POLITECNICO
MILANO 1863

CHERNE 2018 - 14th Workshop on European Collaboration in Higher Education on Radiological and Nuclear Engineering and Radiation Protection *Macugnaga*

IONIZING RADIATION EFFECTS ON POLYMER BIODEGRADATION

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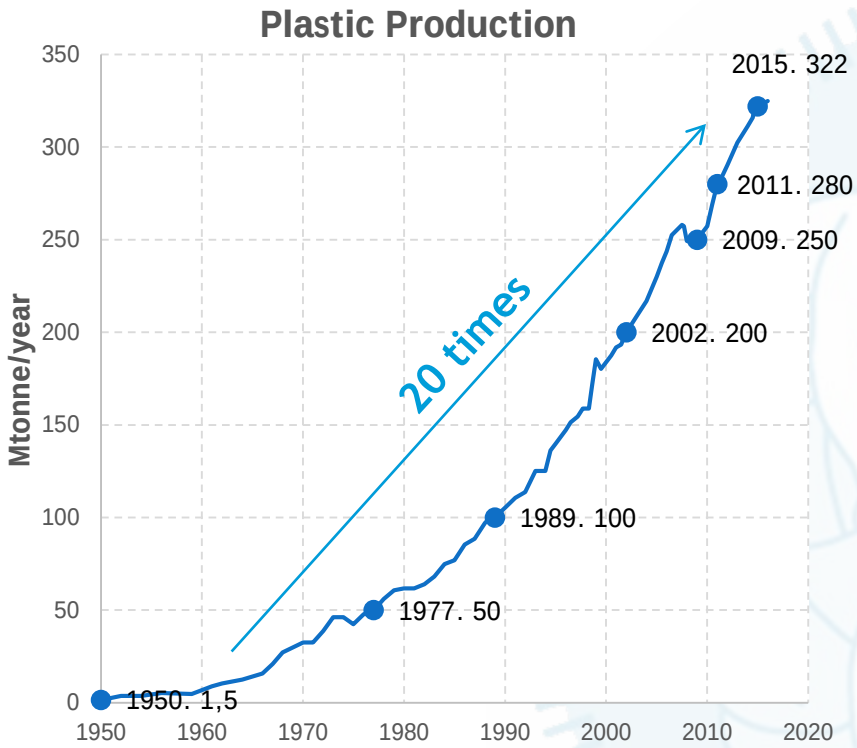
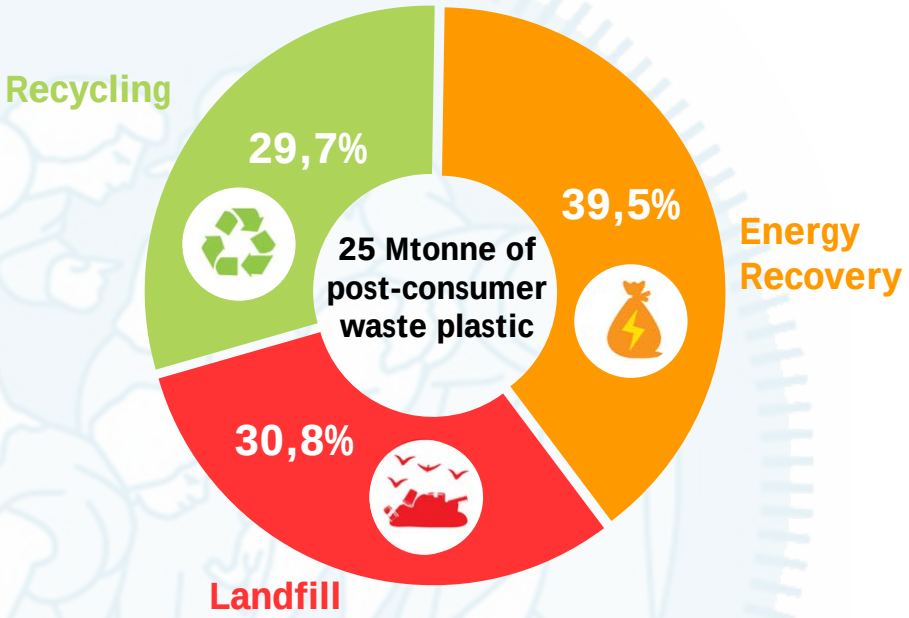
31/05/2018

PLASTICS

In 2015 the plastic production exceeded **322 million tons** all over the world, with **packaging** covering the 26%. However, due to the specific function it **rapidly becomes waste**.





Recycling and incineration are not always practicable and still a huge amount of plastic is disposed into the environment.

Introduction and Motivation

Plastics

Recently great concern has risen about the **health** and **environmental** effects caused by plastic waste.

PLASTICS

With time, plastic does not decompose…

it only becomes smaller generating **microplastics**

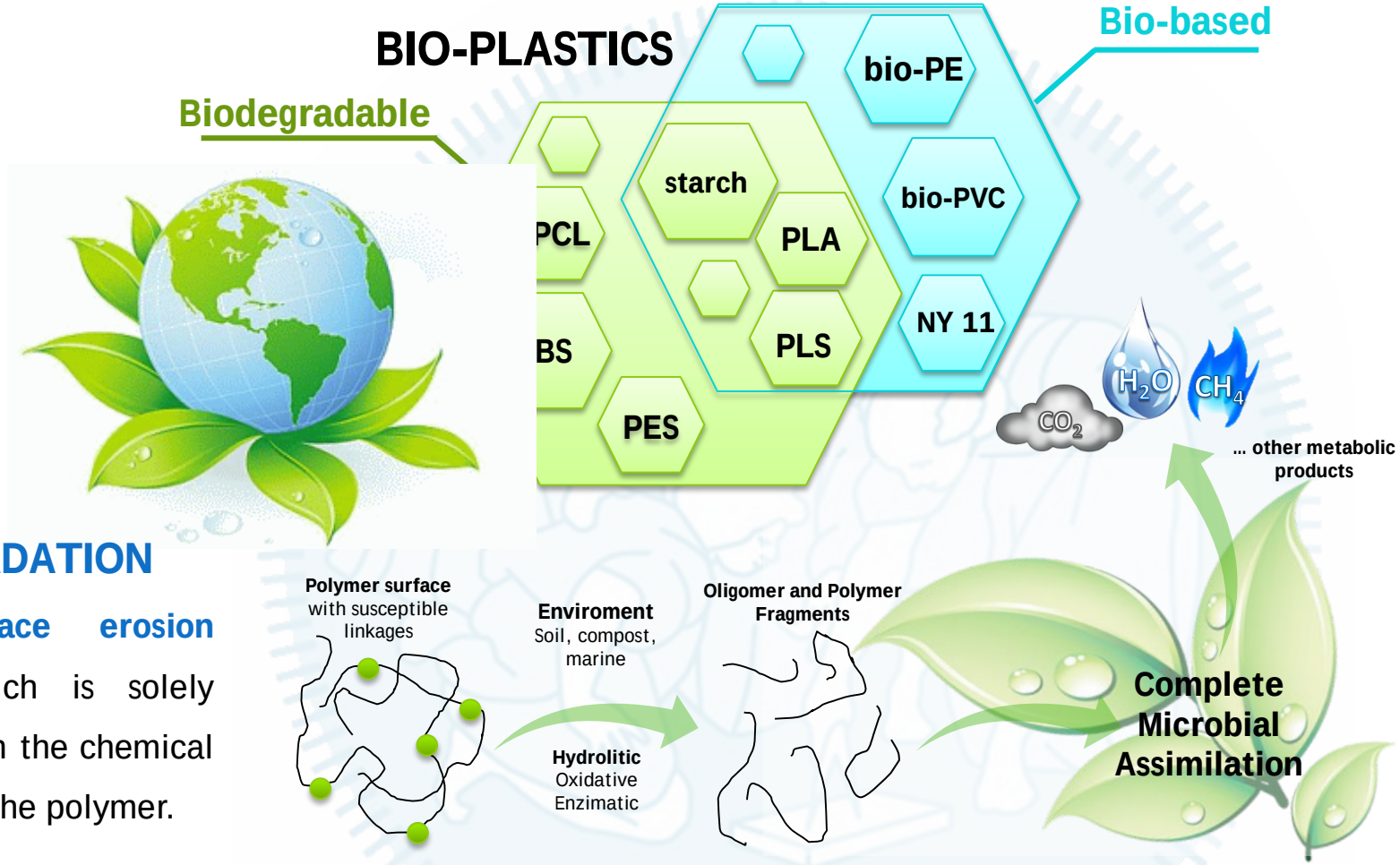
Cause of environmental pollution

How to enhance plastic degradability?

