Gamma/E-beam to new X-Rays: How to compare radiation sterilization technologies on PP, PE and PET ?

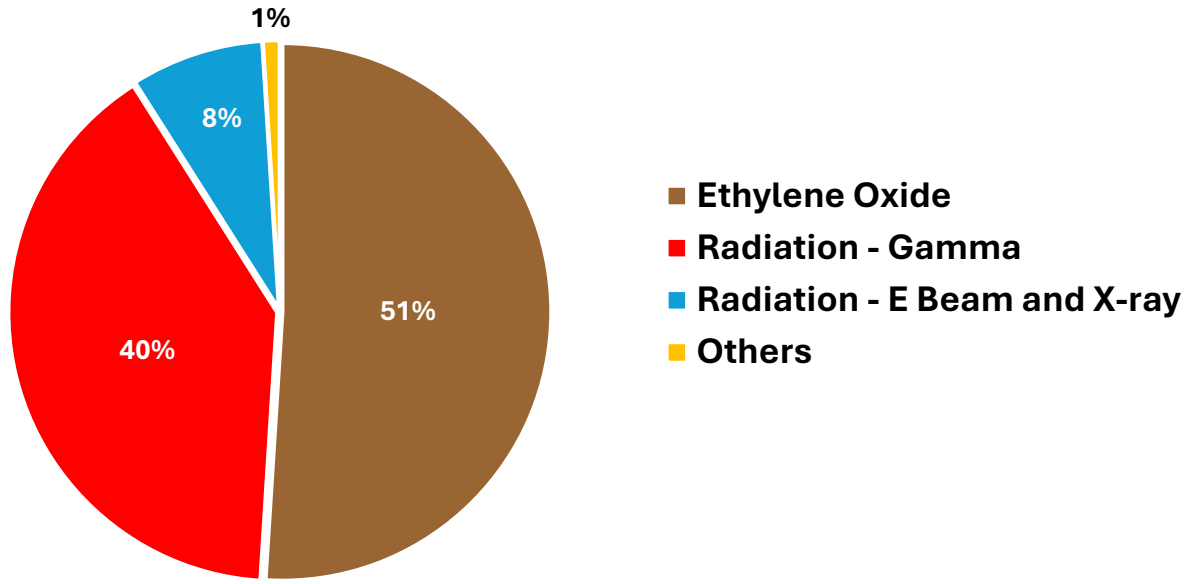
Nicolas Ludwig – Aerial
Sophie Rouif - Ionisos



With the support of:

Introduction
Radiation Sterilization of single use systems

Radiation represents about half of the sterilization market of single-use systems (Gamma, E Beam, and X-rays)



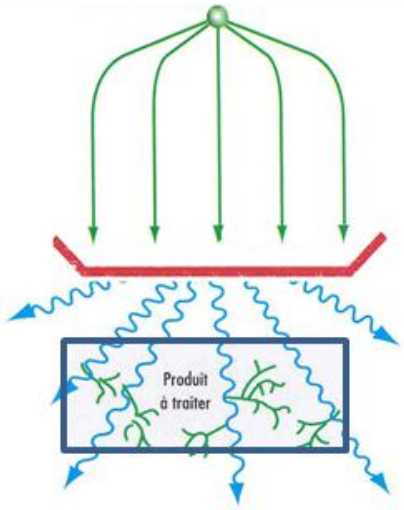
Radiation allows to deposit energy in material depth so that to irradiate through packaging and many layer of products.
Deposited energy per unit of mass is named absorbed **Dose.**
The unit of dose is the gray (Gy), 1Gy = J kg^{-1}

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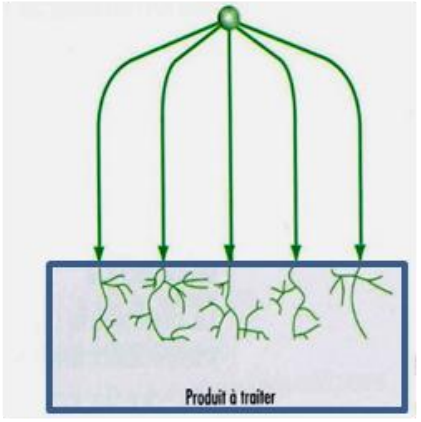
IONISOS

Introduction
Three irradiations technologies

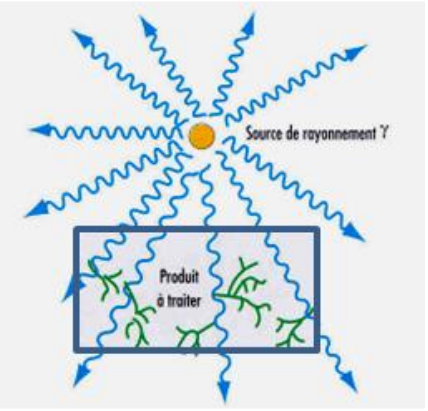
X Ray



E Beam



Gamma Ray



Gamma Ray : Radioactive source – High volume (pallet) – Low dose rate (~ kGy/hour)

E Beam : Electrical source – Intermediary volume (box) – High dose rate (~ kGy/s)

X Ray : Electrical source – High volume (pallet) – Intermediary dose rate (~ kGy/min)

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Presentation of Aerial

Excellence center for radiation processing

Aerial

CRT



IAEA
International Atomic Energy Agency

Aerial

IAEA Collaborating Centre

for

Multidisciplinary Applications of Electron Beam and X Ray Technologies and Related Dosimetry for Radiation Processing and Food Irradiation

2021 – 2025

Label Technologic Resource Center (CRT) by French Ministry

Label Collaborating center by the IAEA (International Atomic Energy Agency)

Based in Illkirch (Strasbourg)

Based upon the skills and knowledge of a multidisciplinary team of 41 individuals (PhDs, engineers, and highly qualified technicians)

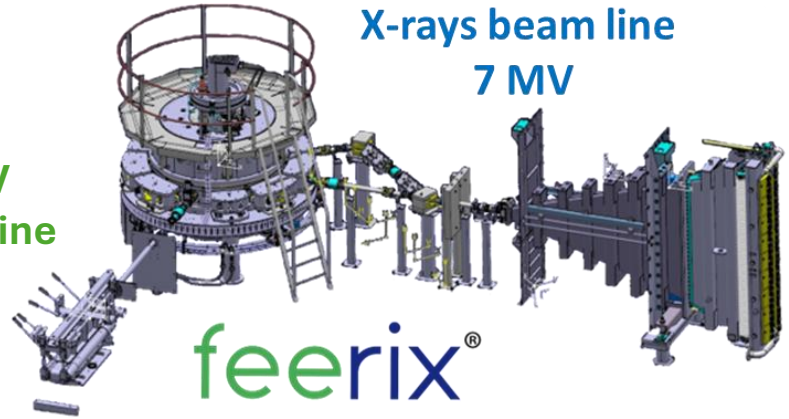
Assistes industries in term of Applied Research, Expertise, and Training

