DE LA RECHERCHE À L'INDUSTRIE

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On the radio-oxidation at high doses of an industrial polyesterurethane and its pure resin

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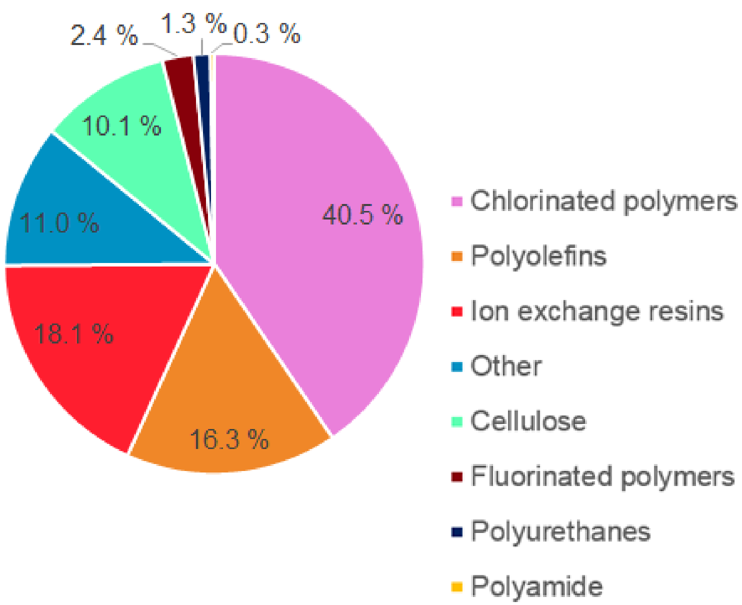
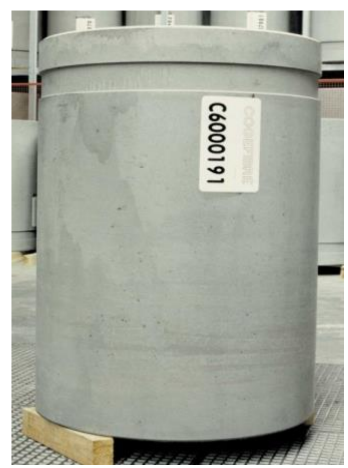
Polymers used in the nuclear industry

A wide variety of polymers in the nuclear industry

Nitrile rubber	Fluoro elastomer	Chlorinated polymer	EPDM	Epoxy	Polyurethane	Acrylic
						
Seals	Seals	Hot cell sleeve Protection sheet	Seals Insulation	Coating Paints	Gloves Cables sheath Insulation	Scotch



=>



Intermediate Level Long Lived Waste (IL-LLW)

=>

Storage and then disposal (future)

Polymers in nuclear waste containers

- Polymers in contact with radionuclides (RN) in the Intermediate Level Long Lived Waste (IL-LLW) packages

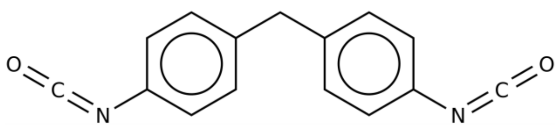
- Main risk associated with storage
  - Gas emission (inflammation, corrosion…)

- Estimate/simulate, over years (up to about 10 MGy), main gases emission
  - Necessity to understand the evolution of the different polymers under irradiation
    - Identification and as much as possible quantification of the degradation products

Chosen polymers

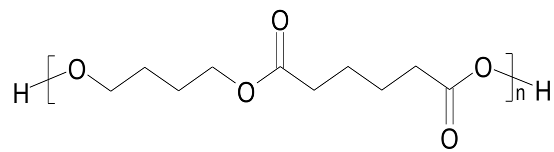
- Industrial polyesterurethane (named hereafter PURm)
  - Constituent of glovebox gloves
  - Composed of 3 segments synthesized from these precursors

hard segment | **extender** | **soft segment**



4,4'-methylene diphenyl diisocyanate

butane-1,4-diol

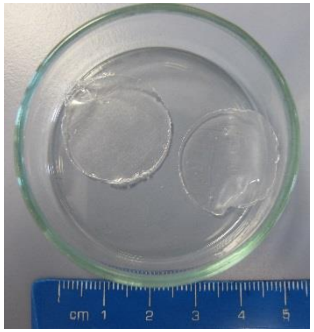


poly(1,4-butylene adipate)

25.5%$_w$ (hard segment)