No chemical, physical or biological processes can efficiently enhance plastics degradation.

PLASTICS

Creation of new polymeric materials satisfying the conditions of **BIODEGRADABILITY**, **BIOCOMPATIBILITY** and release of **LOW TOXICITY** degradation products.



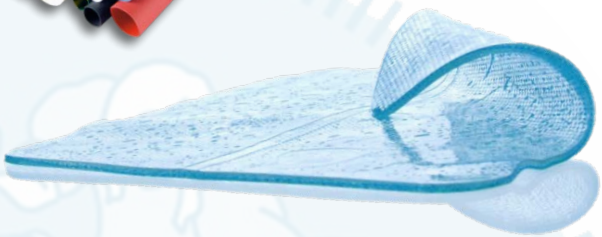
BIODEGRADATION

is a **surface erosion process** which is solely dependent on the chemical structure of the polymer.

IRRADIATION OF POLYMERS

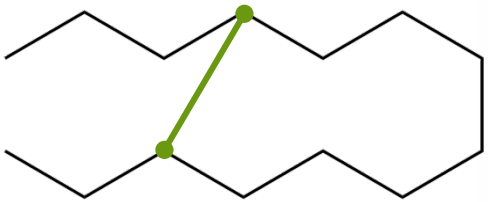
Ionizing radiation is widely used on polymers and it can also **modify** their properties:

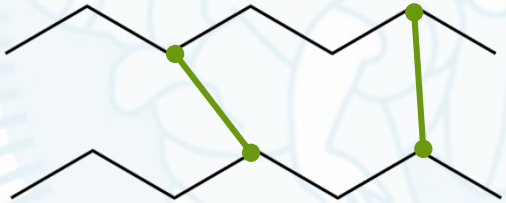
- ***Radiation processing***
- ***Sterilization*** of medical supply
- Packaging for ***food irradiation***
- ***Nuclear and aerospace*** applications



Irradiation causes the creation of very reactive **radicals** and leads to two competing phenomena:

Crosslink





Degradation

OBJECTIVES

- Effects of **gamma radiation** on aliphatic **biopolymers**
  - Characterization of Chemical and Physical modifications
- Impact of ionizing radiations on the rate of **biodegradation**
- Evaluate if a radiation treatment could enhance the biodegradability of conventional and new plastics

COLLABORATIONS

UNIVERSITÀ DI BOLOGNA
Department of Civil, Chemical, Environmental, and Materials Engineering

gammatom Irradiation facility

POLITECNICO DI MILANO
Department of Aerospace Science and Technology
Positron Spectroscopy and Thermal Analysis Laboratory
Chemistry, Material and Chemical Engineering Department "Giulio Natta"

SELECTED SYSTEMS

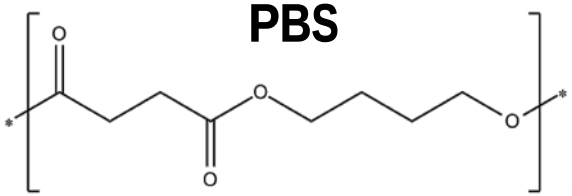
Newly synthesized and conventional aliphatic polymers for **packaging**:

PBS-PTDGS copolymers

BIODEGRADABLE

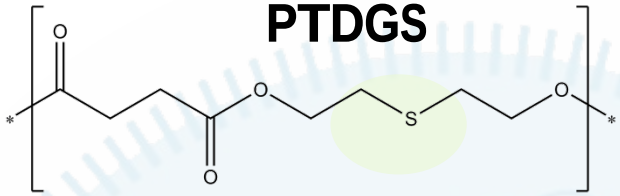
Poly(Butylene Succinate)

PBS



Poly(Thiodiethylene Glycol Succinate)

PTDGS



NEWLY SYNTHESISED

Film 200 µm

Sheet 1 mm

P(BSxPTDSy) y= 10-40

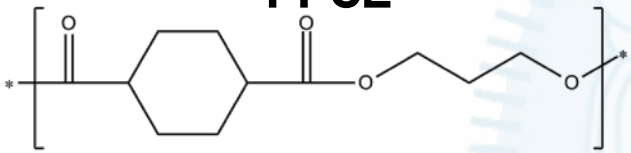
MONTHS

PPCE-PNCE copolymers

SLOW DEGRADING

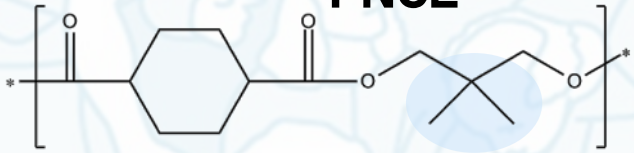
Poly(Propylene Cyclohexanedicarboxylate)

PPCE



Poly(Neopentyl Cyclohexanedicarboxylate)

PNCE



NEWLY SYNTHESISED

Film 200 µm

Sheet 1 mm

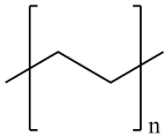
P(PCExNCEy) y= 5-20

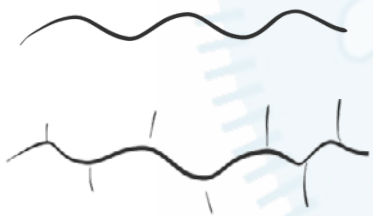
YEARS

PE

RECALCITRANT

Polyethylene





LDPE 15 µm

HDPE 10 µm

COMMERCIAL

DECADES

EXPERIMENTAL ACTIVITY

MOULDING

films 200 µm (Thermo-hydraulic press 5 min @ T_m+30°C)