Presentation of Aerial

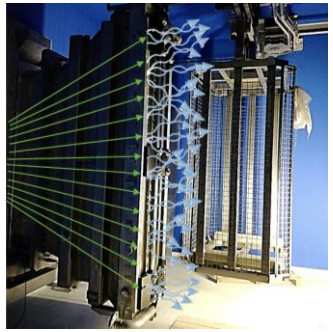
From low to high energy e-beam and X-rays

feerix® industrial-scale facility

- High Power/High volume
- Dedicated 100% to R&D and process development







Other irradiation facilities of Aerial

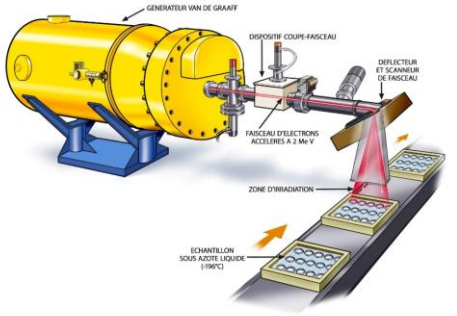
Low Energy E-Beam (80-200 keV)





Low Energy X-rays (10-160 kV)

Medium Energy E-Beam and X-rays (0.5 – 2.2 MeV)



Presentation of Ionisos

Leading European Sterilization supplier

OUR SERVICES

Sterilization

- Eliminate or reduce the bioburden of pathogenic and other microorganisms (e.g. salmonella, listeria, ...); cold sterilization

Crosslinking

- Modify the chemical properties and therefore physical characteristics of materials

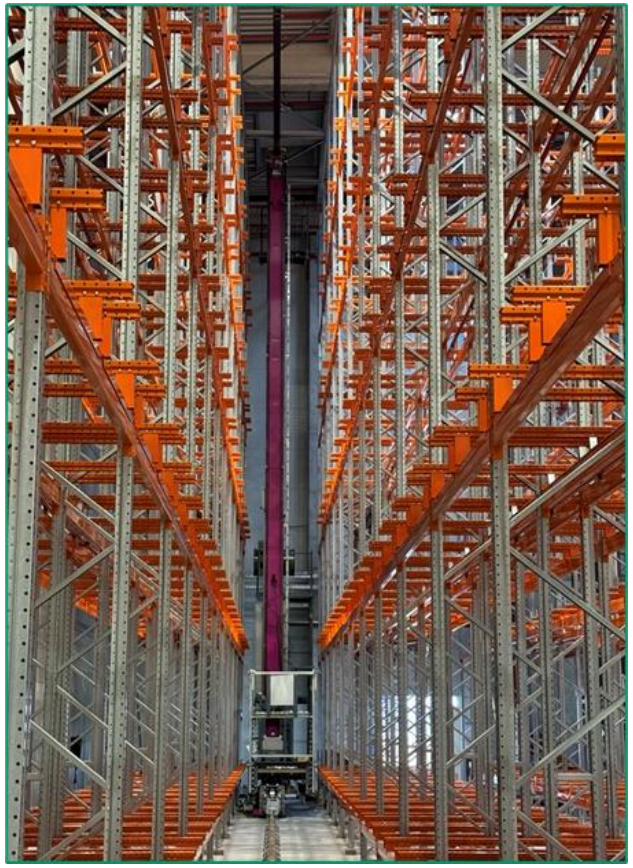
4	10	5	308
TECHNOLOGIES of industrial cold sterilization and crosslinking	**SITES** including our new facility of Henriville in France	**COUNTRIES** France, Germany, Spain, Estonia and Switzerland	**EMPLOYEES**



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Presentation of Ionisos

Upcoming X-ray treatment center - Henriville



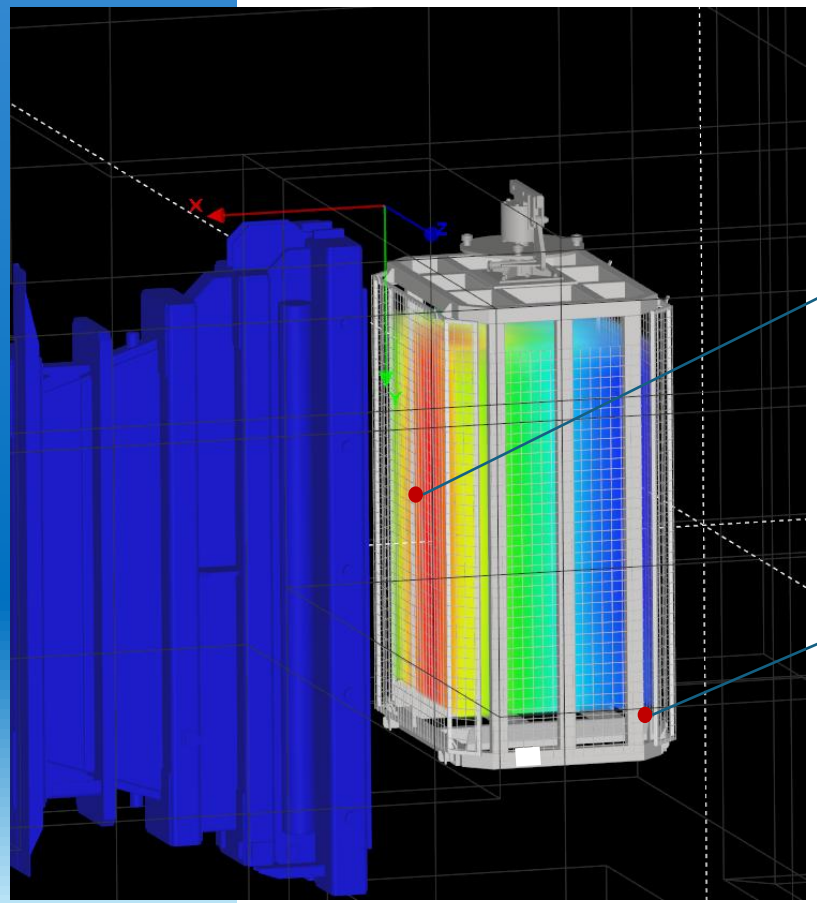
Full automated transtoker, with controlled temperature between 15°C and 25°C