63.4%$_w$ (extender + soft segment)

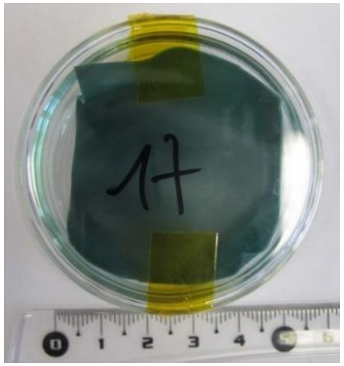
+ 8.9% inorganic fillers
+ 1.8% crosslinking agents
+ 0.4% pigments



- Corresponding pure resin (named hereafter PURe)
  - PURm without charges and additives
    - Evaluation of their effect on the degradation mechanism
    - Identification of a degradation mechanism valid for the entire polymers family

Irradiation conditions

- Gamma irradiations
  - ^{60}Co source (about 0.8 $kGy.h^{-1}$)
    - PURm: 500, 1 000, 4 000, 10 000 kGy
    - PURe: 500, 1 000, 4 000 kGy
  - Homogeneous radio-oxidation conditions
    - Thickness < critical thickness



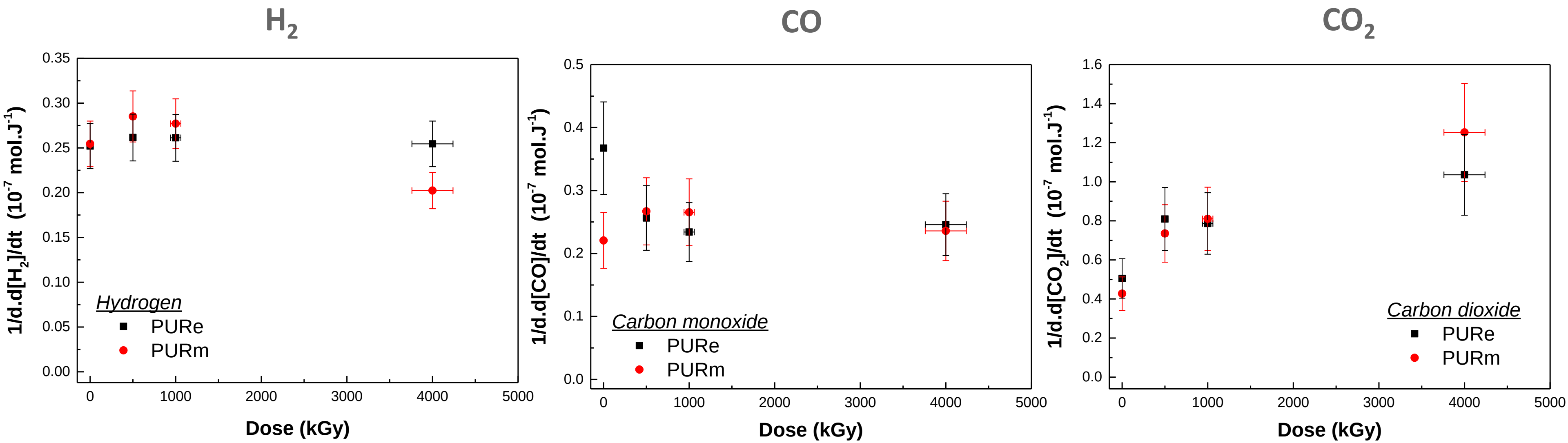
- First-step irradiation
  - Irradiations using open pillboxes

    => Ageing mechanism determination

- Second-step irradiation
  - In closed ampoules under controlled atmosphere
  - Masses estimated to attain
    - Final hydrogen content < 1 $\%_{vol}$ to avoid readdition
    - Final oxygen content > 10 $\%_{vol}$ to ensure homogeneous oxidative conditions

    => Gases quantification at different doses

Gases evolution as a function of dose



- Representation in mol.J^{-1} of energy deposited in the polymeric resin
  - PURe: 100%$_{wt}$ of the material *vs* PURm: 88.9%$_{wt}$ of the industrial material
  - No relevant influence of charges and additives on the gases evolved
- Dose effect up to 4 000 kGy:
  - No dose effect on H_2 and CO release
  - CO_2 increases
    - Formation of carboxylic acids under radio-oxidation [1]
    - These carboxylic acids are then degraded when dose further increases