IRRADIATION

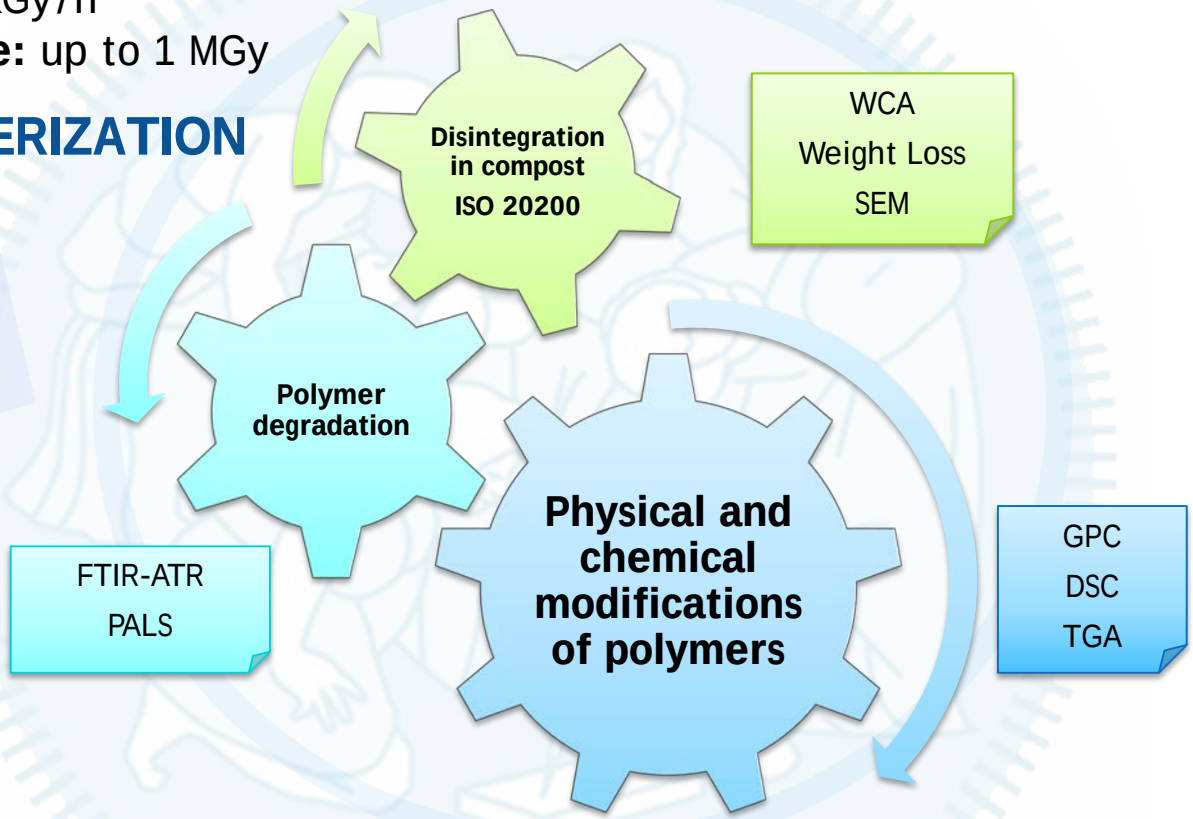
Source γ: Co-60

Environment: Air / Oxygen / Water / Hydrogen Peroxide 2% - 15%

Dose Rate: 2.5 kGy/h

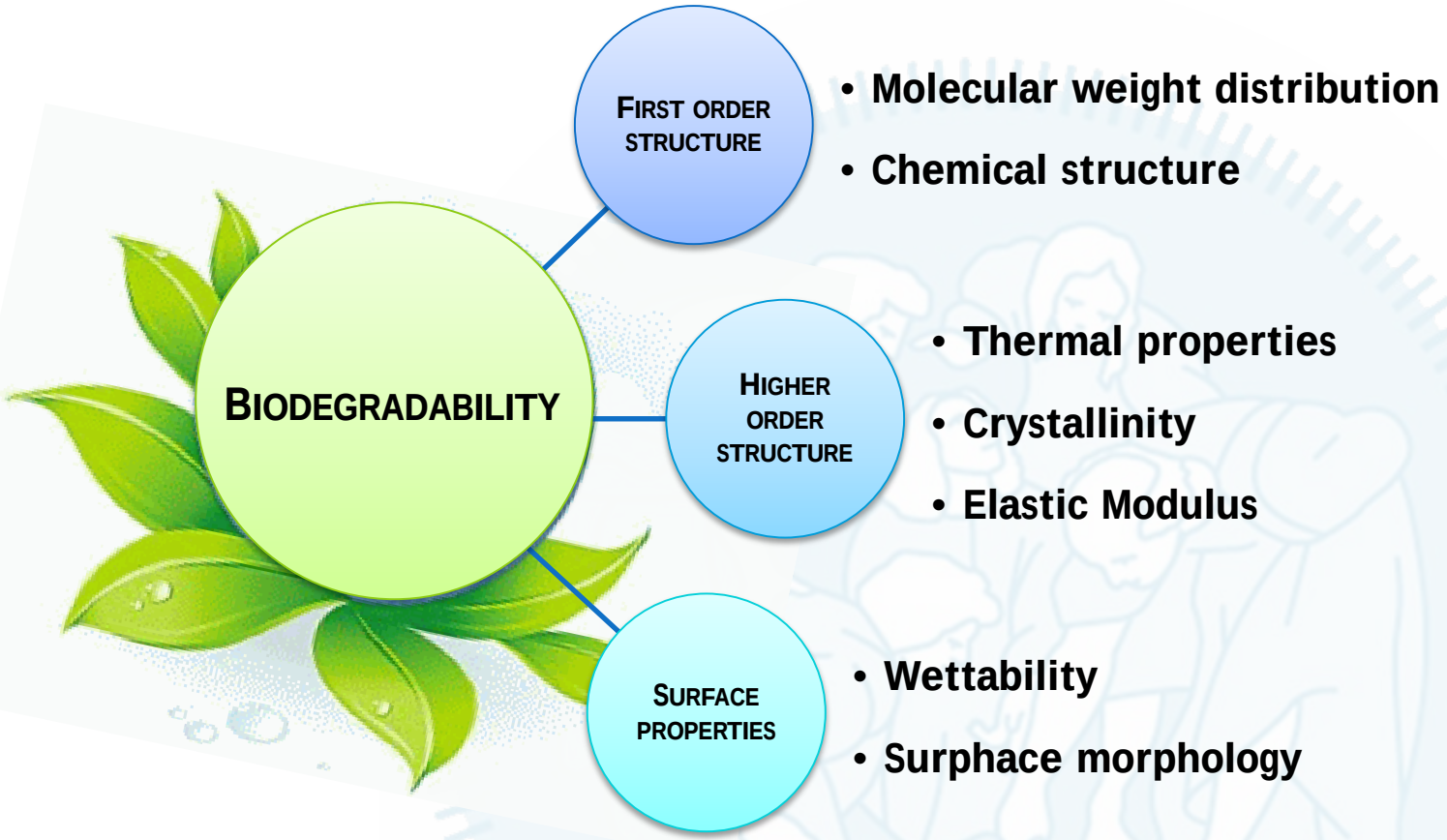
Absorbed Dose: up to 1 MGy

CHARACTERIZATION



EXPERIMENTAL ACTIVITY

The rate of biodegradability depends on both physical and chemical properties:



MOLECULAR WEIGHT: BIODEGRADABLE SYSTEM

Irradiation in **Air**

PBS

Yields of intermolecular crosslink G_x and scissioning G_s:

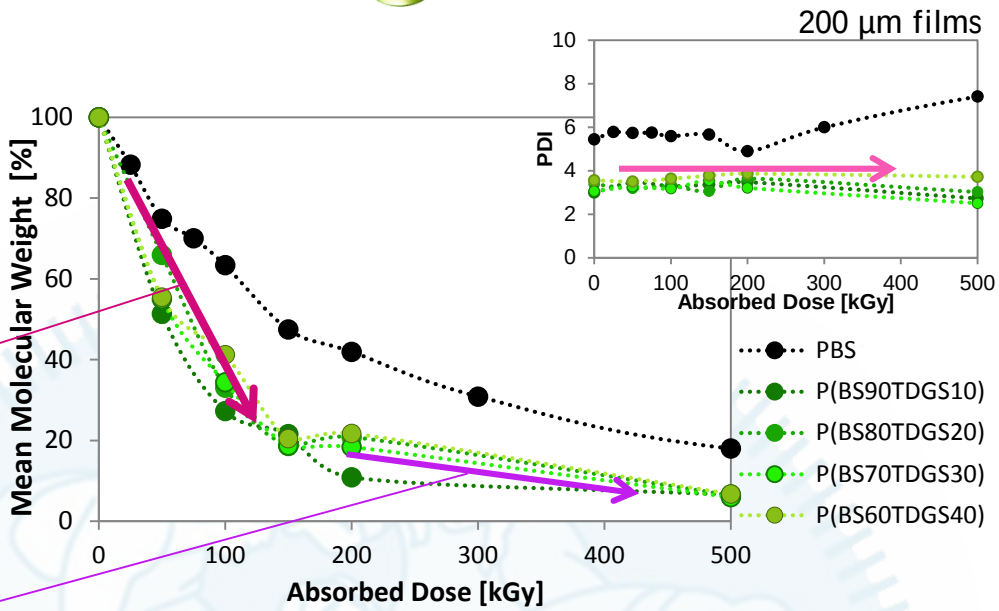
$$\frac{1}{\overline{M_n}} = \frac{1}{\overline{M_{n,0}}} + (G_s - G_x)D_x \cdot 1.038 \cdot 10^{-7}$$