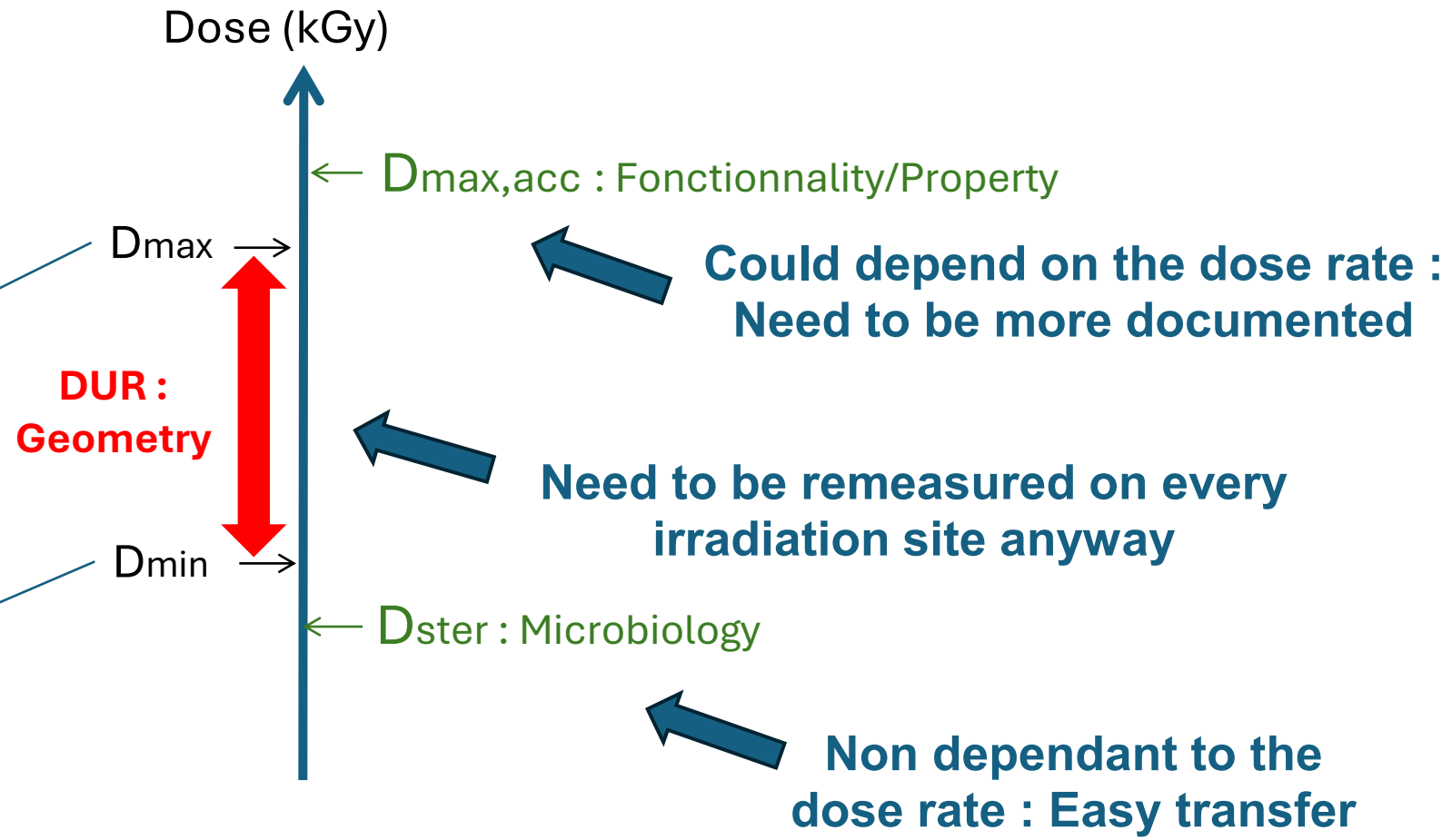


High capabilities of optimization to reach the best DUR (next slide)

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Context
Irradiation process and transferability

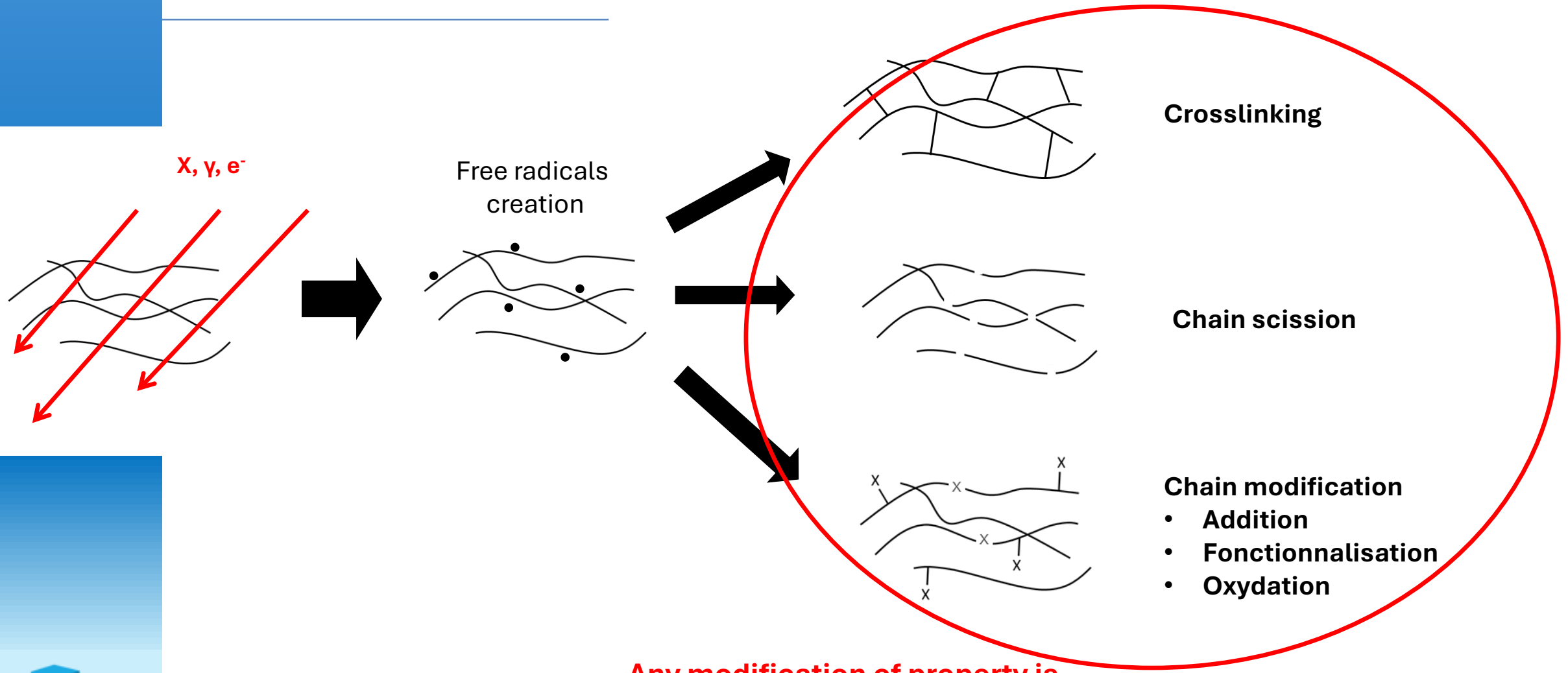




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Context
Radio-induced modifications of polymers



Any modification of property is potentially problematic effects

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EDITOP Project
Overview

Effects of **D**ifferent **I**rradiation **T**echnologies **O**n **P**olymers

IT IS A TEAM PROJECT

- Coordinated Research Project supported by IAEA, 14 countries, many teams are working on MD themselves
  - Possibility to “cross” our trends and results
  - Publication of an IAEA dedicated report at the end

- EDITOP French consortium :
  - 3 research laboratory : IMT Alès, Mines St Etienne, AMU
  - 2 industrials “end users” : Sartorius and Medtronic
  - 1 sterilization service provider : Ionisos
  - 1 technical resource center : Aerial

- Complementary to other initiatives taken worldwide such as Team Nablo (US)

IAEA International Atomic Energy Agency

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IMT Mines Alès École Mines-Télécom

MINES Saint-Étienne

Aix*Marseille université

SARTORIUS

Medtronic

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EDITOP Project
Selection of polymers

Effects of Different Irradiation Technologies On Polymers

Polymers	PP homopolymer 1	PP homopolymer 2	PP homopolymer 3	Polyethylene HDPE	PET 1	PET 2
Additives	Antioxidant	Sliding agent	Clarifying additivation	Antioxidant	Colour modification agents	NC
Manufacturing Claims, sterilization included	Radiation resistant	Ethylene Oxide, Steam	Radiation resistant	Ethylene Oxide	No / good optical properties and food contact compliant	NC
Tacticity	Isotactic at 96%	Isotactic at 93.3%	Isotactic at 97–98%	NA	NA	NA
Melt Flow Index (MFI, 2.16 kg) ($g.10min^{-1}$)	10 (230°C)	19 (230°C)	55 (230°C)	0.4 (190°C)	NC	NC
Melting Point (°C)	164	160	164	170	245	NC
Flexural Modulus (MPa)	1250	1250	1800	-	NC	NC