[1] Lacoste & Carlsson, *J. Polym. Sci. Part A : Polym. Chem.* **30** (1992), 493

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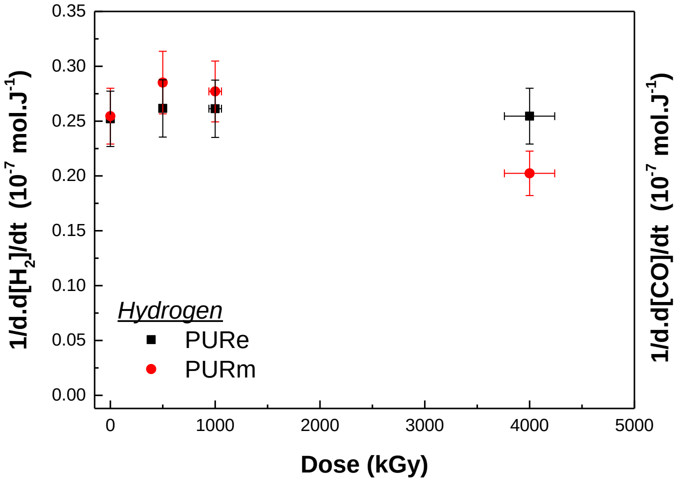
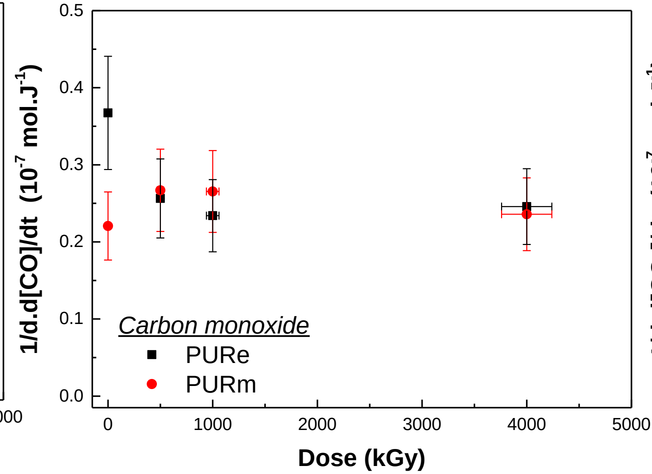
Gases evolution as a function of dose

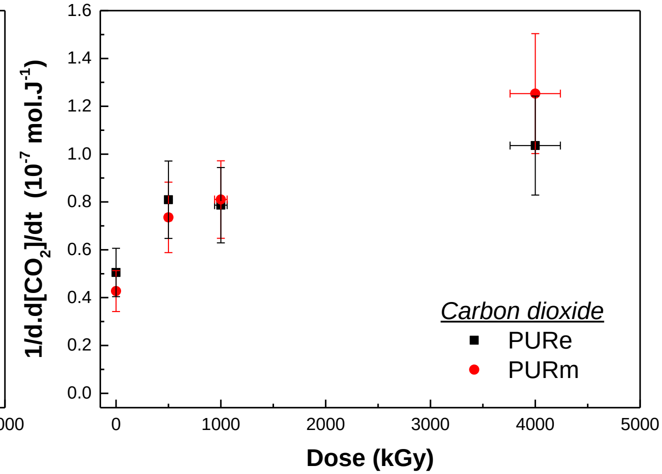
H_2



CO

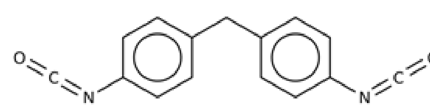


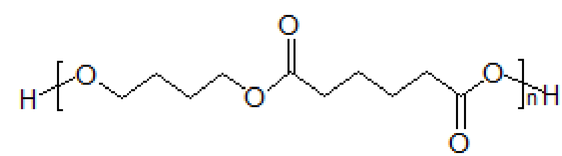
CO_2



- Both PUR relatively stable under irradiation
  - Compared to other polymers found in IL-LLW like PE
    - $G(H_2)_{PE} \approx 3.5 \cdot 10^{-7}$ mol/J vs $G(H_2)_{PUR} \approx 0.25 \cdot 10^{-7}$ mol/J
  - Stability partly due to
    - Aromatic rings from the hard segments [2-4]
    - Esters from the soft segments… [5]