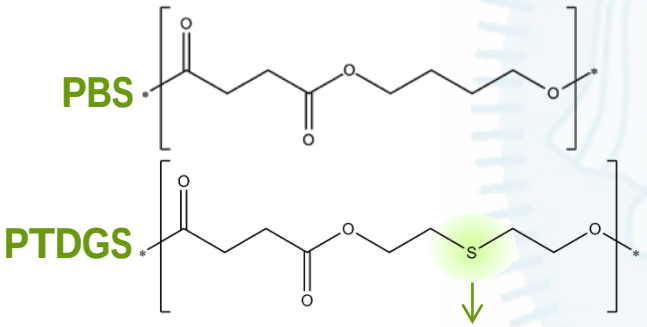
Ionization and excitation

Formation alkyl free radicals

degradation

Hydrogen abstraction increase of **crosslink**





lower ionization potential and weakness of the C-S bond

Degradation higher for the copolymers

Polymer	Dose (kGy)	200 µm G_s	200 µm G_x	200 µm G_s/G_x
PBS	50	1.84	0.35	**5.24**
	100	1.57	0.28	**5.55**
	200	1.82	0.29	**6.35**
	500	2.53	0.51	**5.00**
P(BS60TDGS40)	50	8.76	0.52	**16.73**
	100	4.39	0.53	**8.28**
	200	3.95	0.52	**7.62**
	500	5.05	0.71	**7.08**

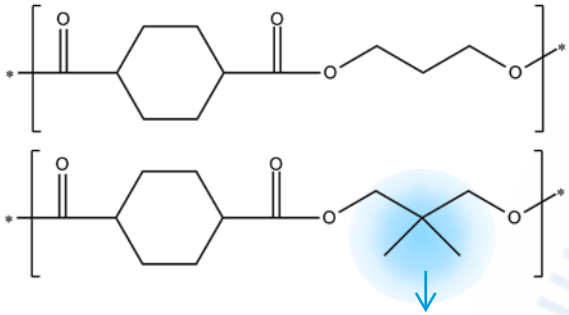
FIRST ORDER STRUCTURE - GEL PERMEATION CHROMATOGRAPHY

MOLECULAR WEIGHT: INTERMEDIATE SYSTEM

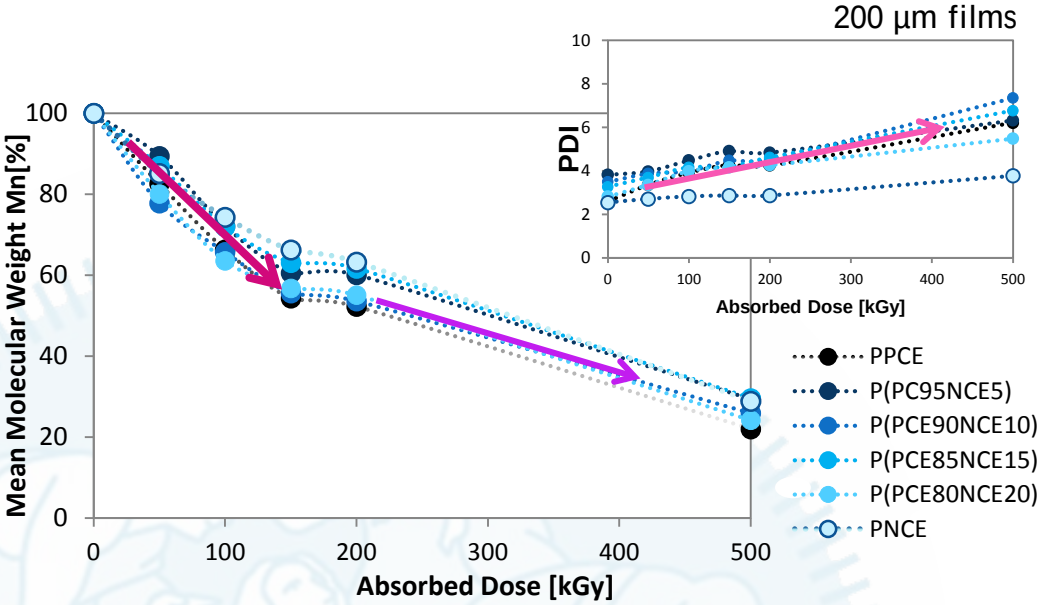
Irradiation in **Air**

PPCE

The introduction of NCE co-unit does not affect the stability of the system.



Favors homolytic chain scission
Steric hindrance limits recombination



$G_s/G_x \approx 4$ indicates an higher presence of crosslink

Not remarkable differences with the samples irradiated in water up to 200 kGy

POLYMER	Dose (kGy)	200 µm G_s	200 µm G_x	200 µm G_s/G_x
PPCE	50	3.93	0.79	4.94
	100	3.45	0.72	4.80
	200	2.70	0.54	5.02
	500	3.68	0.76	4.87
P(PCE80NCE20)	50	2.61	0.58	4.50
	100	3.01	0.67	4.50
	200	2.12	0.46	4.62
	500	3.19	0.63	5.03

FIRST ORDER STRUCTURE - GEL PERMEATION CHROMATOGRAPHY

CHEMICAL MODIFICATIONS

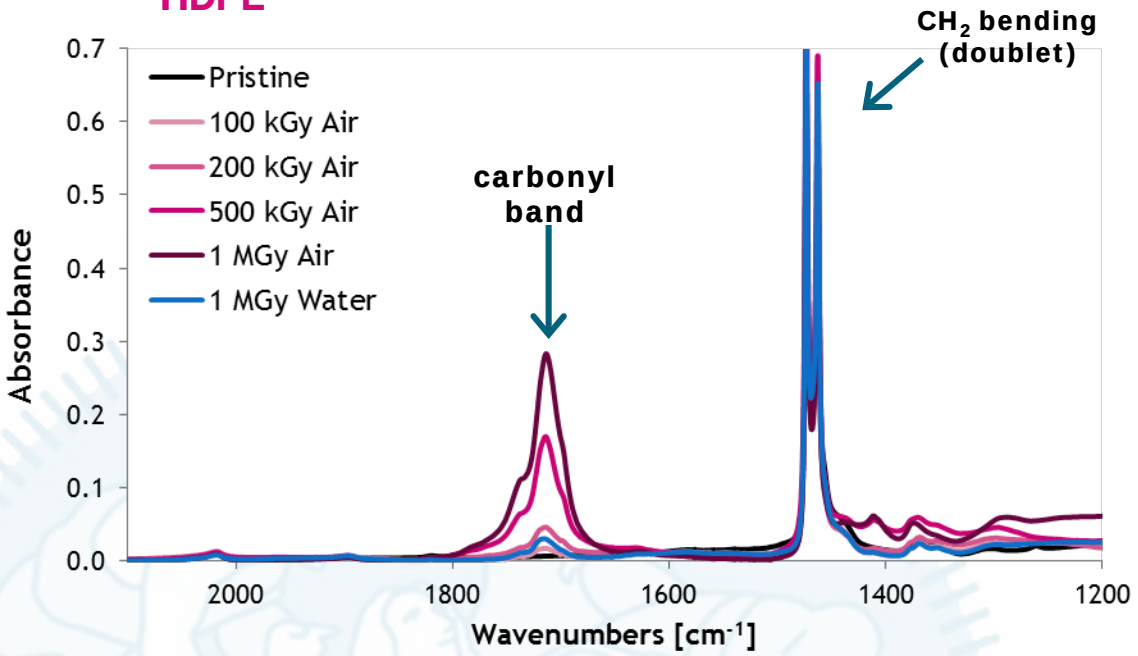
HDPE

- increase of oxidation with increasing the absorbed dose.
- Absorbed doses higher than 100 kGy evidenced higher oxidation.
- hydrogen peroxide solutions and oxygen atmosphere enhances the oxidation with respect to air.

