Introduction and selection of ionizing rays for polymers treatments

POLYRAY

March, 15-16th 2016
Nürtingen, Germany, by IST
more than UV

Service company for the treatment by ionizing radiations:

- Electron Beam (EB or accelerated electrons)
- Gamma Rays (photons from Cobalt 60)

Electron beam
Linac Accelerator

Cobalt 60 source

Activities:

- Sterilization of medical devices and pharmaceuticals: 60 %
- Aseptization of packagings and raw materials: 20 %
- Radiation Chemistry (cross-linking, grafting, radiolysis studies …): 15 %
- Food Ionization: 1 à 5 %

Figures :

- Activity dating back to the creation of Conservatome (Dagneux) in 1956
- Created in 1993 by merging
- n°1 in France, n°2 in Europe
- SME of 70 p

Radiation processing of polymers

IONISOS

Radiation processing with ionizing rays enables different types of chemical modification of polymers, **without adding an initiator**:

- Polymerization of resins, composites, inks, varnishes, adhesives …(see SUN presentation of Dr. Linzer)
- Crosslinking of thermoplastics (PE, PA) (see Dr. Gohs presentation)
- Functionalization of polymer substrates by Grafting (see Fraunhofer presentation by M. Weidauer)

Radiation processing of polymers

IONISOS

Depending on the objective of modification, we can choose a strategy of radiation chemistry :

Chemistry directly triggered under the rays: **simultaneous irradiation**

Free radicals can be created previously and use later after reactivation: **pre-Irradiation**

Without oxygen (N_2, Ar …)

Initiation $S_P \xrightarrow{\text{Ray } \gamma} S_P^{\bullet}$

$S_P^{\bullet} + M \longrightarrow S_{PM}^{\bullet}$

Propagation $S_{PM}^{\bullet} + nM \longrightarrow S_{PMn+1}^{\bullet}$

Le Moël, S. A. and C. Aymes-Chodur *Journal of Polymer Science Part B:* 2001 **39**(13): 1437-1448.

In presence of oxygen

Hydroperoxyde formation

$S_{PH} + O_2 \xrightarrow{\text{Ray } \gamma} S_{POOH}$

Thermal decomposition

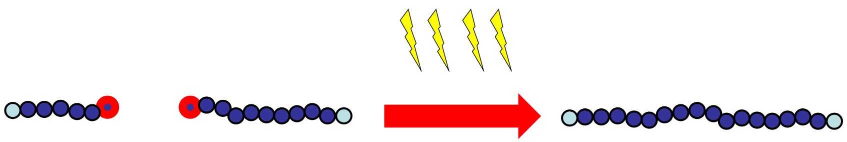
$S_{POOH} \longrightarrow S_{PO}^{\bullet} + {}^{\bullet}OH$

Initiation $S_{PO}^{\bullet} + M \longrightarrow S_{POM}^{\bullet}$

Propagation $S_{POM}^{\bullet} + nM \longrightarrow S_{POMn+1}^{\bullet}$

Strategy of radiation chemistry

Simultaneous irradiation



Currently use for **polymerization, crosslinking and on-line grafting**,

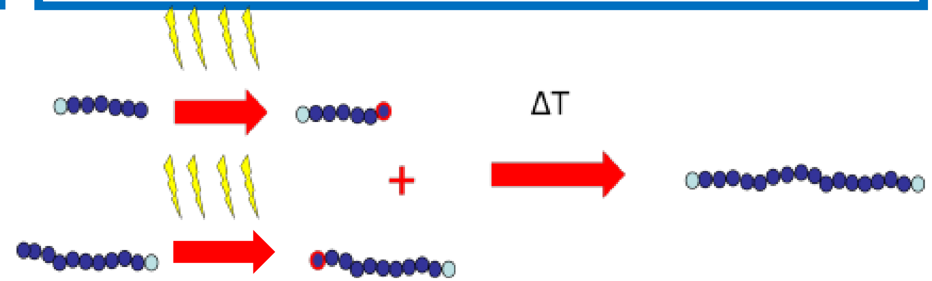
☺ One-step immediate reaction

☺ Higher yield

☺ In case of radiation sensitive polymers, promote addition vs chain breakage

☹ Substantial investment, except if use of sealed emitters.

Pre-irradiation



Currently use for **crosslinking of polymer alloys** and for **grafting**

For example, the reactivation can be operated in a extruder.