      => Both behave as energy and/or radical scavengers





[2] Dannoux et al., *J. Polym. Sci. Part B : Polym. Phys.* **46** (2008), 861

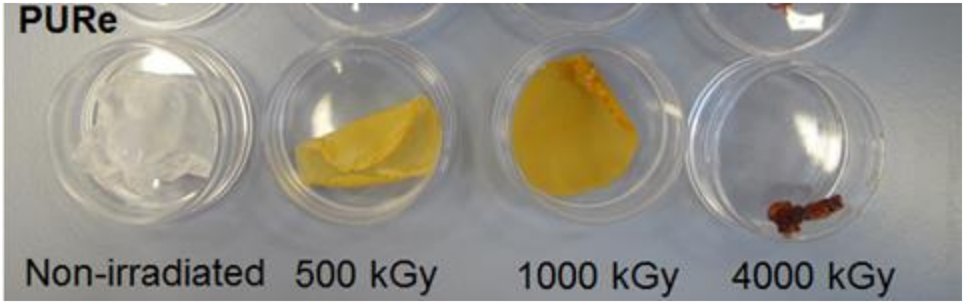
[3] Ferry et al., *J. Phys. Chem. B* **117** (2013), 14497

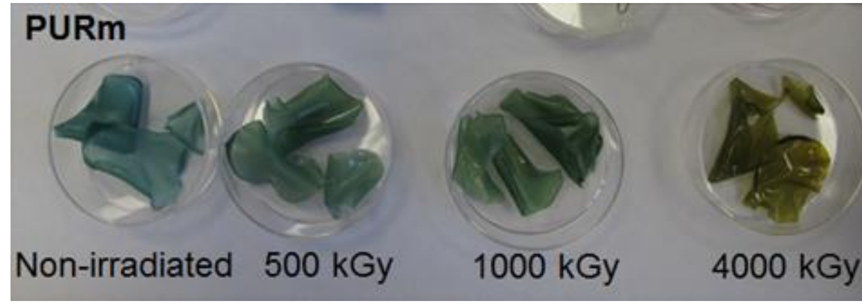
[4] Chang & LaVerne, . *Phys. Chem. B* **104** (2000), 10557

[5] Ferry et al., *Nucl. Instrum. Methods Phys. Res., Sect. B* **334** (2014), 69

Materials evolution as a function of dose

Visual evolution and ultimate analyses





Radio-oxidized polymer	Mean dose (kGy)	Organic elements analysis ($\%_{weight}$)			
		C	H	O	N
PURm	0	56.8	6.7	24.3	3.2
	500	56.7	6.7	24.3	3.2
	1 000	56.5	6.6	24.6	3.2
	4 000	55.3	6.4	26.4	3.2
	10 000	53.8	6.2	28.2	3.0
PURe	0	61.9	7.3	28.1	2.5
	500	61.4	7.3	28.8	2.5
	1 000	61.3	7.2	28.7	2.5
	4 000	60.0	7.1	30.3	2.5

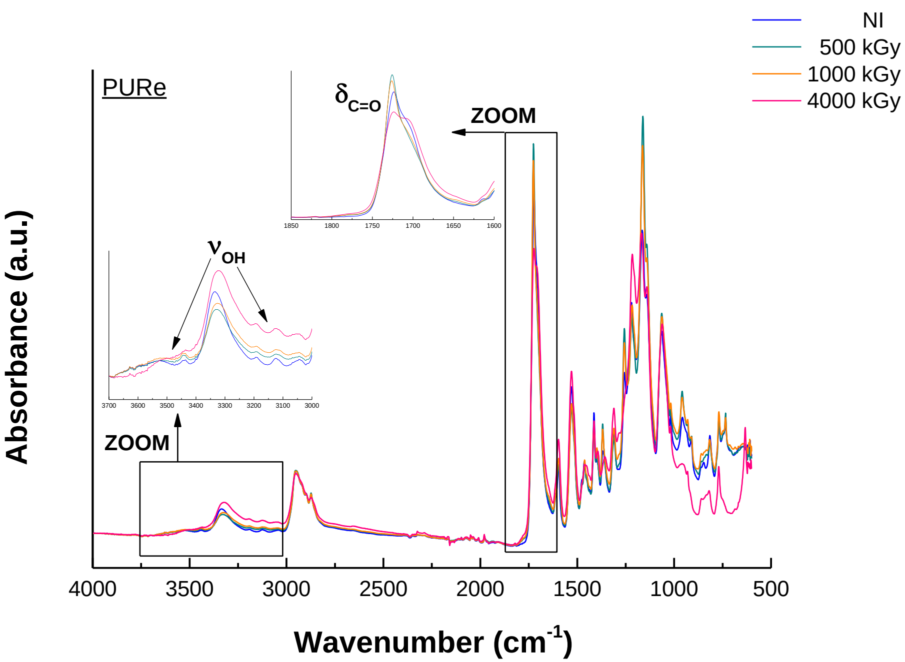
- C & H ↘
  - Gas release (CO, H_2…)
- O ↗
  - New bonds formation (-OH, -OOH, C=O…) [6]
- N →
  - No urethane bond scission
  - Confirmed by the absence of NOx gases