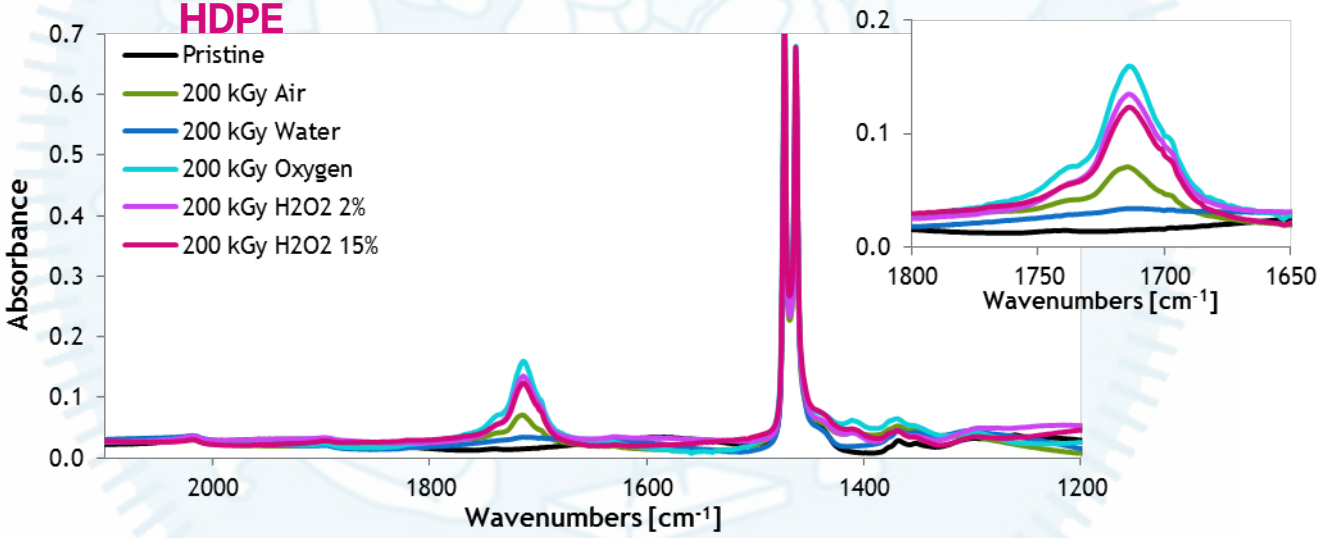
LDPE

- FTIR-ATR: increase of oxidation at absorbed doses above 200 kGy.

HDPE



HDPE

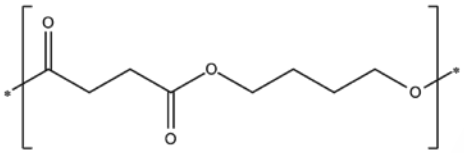


THERMAL PROPERTIES

The thermal stability of all the systems is affected:

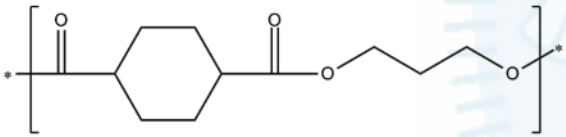
PBS

- Melting temperature constant
- Increse of melting enthalpy
- No differences air/water

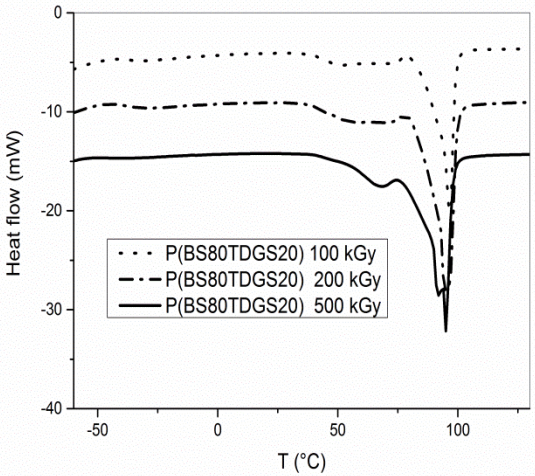


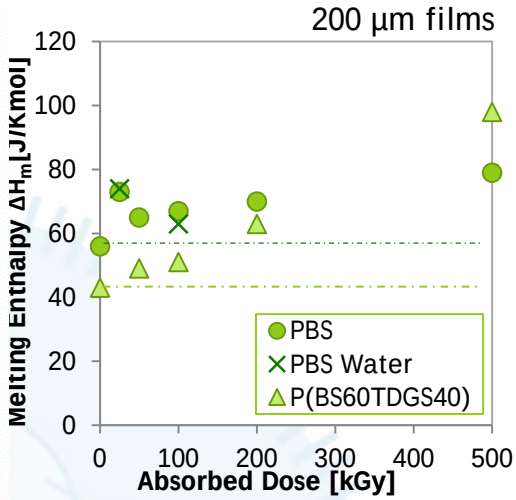
PPCE

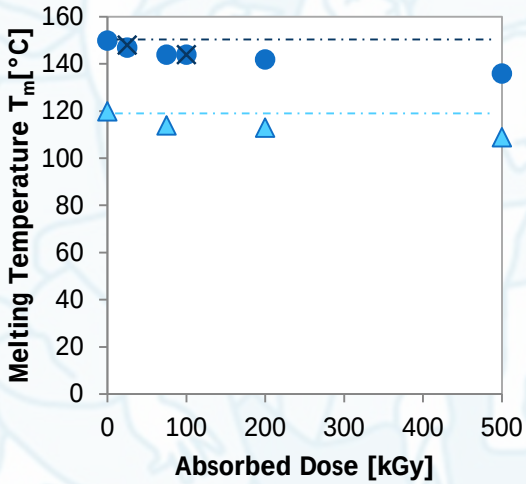
- Slight decrease of melting temperature
- Constant melting enthalpy
- No relevant differences air/water

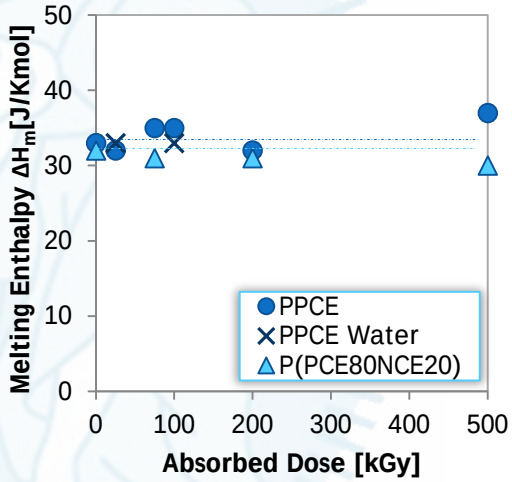


Second melting peak at lower temperature was observed for the treated samples, in particular for copolymers of PBS and PPCE.









HIGHER ORDER STRUCTURE - DIFFERENTAL SCANNING CALORIMETRY

THERMAL PROPERTIES: ENVIRONMENT

Crystallinity increases for all the irradiation environments and remains constant above 200 kGy

