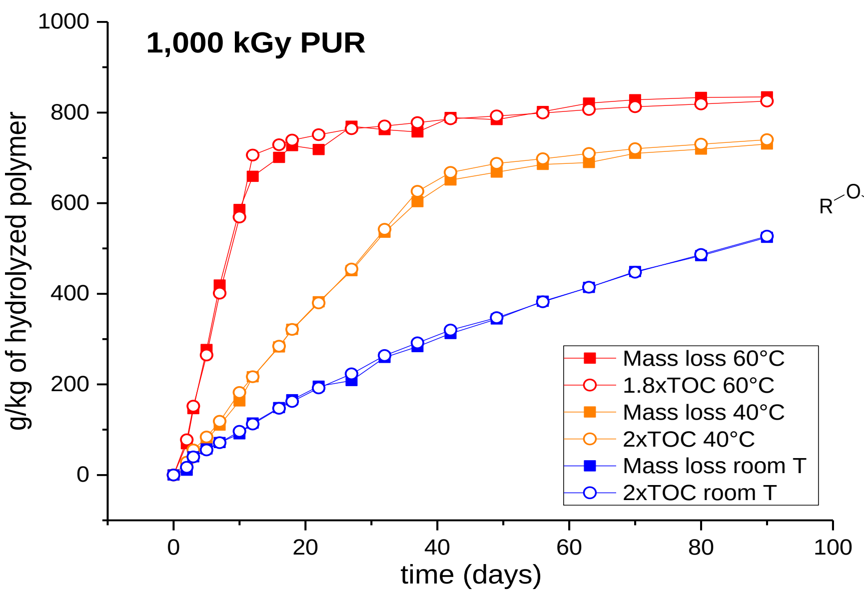
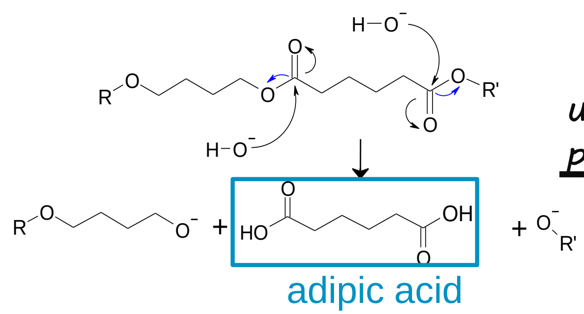
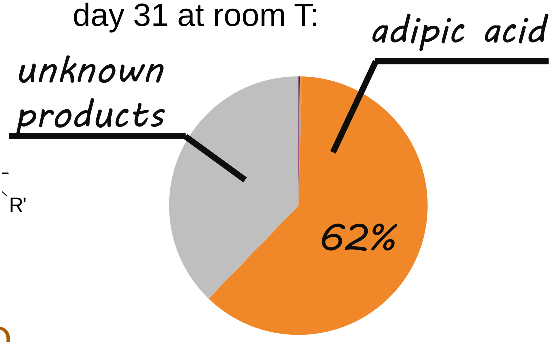


- Total Organic Carbon = TOC is proportional to mass loss





Mass balance of hydrolysis solution of 1,000 kGy PUR at day 31 at room T:



Degradation product $C_xH_yO_z$

$$\frac{mass\ loss}{mass\ of\ carbon} = \frac{x m_C + y m_H + z m_O}{x m_C} \approx 2$$

→ **adipate $C_6H_8O_4$ corresponds**

For more details about mass balances: Fromentin et *al.* (2016) *Polymer Degradation and Stability*, **128**, 172-181

MODELLING THE SOLUBLE FRACTION RELEASE

Yoon's model

- **Hypotheses:**
  - Hydrolysis of each chain occurs with equal probability.
  - Water diffusion into the polymer does not limit hydrolysis.
  - Water-soluble products are immediatly leached out of the polymer.
  - Hydrolysis is a complete reaction.