[6] Ferry et al., Ionizing Radiation Effects in Polymers, in: *Reference Module in Materials Science and Materials Engineering,* Elsevier (2016), 1

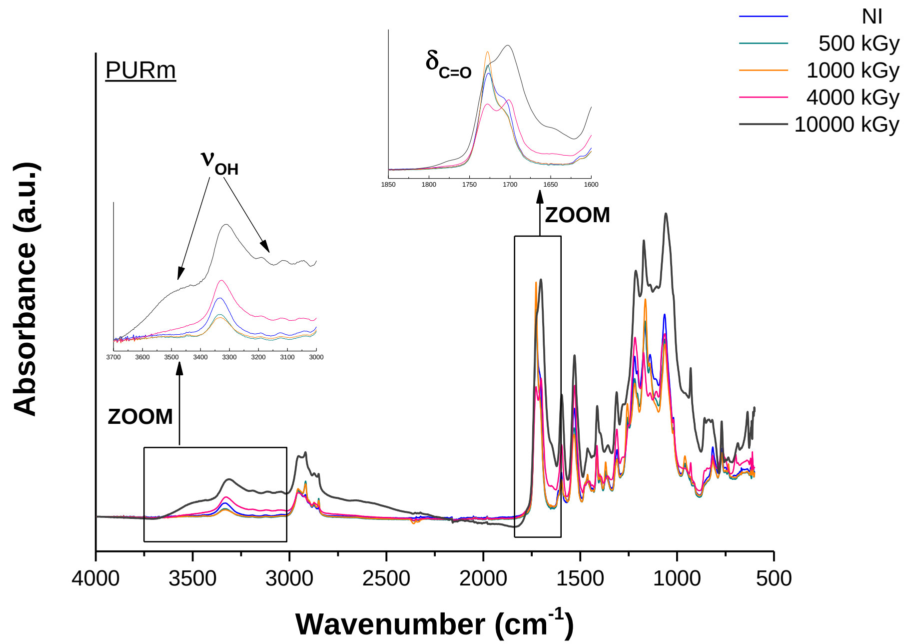
Materials evolution as a function of dose

Infrared spectroscopy (FTIR)