😐 2-steps reaction

☹ Lesser yield

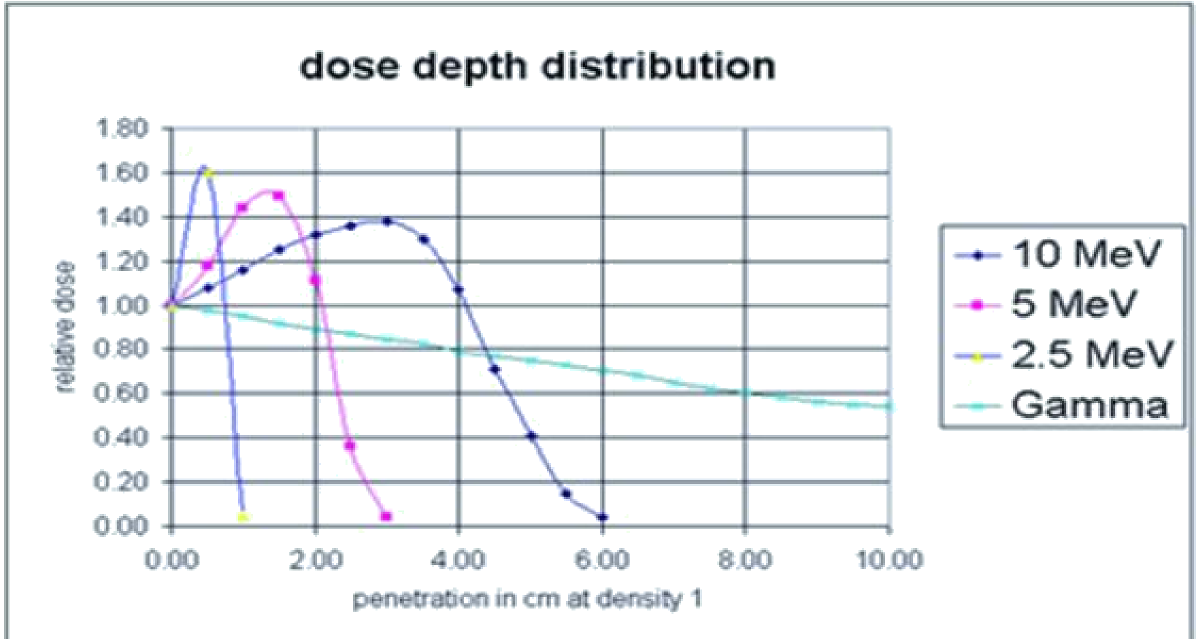
☺ Higher control of secondary reactions (chain breakage)

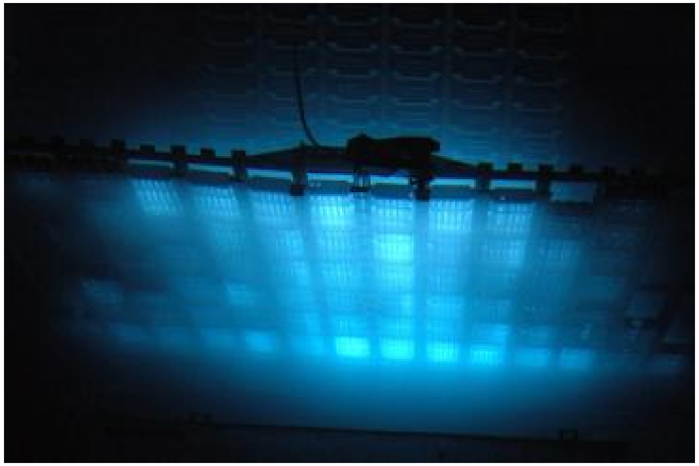
☺ Generally possible on existing facilities (services company).

Radiation technologies

Gamma Rays:

- Products generally process with an overhead conveyor, adapted to large products (1 m).
- Low dose rate = time for secondary reactions
  → in presence of oxygen, adapted for PRE IRRADIATION strategy
- Very high penetration due to the electromagnetic nature of the photons emitted by a cobalt 60 source.

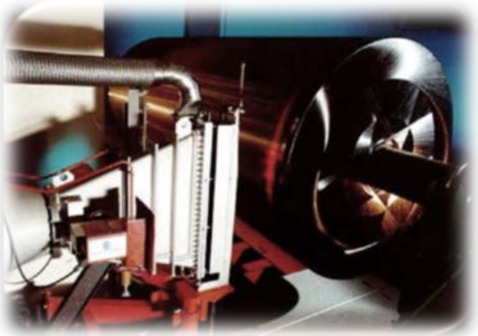




Radiation technologies

Electron beam:

- Products generally process continuously under the beam.

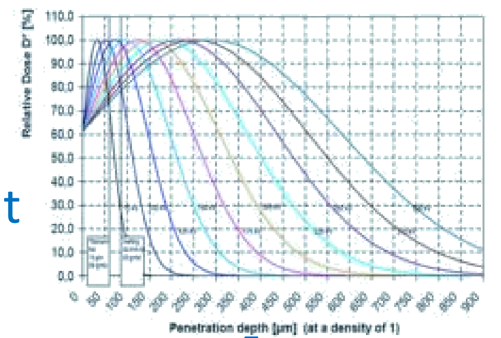


- Penetration is correlated to the energy of the incident electrons
- Treatment dose = quantity of electrons per surface unit measured in Gray (1 Gray = 1 Joule / kg = 1 W.s / kg)
- Dose = k . beam current / product speed (at given energy)

➡ Treatment parameters are electrically controlled

- Cold process (temp rise = 2,4°C / 10kGy)

(See Electron Beam presentation of Dr Bielmann)