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EDITOP Project
Irradiation and experimental protocol

Sample preparation

PE – PP – PET / Different grades or preparation

Irradiation

Radiation Technology	Doses	Facilities	Dose rate
Gamma Ray □	Different dose levels between 30 and 100 kGy. Target dose +/- 10%	IONISOS Dagneux, 2 MCi	1-5 kGy/h
E-Beam △		AERIAL Strasbourg 10 MeV, 50 kW	~ 1-10 kGy/s
X-Ray ○		AERIAL Strasbourg 7 MeV, 100 kW	20-80 kGy/h

Accelerated aging

Aging in an oven to obtain sample aged between 1-2 years in order to mimic shelf life and real usage.

Post irradiation analysis

Optical analysis	Colorimetry	Goniometer		
Chemical and molecular characterisation	ESR	IR analysis	Gel content	Analysis of extractibles
Mechanical, thermal and rheological characterisation	Tensile test	Rheology	DSC	Dynamic Mechanical Analysis

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EDITOP Project
Irradiation and experimental protocol

Sample preparation

PE – PP – PET / Different grades or preparation

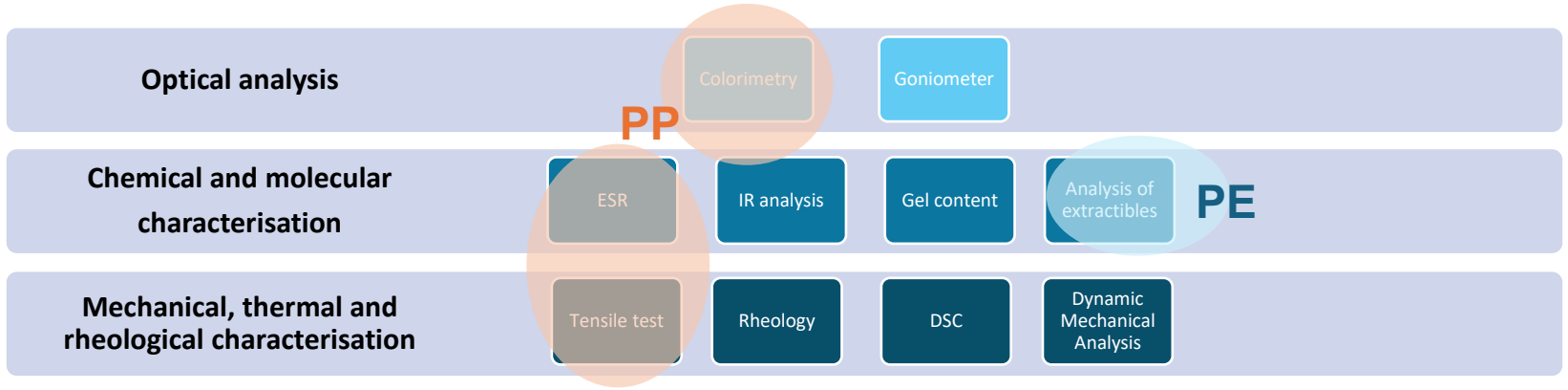
Irradiation

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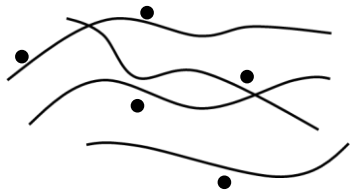
Every results cannot be presented. We will focus on results of first interest

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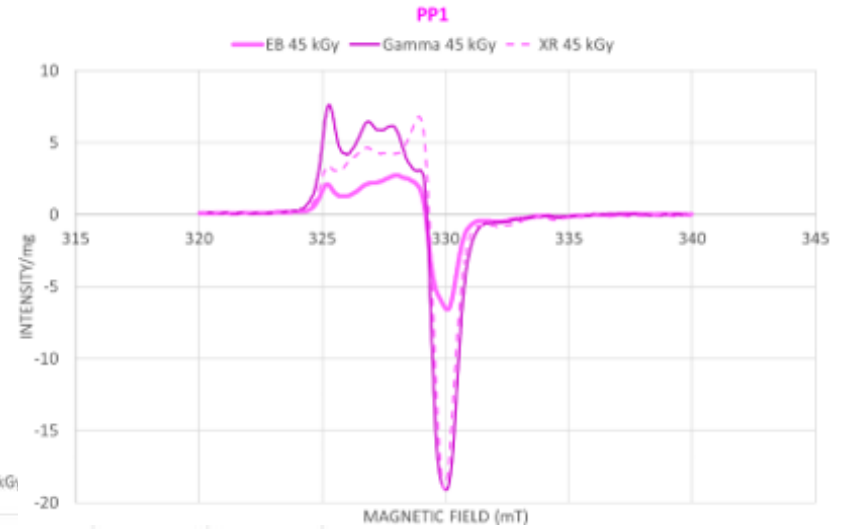
Results and discussions
Mains trends and results on PP

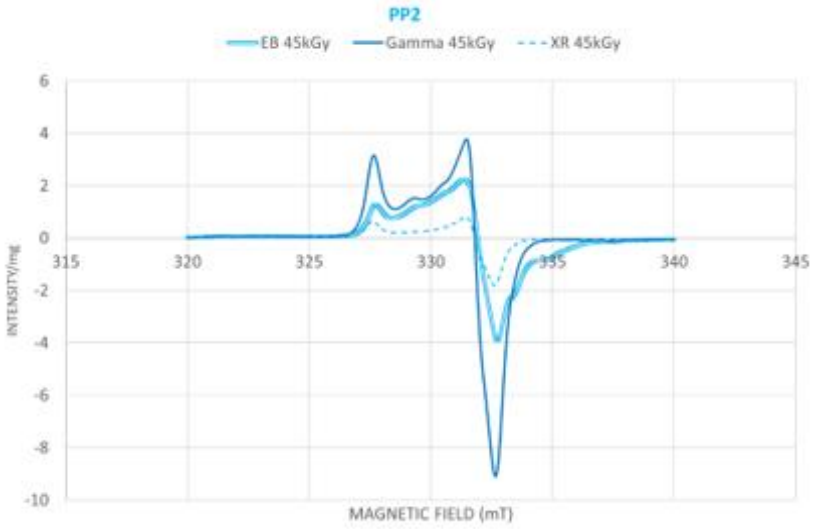
EPR : Visualisation and quantification of radicals