PURe



PURm

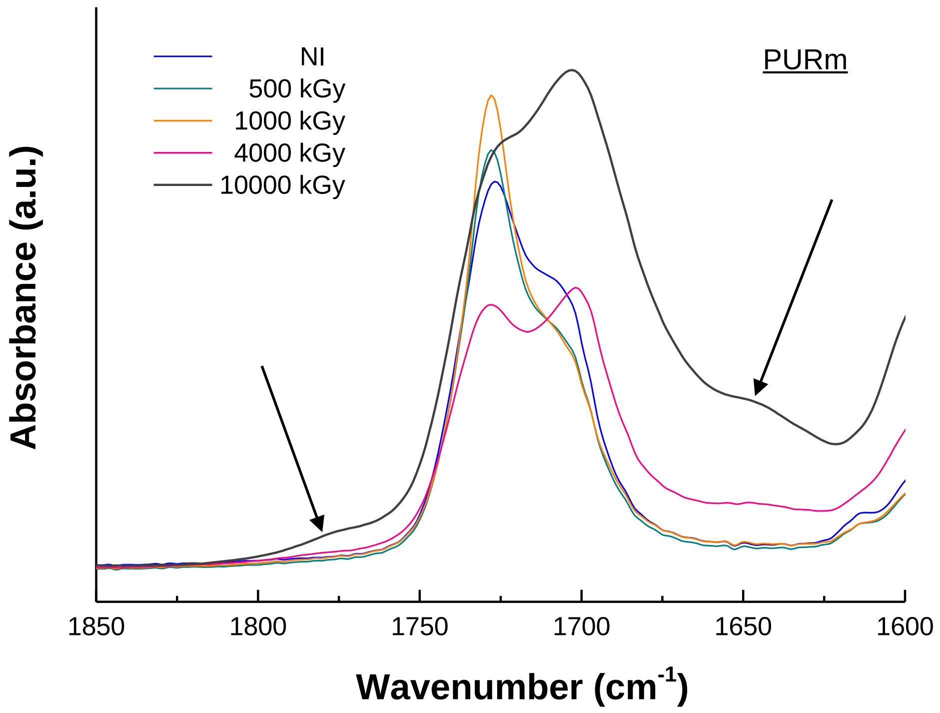


- Formation of new bonds in both PUR up to 4 000 kGy
  - 3600-3000 cm^{-1}: ν_{OH}
  - 1800-1650 cm^{-1}: $\delta_{C=O}$

Materials evolution as a function of dose

Infrared spectroscopy (FTIR)

- Particular case : PURm at 10 000 kGy
  - Shoulder at 1780 cm^{-1}
    - Could be lactones [7]
  - Band at 1640 cm^{-1}
    - C=C double bonds
    - Surprising under homogeneous oxidative conditions
    - Maybe conjugated bonds (by correlation with the visual evolution, *i.e.* yellowing of the irradiated polymers)

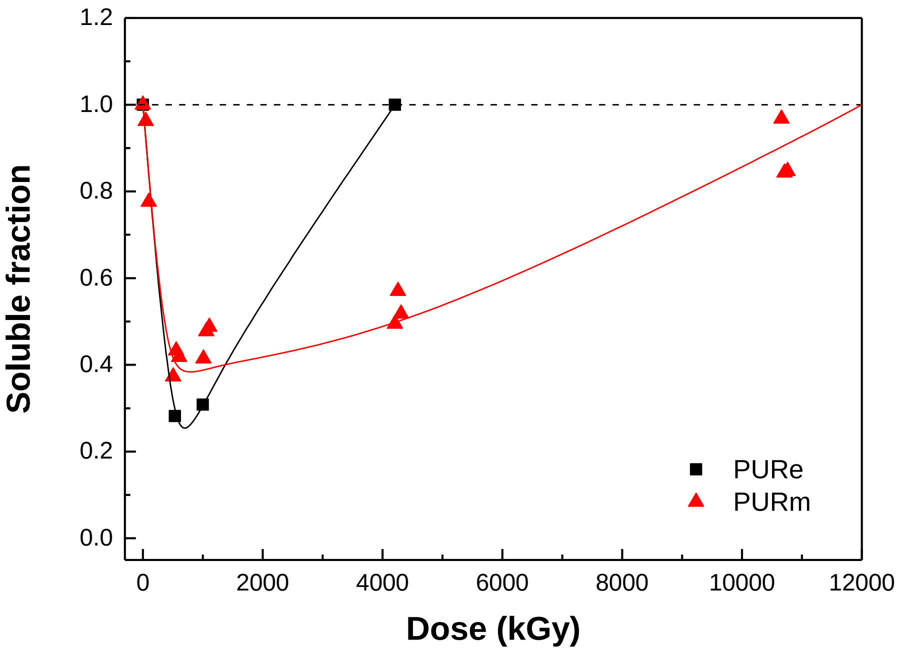


- All infrared band attributions (containing carbon) confirmed by C-1s XPS analyses

[7] Carlsson et al., Identification of products from polyolefin oxidation by derivatization reactions, in: *Chemical reactions on polymers*, American Chemical Society (1988), 376