- Involved reactions:

$$P_2 + W \rightarrow 2P_1$$
$$P_3 + W \rightarrow P_1 + P_2$$
$$\cdots$$
$$P_n + W \rightarrow P_r + P_{n-r} \quad (r = 1, \ldots, n-1)$$

- Induced rates:

$$\frac{d[P_1]}{dt} = 2k_H[W]\sum_{i=2}^{\infty}[P_i]$$
$$\frac{d[P_2]}{dt} = -k_H[W][P_2] + 2k_H[W]\sum_{i=3}^{\infty}[P_i]$$
$$\cdots$$
$$\frac{d[P_n]}{dt} = -(n-1)k_H[W][P_n] + 2k_H[W]\sum_{i=n+1}^{\infty}[P_i]$$

Yoon et *al.* (1997) *Polymer*, **38**, 3573-3579

MODELLING THE SOLUBLE FRACTION RELEASE

Yoon's model

- After mathematical geniuses work:

$$\frac{[P_1]}{\lambda_1} = 1 - 2\left(1 - \frac{1}{\mu_{n0}}\right)e^{-\tau} + \left(1 - \frac{2}{\mu_{n0}}\right)e^{-2\tau}$$

$$\frac{[P_2]}{\lambda_1} = \left(1 - \frac{1}{\mu_{n0}}\right)e^{-\tau} - 2\left(1 - \frac{2}{\mu_{n0}}\right)e^{-2\tau} + \left(1 - \frac{3}{\mu_{n0}}\right)e^{-3\tau}$$

$$\dots$$

$$\frac{[P_k]}{\lambda_1} = \left(1 - \frac{(k-1)}{\mu_{n0}}\right)e^{-(k-1)\tau} - 2\left(1 - \frac{k}{\mu_{n0}}\right)e^{-k\tau} + \left(1 - \frac{(k+1)}{\mu_{n0}}\right)e^{-(k+1)\tau}$$

with $\lambda_k = \sum_{n=1}^{\infty} n^k [P_n]$, $\tau = \int_0^t k_H [W] dt$, $\mu_{n0} = \frac{\sum_{i=1}^{\infty} i[P_i]}{\sum_{i=1}^{\infty} [P_i]} = \frac{\lambda_1}{\lambda_0}$

- Considering that μ_{n0} is very high and that only P_1 is water-soluble:

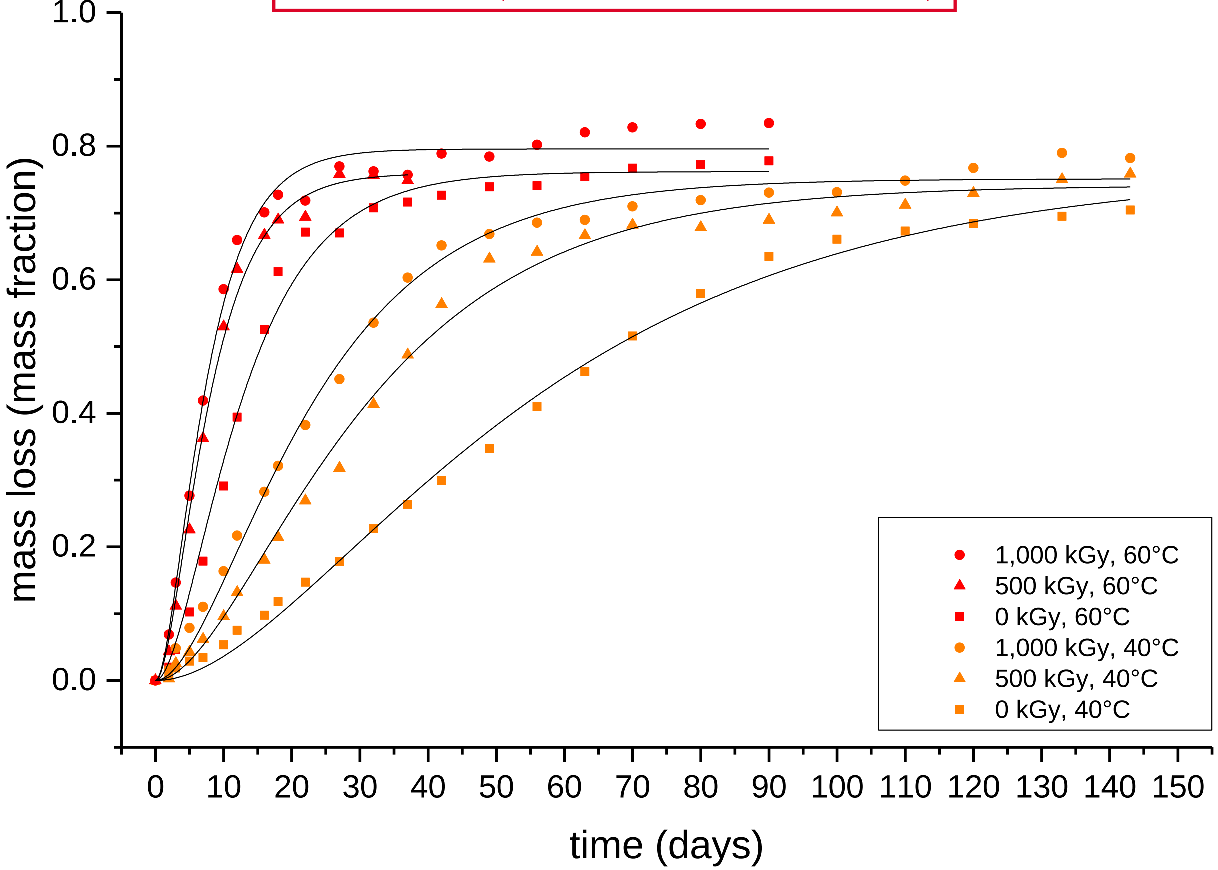
$$[P_1] \approx \lambda_1 (1 - 2e^{-k_H t} + e^{-2k_H t})$$