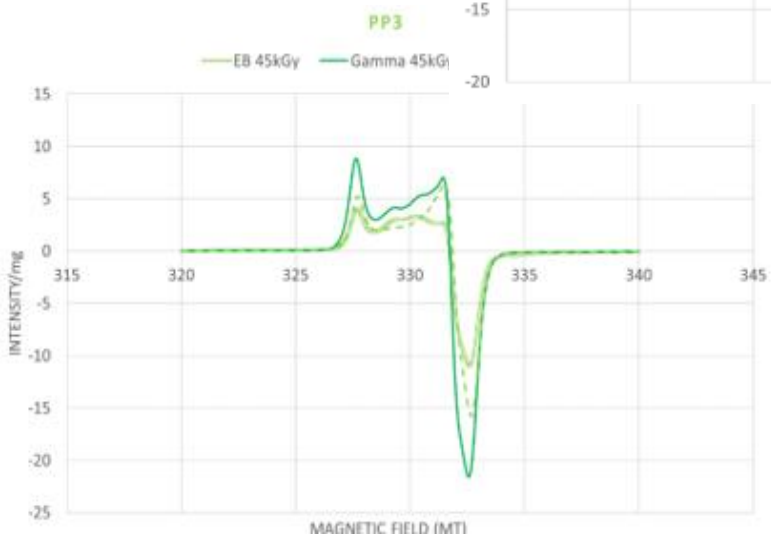


For a 45 kGy, (typical max dose in a sterilization process). ESR curves are similar in shape and intensity

Similar radicals are generated by irradiation, whatever is the PP grade or the radiation technologies





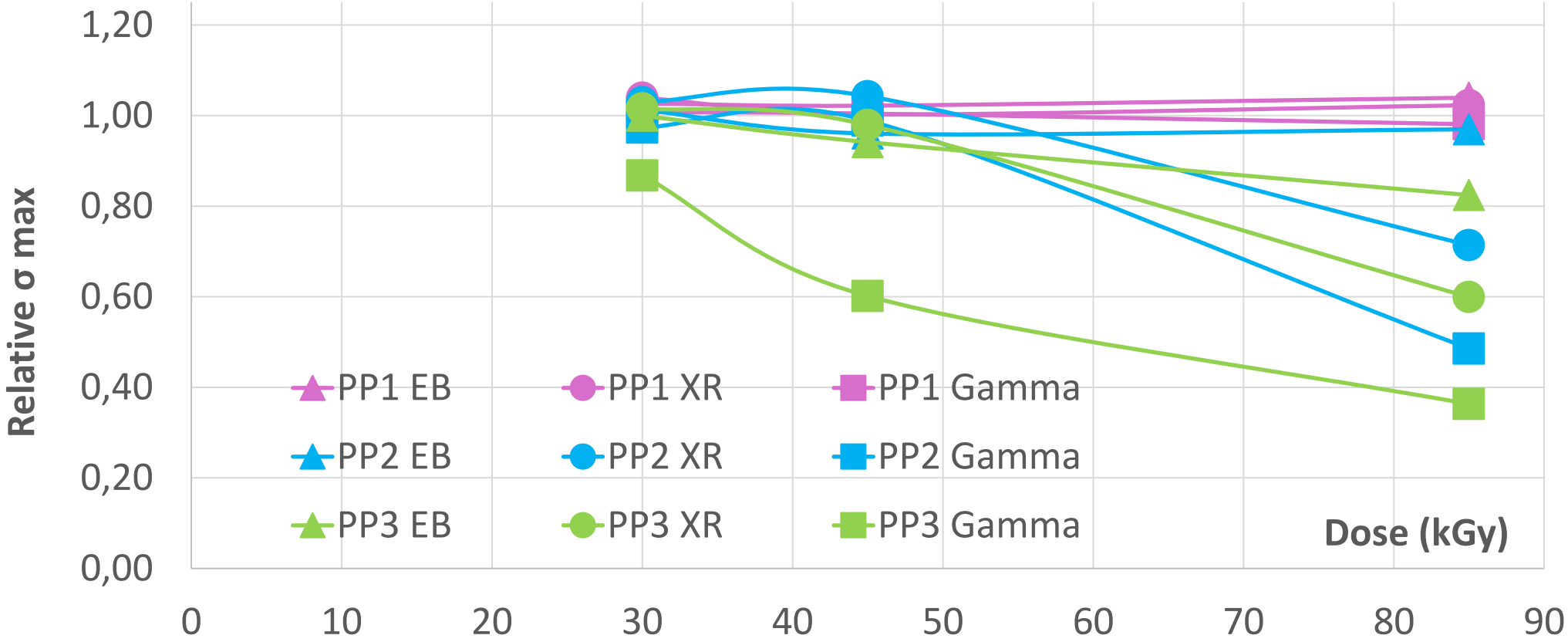


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Results and discussions

Mains trends and results on PP: **tensile test**



Radiation Technology

Gamma Ray

E-Beam

X-Ray

Behaviour	PP1	PP2	PP3
Dose-related	N	> 45 kGy	Y
Dose rate related	N	> 45 kGy	Y

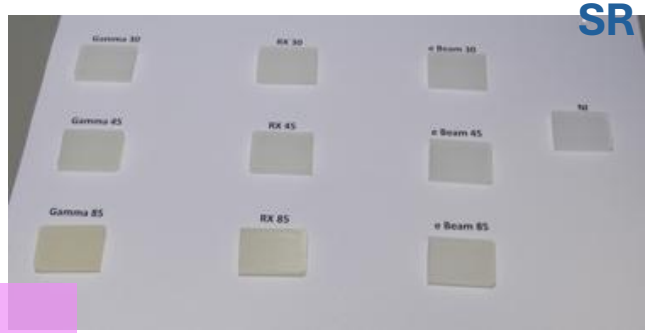
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Results and discussions

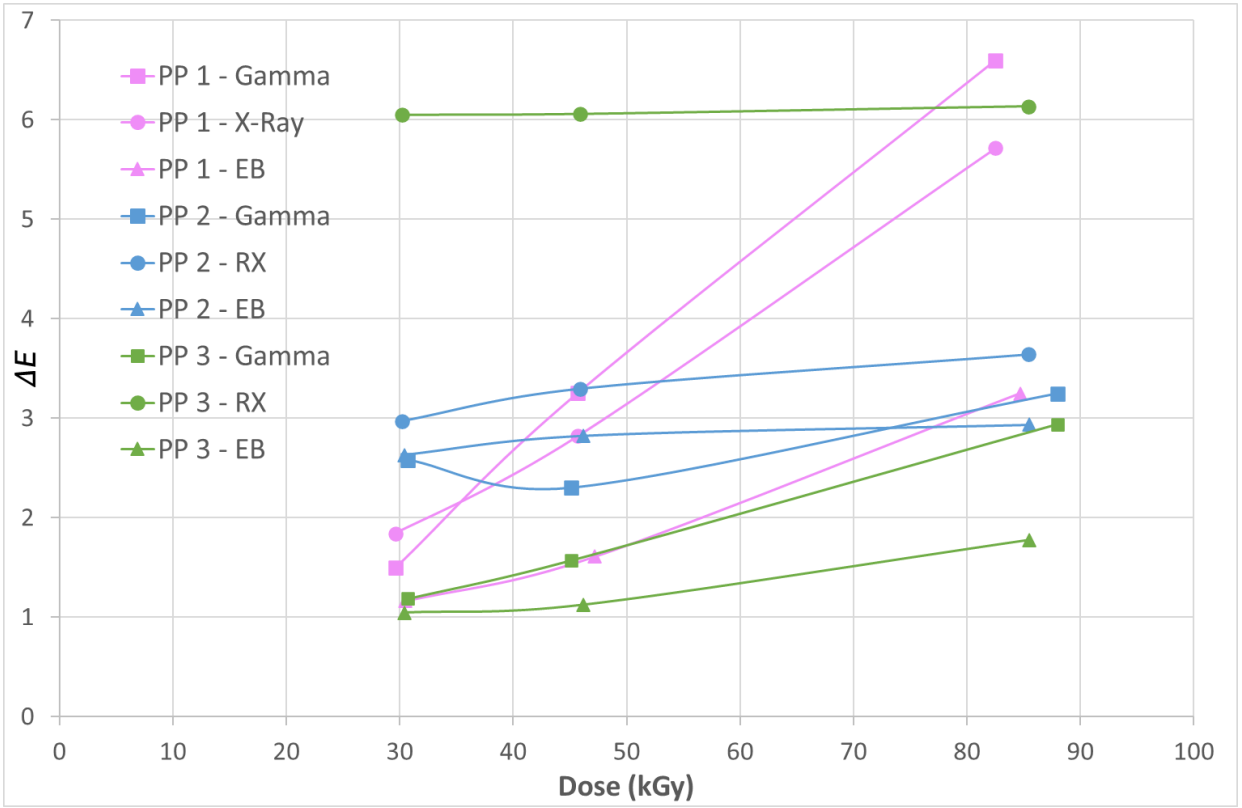
Mains trends and results on PP: **colorimetry**