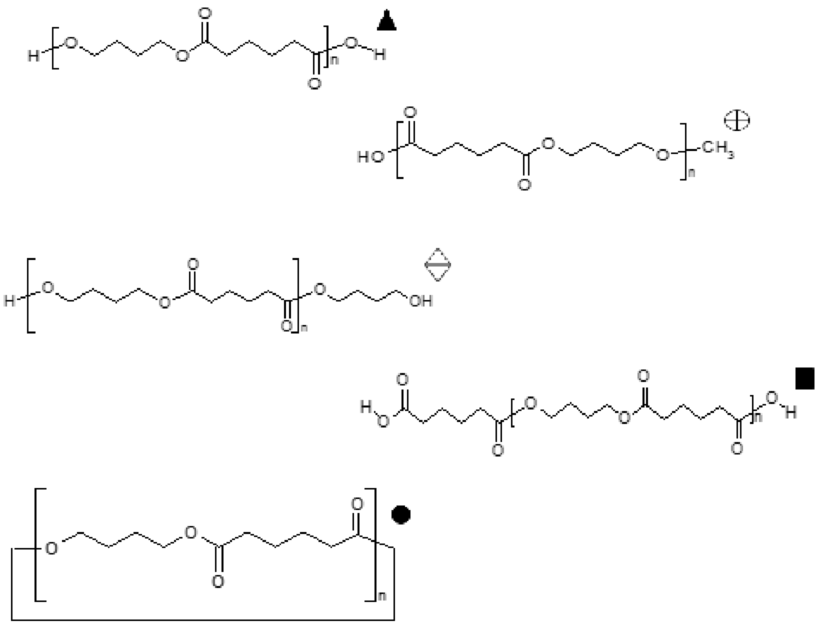
Materials evolution as a function of dose
Soluble fraction (in THF)

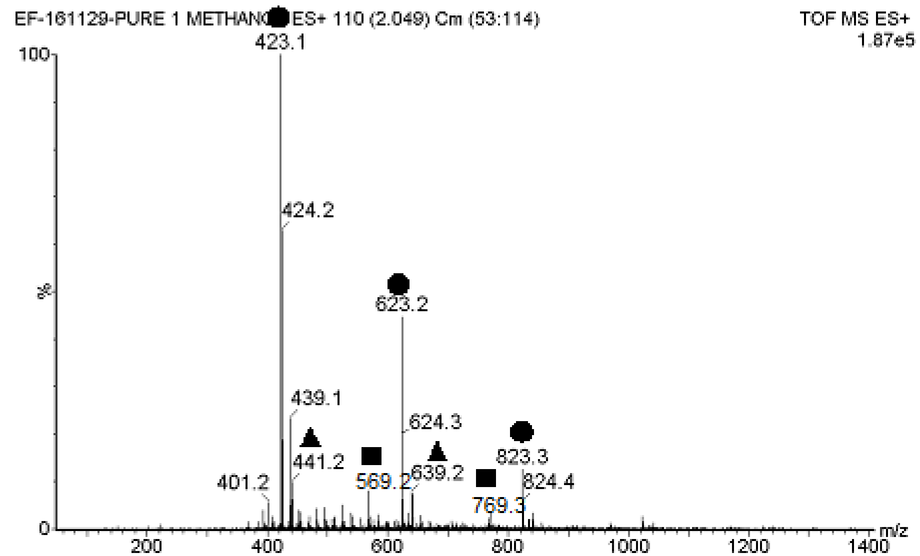
- Soluble fraction in THF followed as a function of dose for both polymers
  - Non-irradiated polymers
    - Totally soluble
  - Up to about 500 kGy
    - Ratio scission/crosslinking ↘
  - By about 500 kGy
    - Ratio scission/crosslinking ↗
    - Total solubility attained again at ≈ 4 000 kGy for PURe and at doses higher than 10 000 kGy for PURm
- Evolution of the ageing mechanism as a function of dose
  - Evaluation of the polymers behavior at these high doses
- *First evidence of a difference between the two PUR*

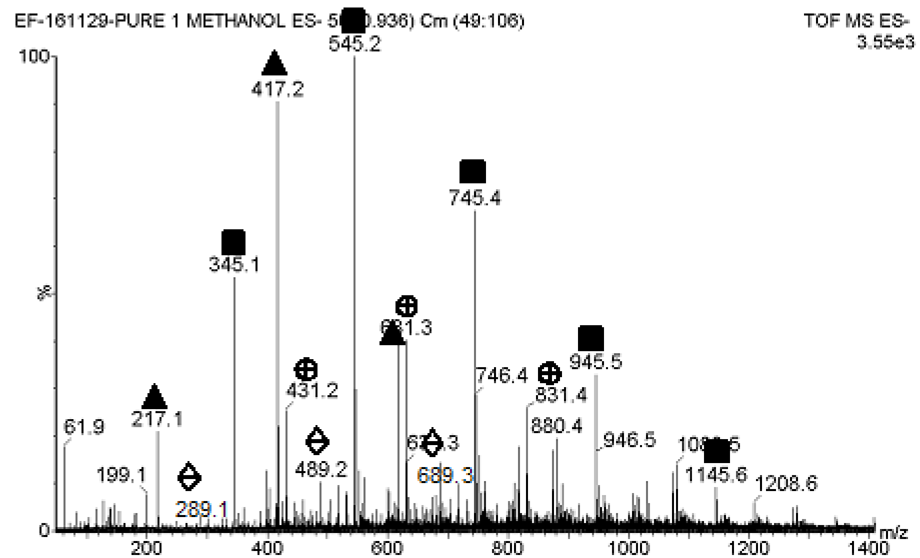


Low molecular mass trapped molecules identification

- Attempt to identify the molecules trapped in the polymer
  - Extraction in methanol
  - ESI-MS of the extracted molecules