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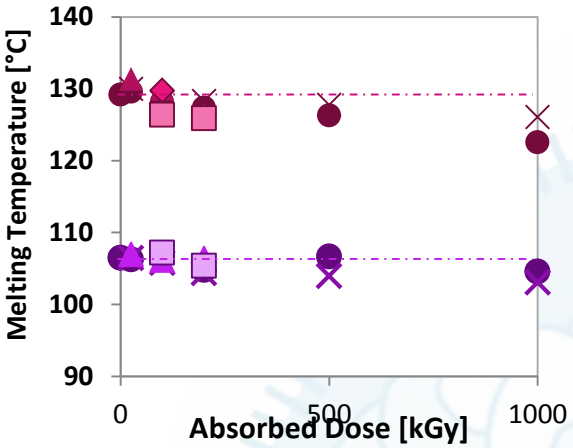
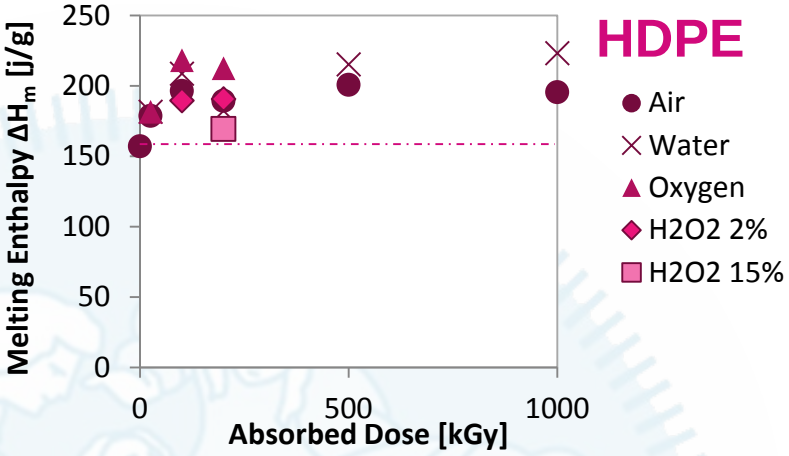
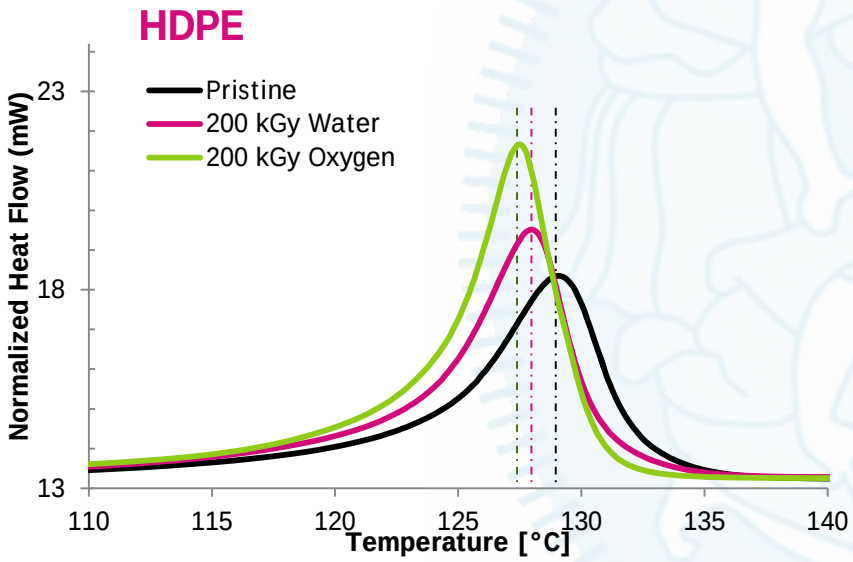
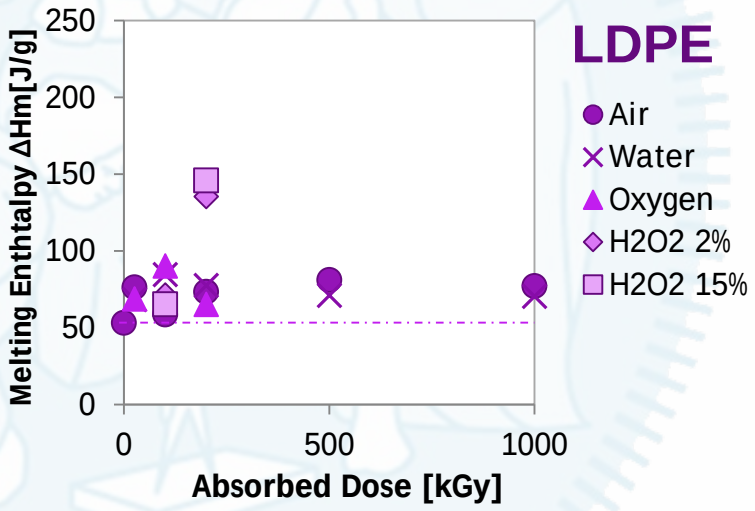








HIGHER ORDER STRUCTURE - DIFFERENTAL SCANNING CALORIMETRY

WETTABILITY

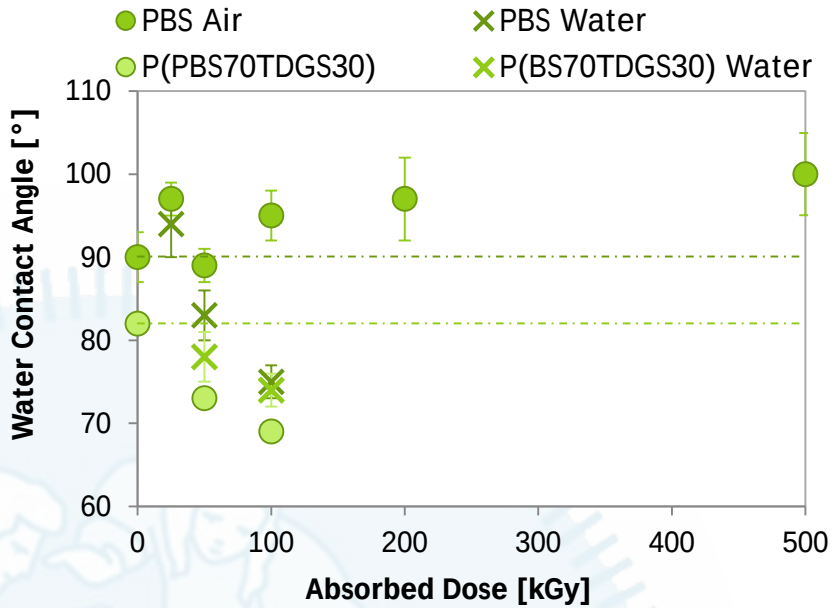
Water Contact Angle measurements show a different effect of radiations:

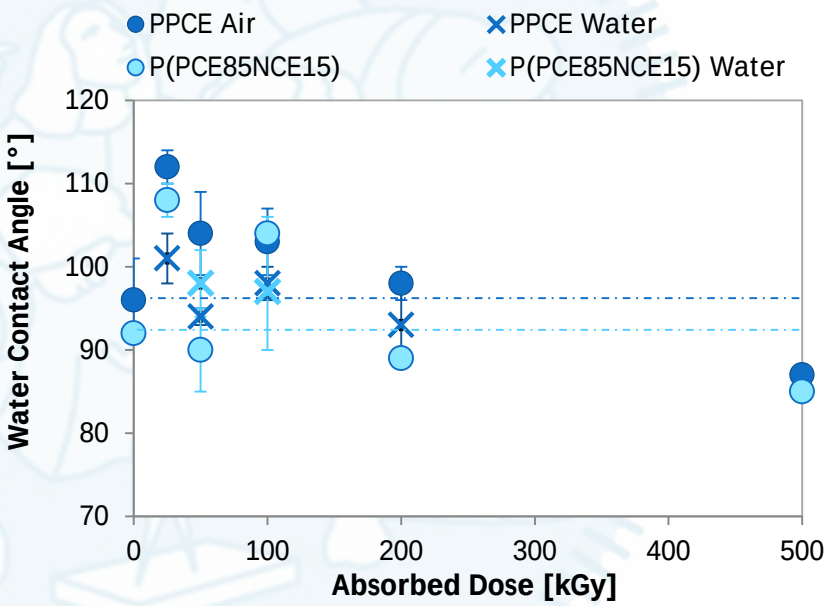
PBS

- Irradiation in air does not increase PBS hydrohilicity
- Positive effect for irradiation in water
- Irradiation enhanced copolymers wettability

PPCE

- Wettability increased only for absorbed doses over 200 kGy
- No improvement for the copolymers