SR



PP1

A yellowing is observed upon irradiation which increases with the dose. Technologies may lead to some modification.





PP2



PP3

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IMT Mines Alès
École Mines-Télécom

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Results and discussions

Mains trends and results on PP

	PP in general at T0
Tensile test	Be careful of the grades where an impact of radiation can be observed in relation with dose and dose rate.
Colour	
DSC	No significant effect
DMA	
ESR	

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Material and methods

Mains trends and results on HDPE: **extractibles**

	Matrices detected	Non-irradiated	EB 100 kGy	Gamma 100 kGy	X-ray 100 kGy
VOC by GCMS	Aldehydes	*Nonanal*		*Nonanal;* ***Decanal***	
	mg/g	*0.15*	*0.29*	*0.43*	*0.41*
	Ester/ether	*ND*	*Close to Butyl 2-methylbutanoate*	*Oxygenated compound (m/z=73; 101; 117); Close to Butyl 2-methylbutanoate*	*ND*
	Aromatic esters	*ND*	*ND*	*Dipropylene glycol dibenzoate; Diethylene glycol dibenzoate*	
		ND	*ND*	*Oxygenated aromatic compound (m/z 103-131);*	
	TOTAL VOC (mg/g)	***0.15***	***0.44***	***1.05***	***0.67***
SCOV by UPLC/TOF-MS	Acids	*Myristic Acid; Hexadecenoic Acid; Pentadecanoic Acid; Linoleic Acid; Palmitic Acid **			
		*Oleic Acid *; Stearic acid*		***Decanoic acid****; Undecanoic acid; Dodecanoic acid; Stearic acid **	***Decanoic Acid****; Dodecanoic Acid;*
	mg/g	*14.11*	*5.04*	*26.41*	*8.39*
	AO degradation	*3,5-Di-tert-butyl-4-hydroxybenzaldehyde*			
	mg/g	*0.43*	*0.59*	*0.77*	*0.64*
	Amides	*Erucamide*	*ND*	*ND*	*ND*
	Aromatic Esters	*ND*	*Diethylene glycol dibenzoate; Dipropylene glycol dibenzoate*		
	mg/g		*0.52*	*0.53*	*0.44*
	TOTAL SCOV (mg/g)	***16.11***	***6.63***	***27.98***	***9.76***

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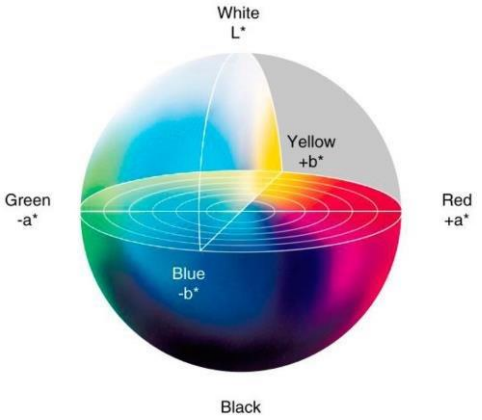
Results and discussions

Mains trends and results on HDPE

	T0	T12
Tensile	No significant impact from the technology, dose, or dose rate on the samples: Results close to the non-irradiated condition. Except for elongation at break: increase with dose and dose rate	No significant impact from the technology, dose, or dose rate on the samples: Results close to the non-irradiated condition. The evolution of elongation at break indicates a **behaviour consistent with time-induced crosslinking.**
Color	Analysis in progress.	Analysis in progress.
DSC	No significant effect.	No significant effect.
DMA	No significant effect of dose or technology, **except for EB: sign of crosslinking with dose.**	Analysis in progress.
ESR	Analysis in progress.	NA
Extractibles	Gamma >> NI, EB, X-ray	NA