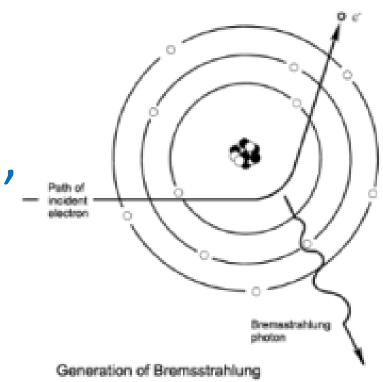
Energy determines Penetration

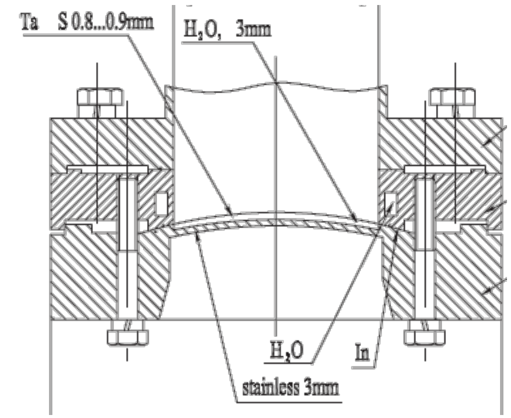
Power determines Throughput

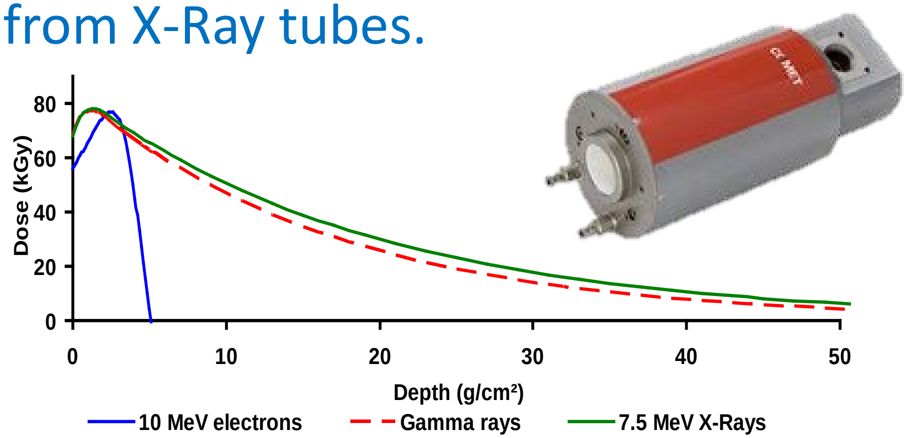
Radiation technologies

X Rays:

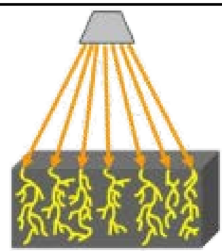
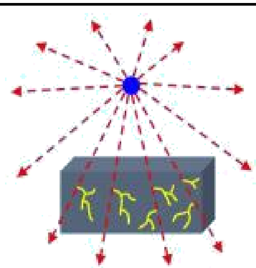
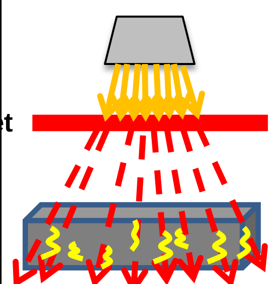
- Generated by electrons decelerated (bremsstrahlung) in high atomic number material (generally Tantalum),
- EB @150kW ≈ 12kW X-rays ≈ 1MCi, need high power EB to compete with large gamma centers,
- Dose can be adjusted (rotation, speed adjustment, collimators,…),
- Some applications directly derived from X-Ray tubes.







Summary

Radiation		Penetration depth	Incident Energy	Power	Dose rate
EB		Medium (from several µm to several cm)	80 keV to 10 MeV (low / medium / high)	1 kW to 700kW	kGy. Seconds
Gamma		High (≈ 1m)	Co^{60} : 1,17 and 1,33 MeV	Source activity (in Curies Ci)	From 0,5 to 25 kGy/h (2 kGy/h in average on an industrial facility)
RX	target 	High (≈ 1m)	Correlated to the energy of the EB used to generate RX	12kW for an EB of power 150kW	kGy. Minutes

NACRE

Industrial Irradiation Consulting and Services

in association with

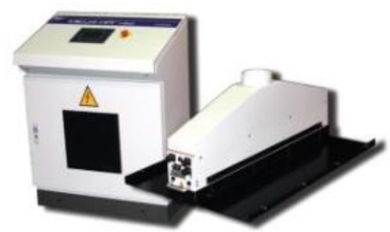
RADSYS

NEW ENERGY, NEW PERFORMANCE

Offering high level expertise in

InfraRed (IR/NIR)

Ultra Violet (UV)



Electron Beam (EB)

Process Development

- Process Consulting
- Proof of Concept Trials
- Process Development
- Short-Run Production

Process Integration

Taylor-made solutions

Machine Maintenance

Customer Service

Training

Thank you for attention

Sophie ROUIF
IONISOS
Parc Dombes Côtière
Activités
01120 Dagneux
sophie.rouif@ionisos.fr

Francis MARTIN
NACRE
21 rue des Alouettes
78700 Conflans
Sainte-Honorine
fm@nacre.fr

POLYRAY