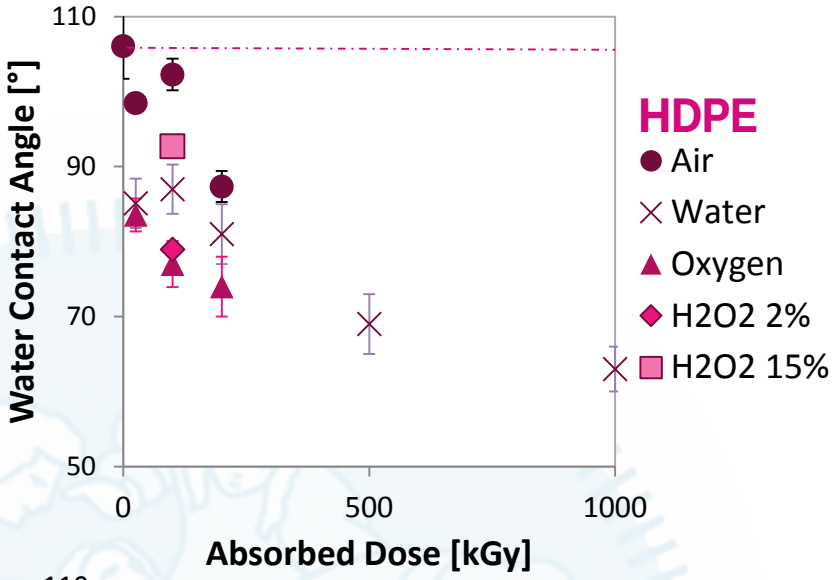


RESULTS

WETTABILITY

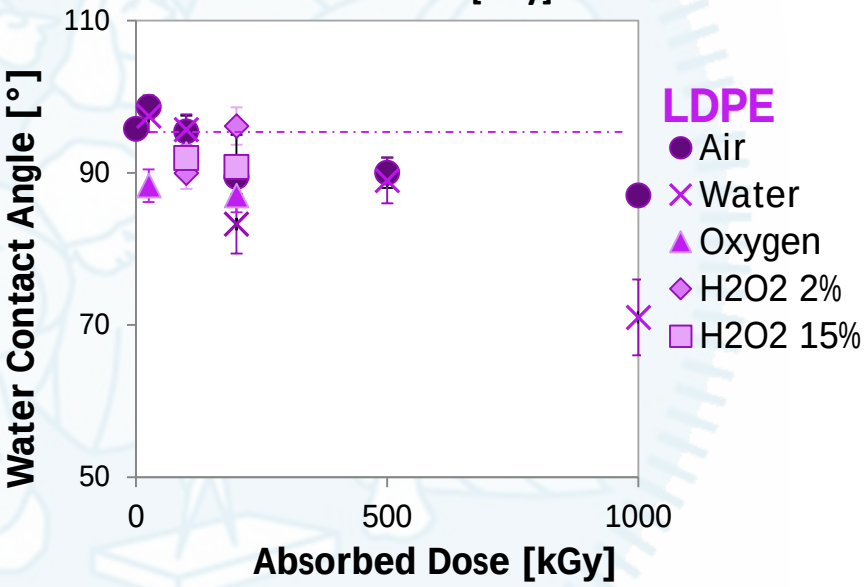
HDPE

- hydrophilicity is strongly enhanced, especially when irradiated in water and oxygen



LDPE

- wettability is slightly enhanced
- relevant decrease at 1 MGy in water



SURFACE PROPERTIES – WATER CONTACT ANGLE

BIODEGRADABILITY

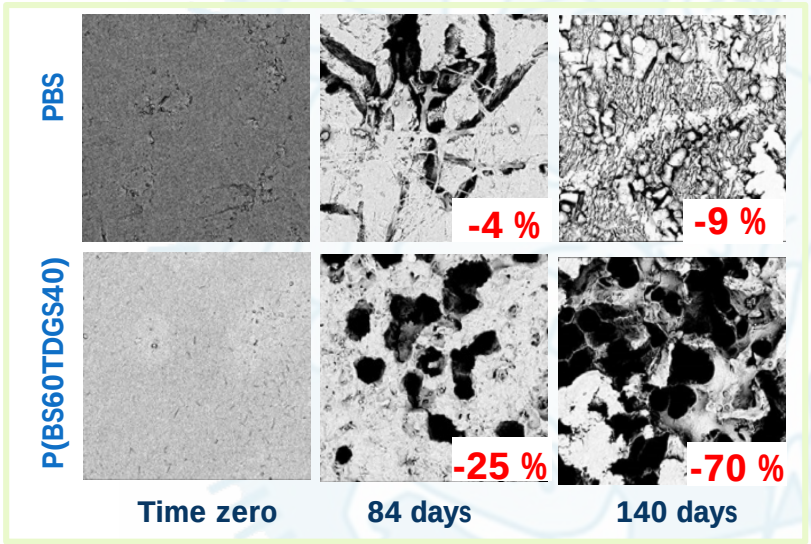
The degree of disintegration in compost of the irradiated samples were investigated with a procedure based on the standard **ISO 20200**

From literature…

Pristine samples

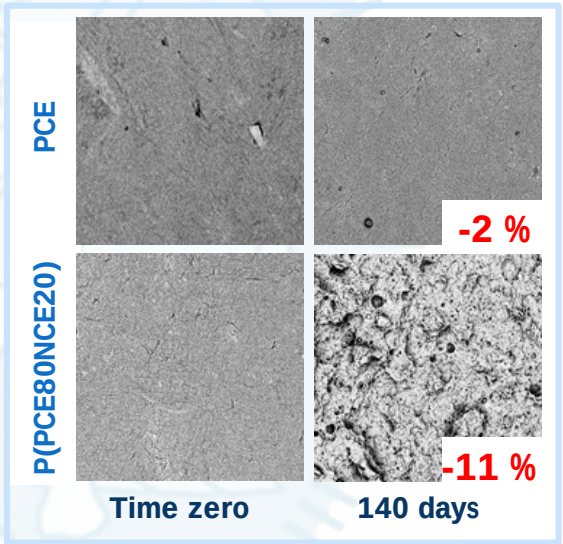
COMPOSTING TEST

PBS-PTDGS System[2]



PPCE-PNCE System[1]

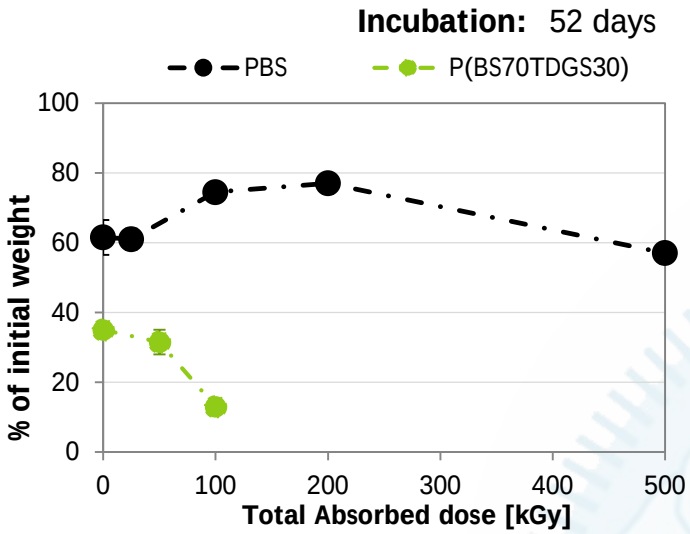
SEM images on films of 200 µm.



[1] L. Genovese et al. eXPRESS Polymer Letters 9 (2015), pp. 972-983

[2] L. Genovese et al. Polymer Degradation and Stability xxx (2016) pp- 1-11 Article in press

BIODEGRADABILITY: BIODEGRADABLE



PBS

Biodegradability in compost is favored when irradiated in water, at 25 kGy (residual weight 44%)