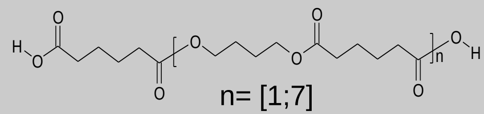
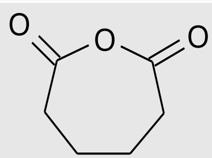
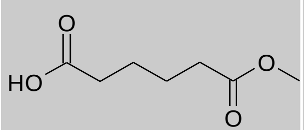
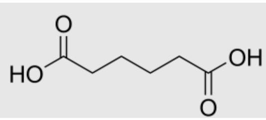
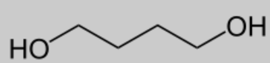
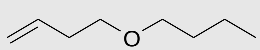
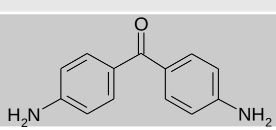






- Identification of oligomers from soft segments

Low molecular mass trapped molecules identification

Kind of molecules		Example of molecules	
Oligomers			
Esters	Lactonized		2,7-oxepanedione (lactonized adipic acid)
	Non lactonized		Monomethyl adipate
Carboxylic acids			Adipic acid
<u>One</u> alcohol			Butane-1,4-diol
<u>One</u> ether			Butoxybutene
<u>One</u> aromatic molecule			Bis(4-aminophenyl)methanone

- Lactones and double bonds
  - Confirmation of their presence (FTIR spectra analysis)
- Aromatic molecule
  - Observed only from PURm radio-oxidized at 10 000 kGy
  - *First and only evidence of the hard segments decomposition*

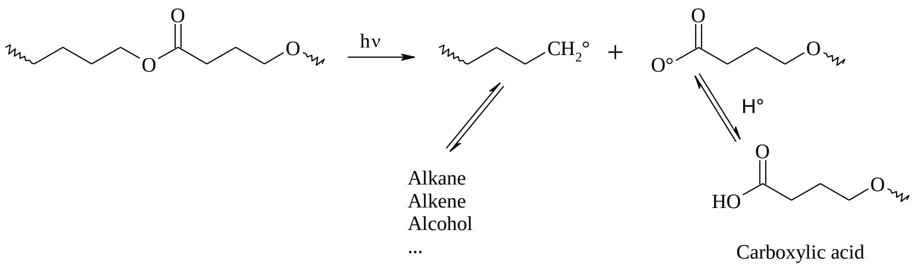
Conclusions

Polyesterurethane ageing mechanisms

- Radio-oxidation of PUR: degradation mechanisms *up to 10 MGy*
  - Dose effect moderated (energy and/or radical scavengers)

- For pure resin (PURe) as for industrial material (PURm)
  - Quantification of the main gases evolved
    - H_2 and CO → and CO_2 ↗
  - New bonds in the polymers
    - Lactones, ketones, alcohols, hydroperoxides… but also double bonds
  - Low molecular mass molecules trapped
    - Oligomers, adipic acid… mainly issued from soft segments

- Degradation mechanism of the aromatic polyesterurethanes under radio-oxidation
  - Ester bonds scissions



Conclusions

From one polymer to the nuclear waste safety

- Charges and additives presence effect
  - Separation of the effect of radio-oxidation on the resin and on the other components of an industrial polymer
    - Degradation mechanism for one polymer family
    - No irradiation of all materials
    - Verification with few experiments

- Quantification of the radiation chemical yields of gases
  - Integration into a simulation program

- All the main polymer families encountered in IL-LLW studied
  - Chlorinated polymers, polyolefins…

Thank you for your attention

Acknowledgements

- S. Rouif (IONISOS), P. Le Tutour (LABRA) & V. Labed (GAMMATEC) for their helpful collaboration during irradiations
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