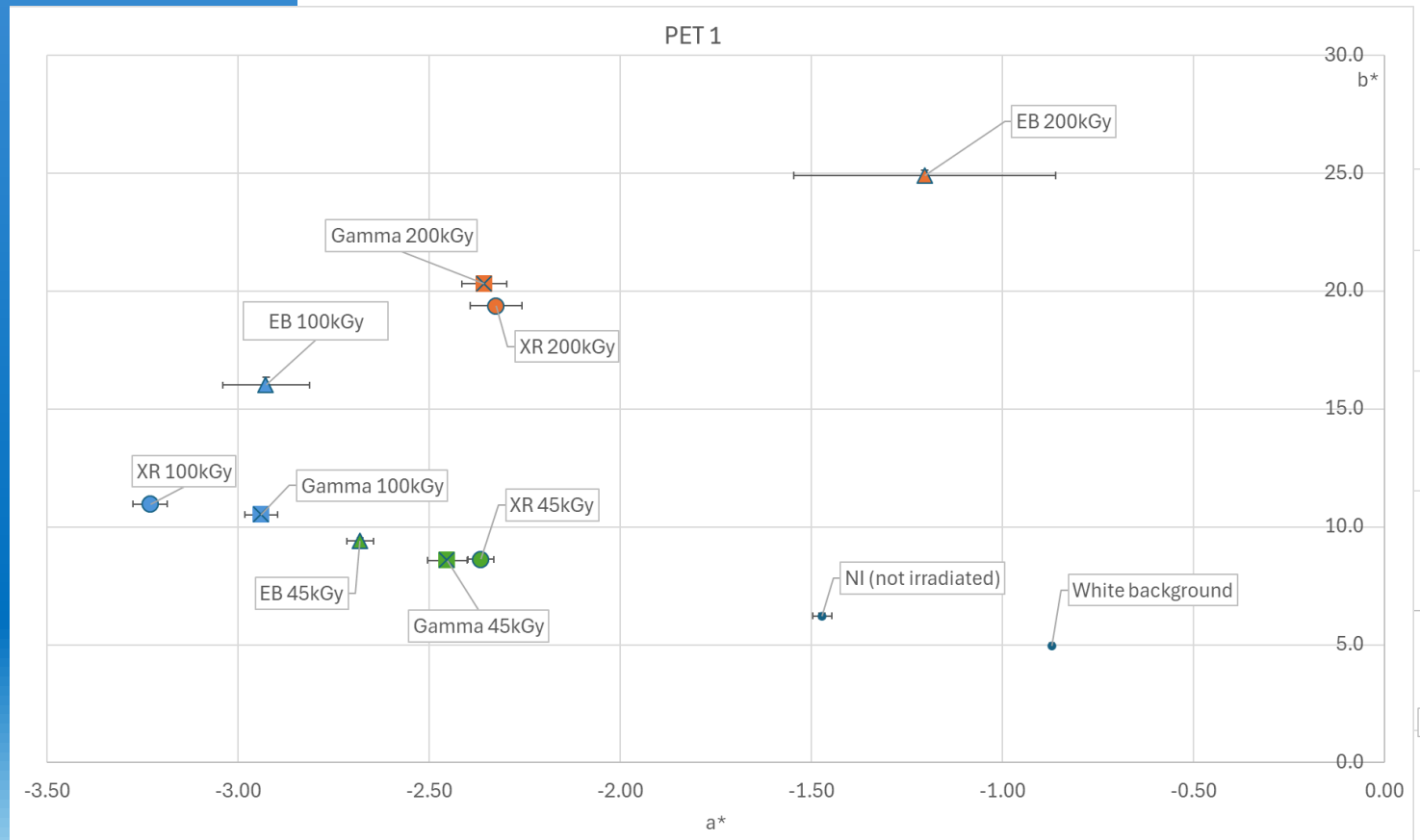
Results and discussions

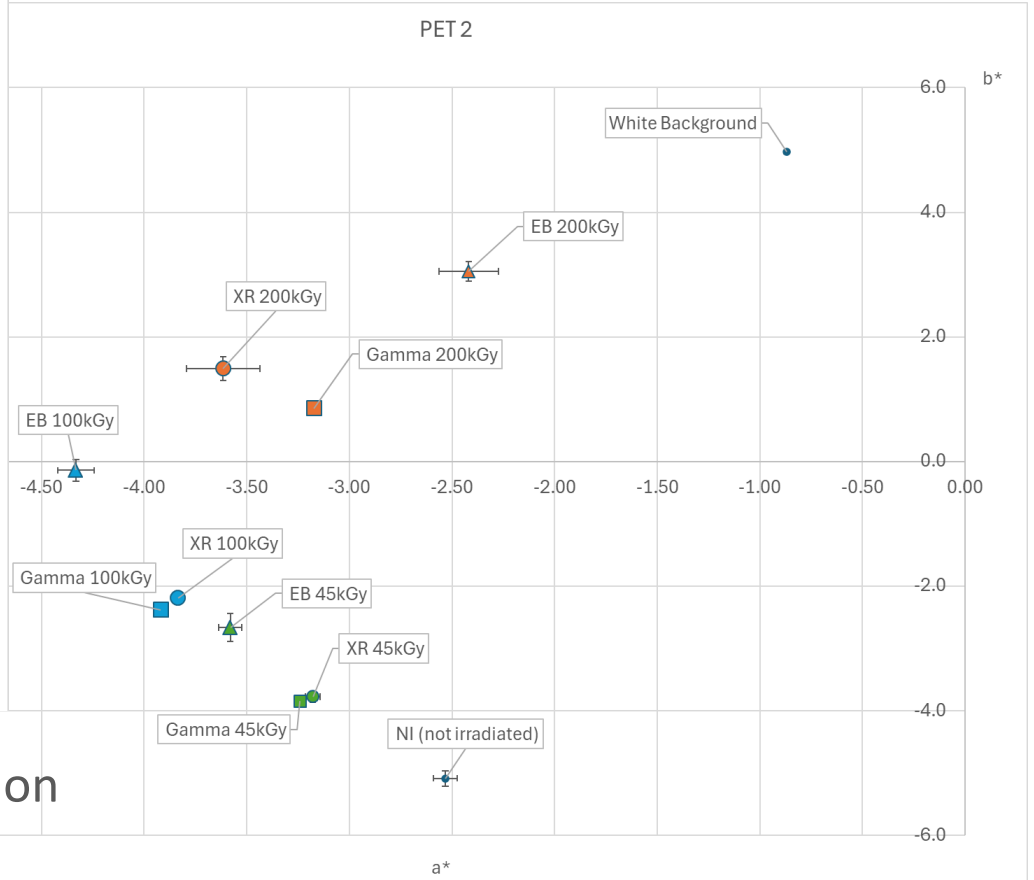
Mains trends and results on PET: **colorimetry**



SR

IMT Mines Alès
École Mines-Télécom





Trend: starting from 100 kGy, the impact of E-Beam on yellowing is greater than with gamma and X-ray.

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Results and discussions
Mains trends and results on PET

PET 1 & 2	T0	T16
Tensile	No significant impact from the technology, dose, or dose rate on the samples. Results close to the non-irradiated condition. Except for elongation at break (sign of crosslinking from 100 kGy).	No significant impact from the technology, dose, or dose rate on the samples: Results close to the non-irradiated condition. The evolution of elongation at break indicates a behaviour consistent with time-induced crosslinking in all samples.
Color	Trend: starting from 100 kGy, the impact of EBeam on yellowing is greater than with gamma and X-ray.	Analysis in progress.
DSC	No significant effect.	
DMA	No significant effect.	Analysis in progress.
InfraRed	Analysis in progress.	Analysis in progress.
ESR	Spin/g: EB > X-ray > Gamma / trend to confirm	NA

Conclusion

Positive leverages of transference to New X-RAY



- **To predict the dose rate effects** on materials when converting from one irradiation technology to another;

- facilitate the transfer necessary for the emergence of machine-based radiation technologies.



- Potential **transition of some products made of PP, PE or PET from existing E-beam or Gamma sterilization technology to new X-ray.**

- With the grades studied here, all that remains to be done is to validate it.



Both 3 plastics are relevant to be recycled in a **circular economy**.

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Thank you !!



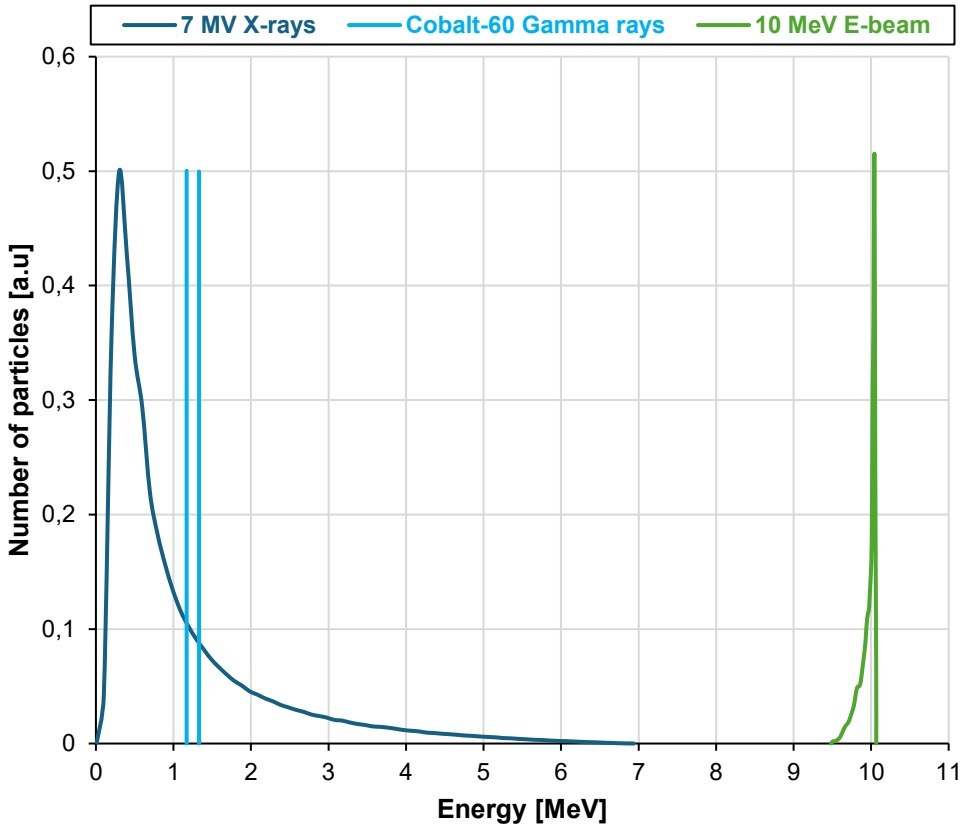
Nicolas Ludwig - Aerial
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sophie.rouif@ionisos.com