Yoon et *al.* (1997) *Polymer*, **38**, 3573-3579

MODELLING THE SOLUBLE FRACTION RELEASE

- Yoon's model applied to our experimental data
  - 40 and 60°C → the model matches

$$[P_1] \approx \lambda_1 (1 - 2e^{-k_H t} + e^{-2k_H t})$$



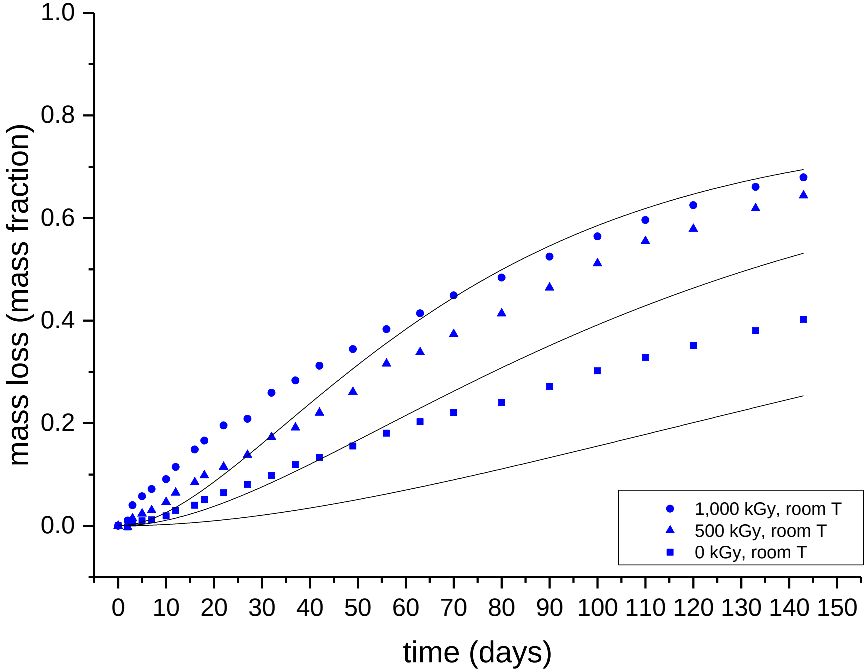
$$k_H = A \times e^{-\frac{E_a}{RT}}$$

Dose (kGy)	Activation energy between 40 et 60°C (kJ.mol^{-1})
0	64
500	59
1,000	49

Yoon et *al.* (1997) *Polymer*, **38**, 3573-3579

MODELLING THE SOLUBLE FRACTION RELEASE

- Yoon's model applied to our experimental data
  - Room temperature → the model does not match…