COPOLYMERS

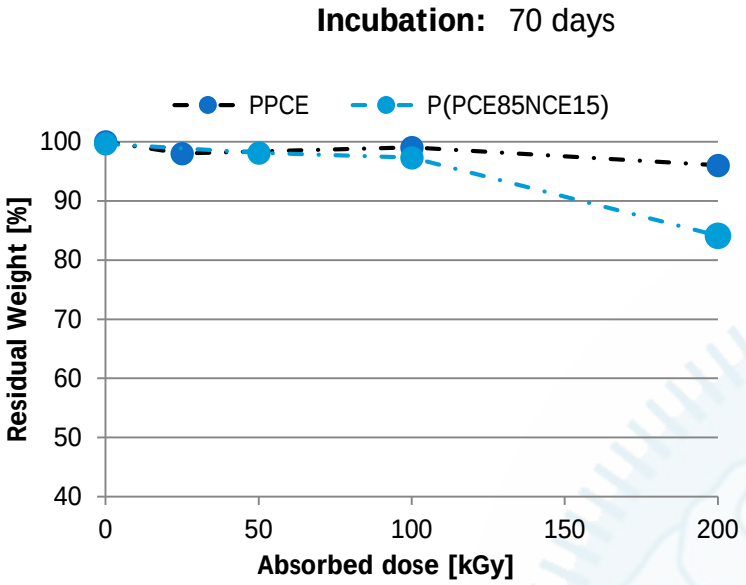
Increased disintegration

Higher with the TDGS content

M.Negrin et al. (2017) *Rad. Phys. Chem.* In press

COMPOSTING TEST

BIODEGRADABILITY: SLOW DEGRADING



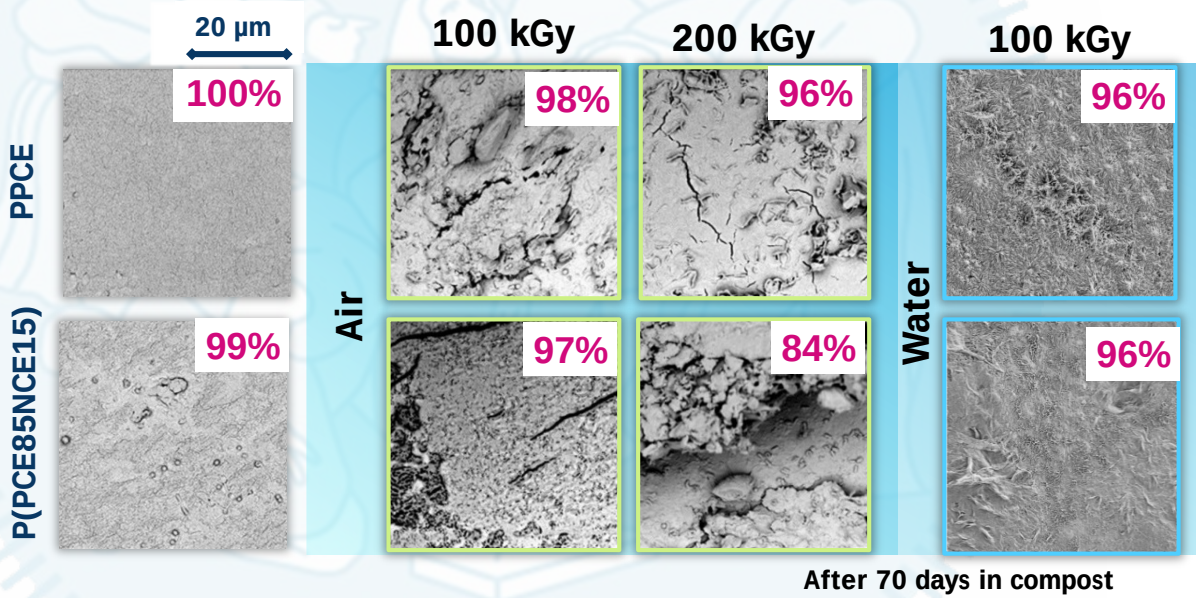
PPCE

Absorbed doses over 200 kGy lead to major improvements

Treatment in water seems to be favorable

COPOLYMERS

Faster biodegradation



COMPOSTING TEST

RECALCITRANT

PE biodegradation rate is about 20 years…
different techniques to monitor the beginning of the degradation process:

DSC - Further increase of ΔH_m
FTIR - Increase of the absorbance of C=O band

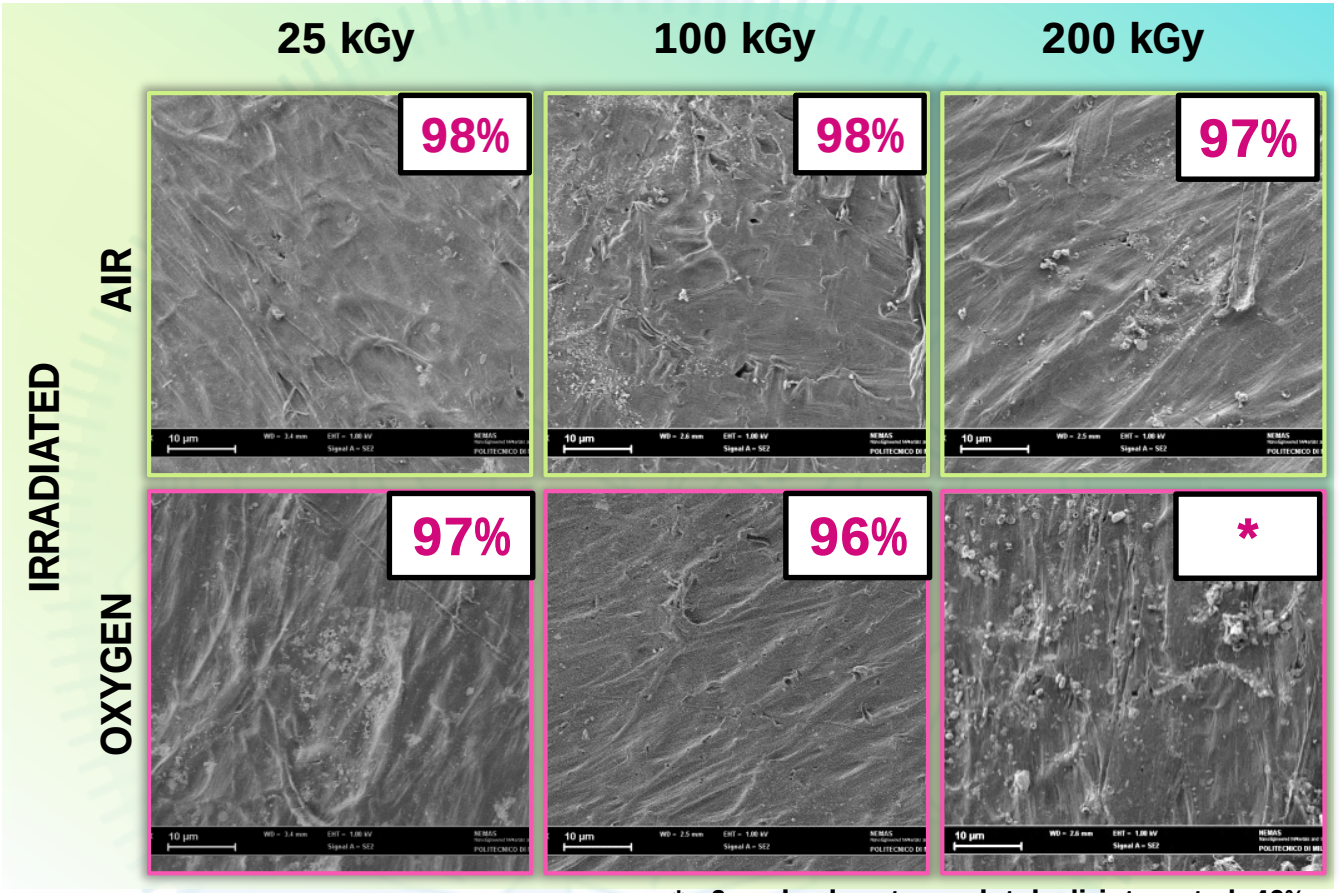
Incubation period: *180 days*

HDPE

- Samples irradiated in water did not show any improvement;
- biodegradability is slightly affected;
- the highest degradation is observed in oxygen.

LDPE

- less degraded than HDPE films;
- small evidences only above 200 kGy.



* Sample almost completely disintegrated~40%

COMPOSTING TEST

CONCLUSIONS

Can ionizing radiation enhance plastic biodegradability?

- According to the polymer structure, different absorbed doses and/or irradiation environments could be required to affect biodegradation;
- Radio-induced decrease of **molecular weight** and increase of surface **wettability** enhance biodegradability, even in the case of slow degrading polymers;
- The radiation induced modifications of the **crystalline fraction** seem not to produce a negative effect on biodegradability;
- It is worth noting that irradiations in **oxidative conditions** at relatively low absorbed doses strongly affect PE wettability.

Future activities

- Assess the time to complete degradation;
- Optimize the composting steps: enzymes/composting strategy;
- Combination with other degradation process: thermal degradation, .. ;
- From biodegradation to compostability.


Thank
you