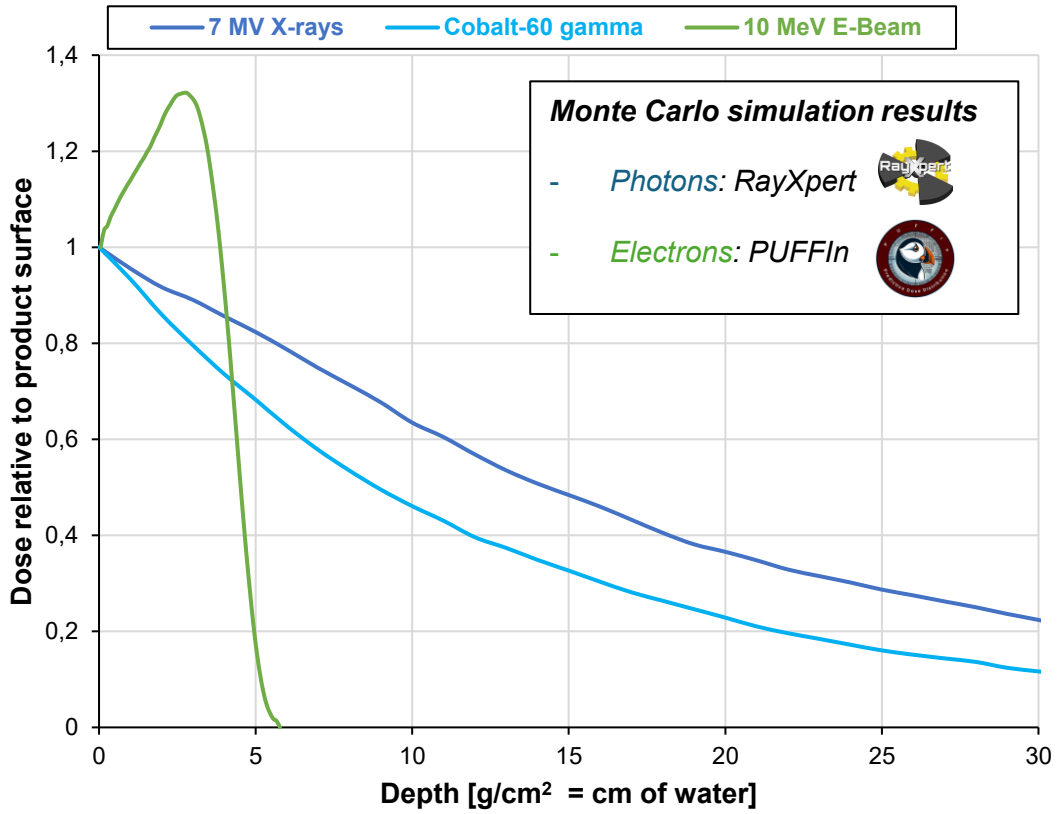
Conclusion
Context and Objectives

Energy distribution



7MV X-ray average energy ~ 1.1 MeV
^{60}Co gamma average energy ~ 1.25 MeV

Dose distribution



In some cases, a double-sided irradiation is needed to ensure a more homogeneous dose distribution

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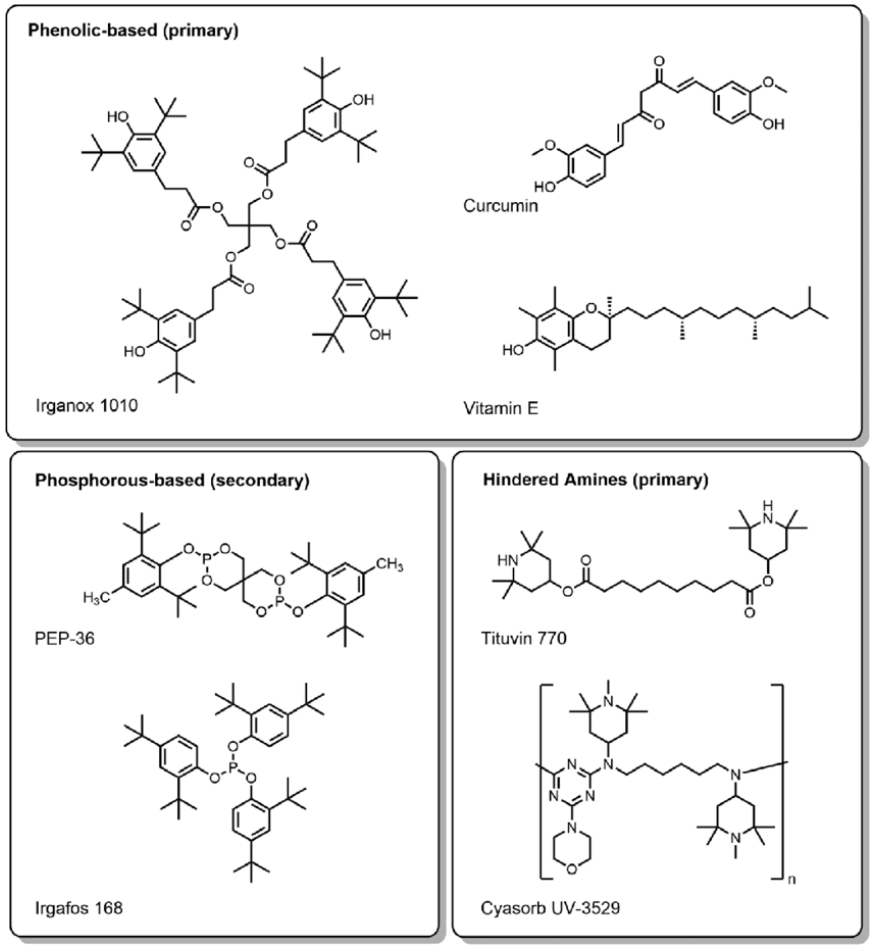
Influencing parameters
Influence of material compositon

- **ADDITIVES : Antioxidants**

Antioxidants are able to trap radical and stabilize material against radiation

- **Case of polyolefins:**
  - Phenolic oxidants are sensitive
  - Hindered Amines are more radiotolerant

- **Each formulation of plastic can behave differently**



There is a need to generate dataset on available commercial plastics to compare irradiation technologies

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