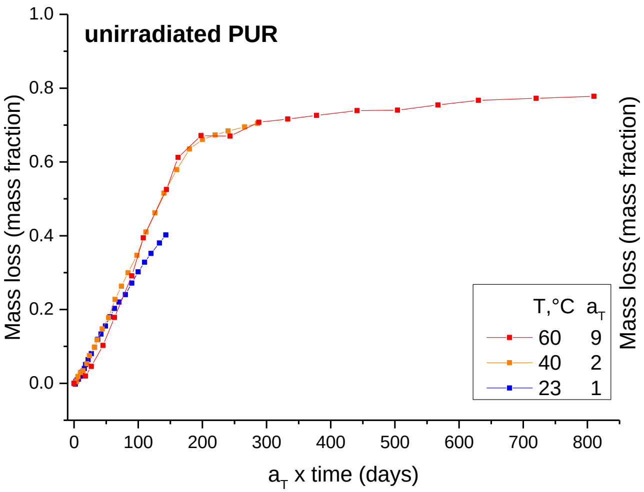


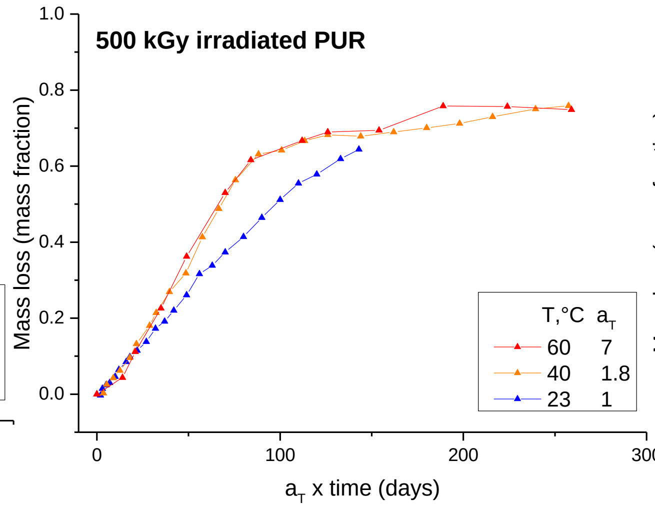
→ **Temperature affects the way** **water-soluble products are released.**

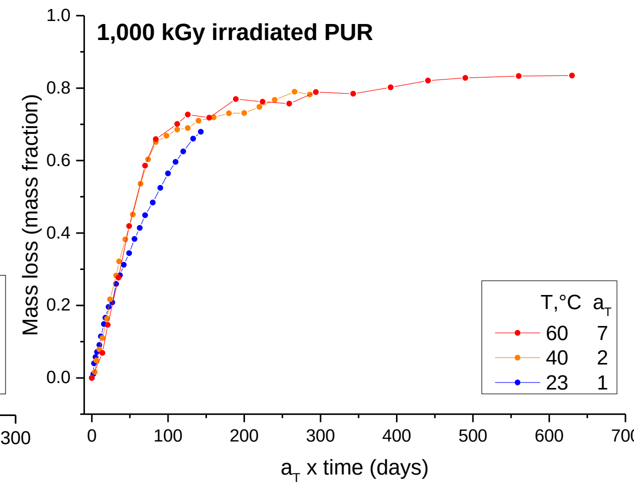
→ **It is observed at all doses.**

MODELLING THE SOLUBLE FRACTION RELEASE

- Time-temperature superposition approach







Data at room temperature cannot be overlaid by data at 40 and 60°C.

→ it confirms that the release of water-soluble products is different at room temperature.

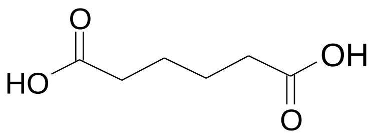
The methodology is explained in Bernstein and Gillen (2010) *Polymer Degradation and Stability*, **95**, 1471-1479.

HYPOTHESES FOR THIS DISCREPANCY

- Discrepancy: the degradation at room temperature is **faster** than expected. Something **speeds up** the reaction **or** the process is **different** at this temperature value.

- Hypotheses for this discrepancy:
  - Some of the Yoon's model hypotheses are not valid:
    - Reaction on surface (versus bulk reaction).
    - Water concentration inside the PUR depends on temperature.
  - There are two competing processes (hydrolysis is the predominant process at " high " temperature):
    - Plasticizing by water : PUR more porous.
    - Remained synthesis reactants and additives leaching at the first steps of the degradation.
    - Autocatalysis by degradation products i.e. adipic acid.*

$$D_{23°C} < D_{40°C} < D_{60°C}$$



* Salazar et *al.* (2003) *Journal of Polymer Science: Part A: Polymer Chemistry*, **41**, 1136-1151.

CONCLUSION

- Unirradiated, 500 and 1,000 kGy irradiated PUR hydrolyzed at room temperature (≈23°C), 40 and 60°C:
  - Mass loss and Total Organic Carbon (TOC) show the same evolution.
  - The ratio between mass loss and TOC confirms that adipic acid is the main product.

- Whatever the dose, the release of soluble fraction at 40 and 60°C follows Yoon's model which means that the ester groups mainly hydrolyzed with equal probability and diffusion does not limit hydrolysis.

- The release of soluble fraction at 23°C does not follow Yoon's model. Several hypotheses to explain this discrepancy: autocatalysis? Plasticizing? Change in water concentration?

- Perspectives: improving the Yoon's model to cover the largest range of temperature.

=> Better understanding of the PUR hydrolysis kinetics. Next step: identifying the degradation products that can complex the radionuclides.

Thank you for your attention.

Any questions?

ACKNOWLEDGMENT

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More details on this subject :
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