The Abdus Salam International Centre for Theoretical Physics

2227-1b

Joint ICTP-IAEA Workshop on Radiation Resistant Polymers

14 - 18 March 2011

"The use of gamma irradiation for biopolymers development for food packaging application"

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Workshop on Radiation Resistant Polymers

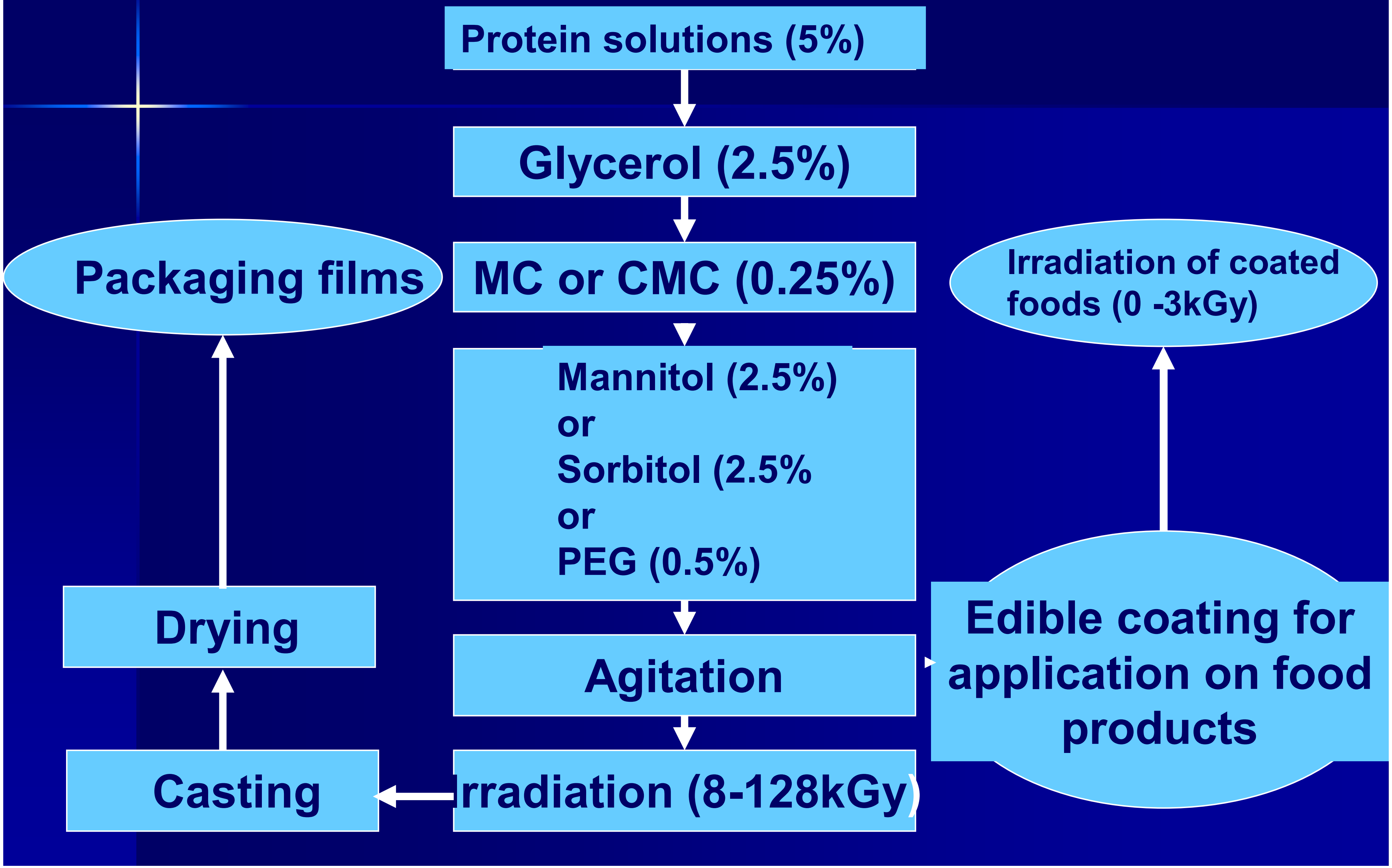
Trieste, March 14-18, 2011

Production of crosslinked natural polymers containing WPi and caseinate proteins using γ-irradiation for the development of bioactive coating and packaging

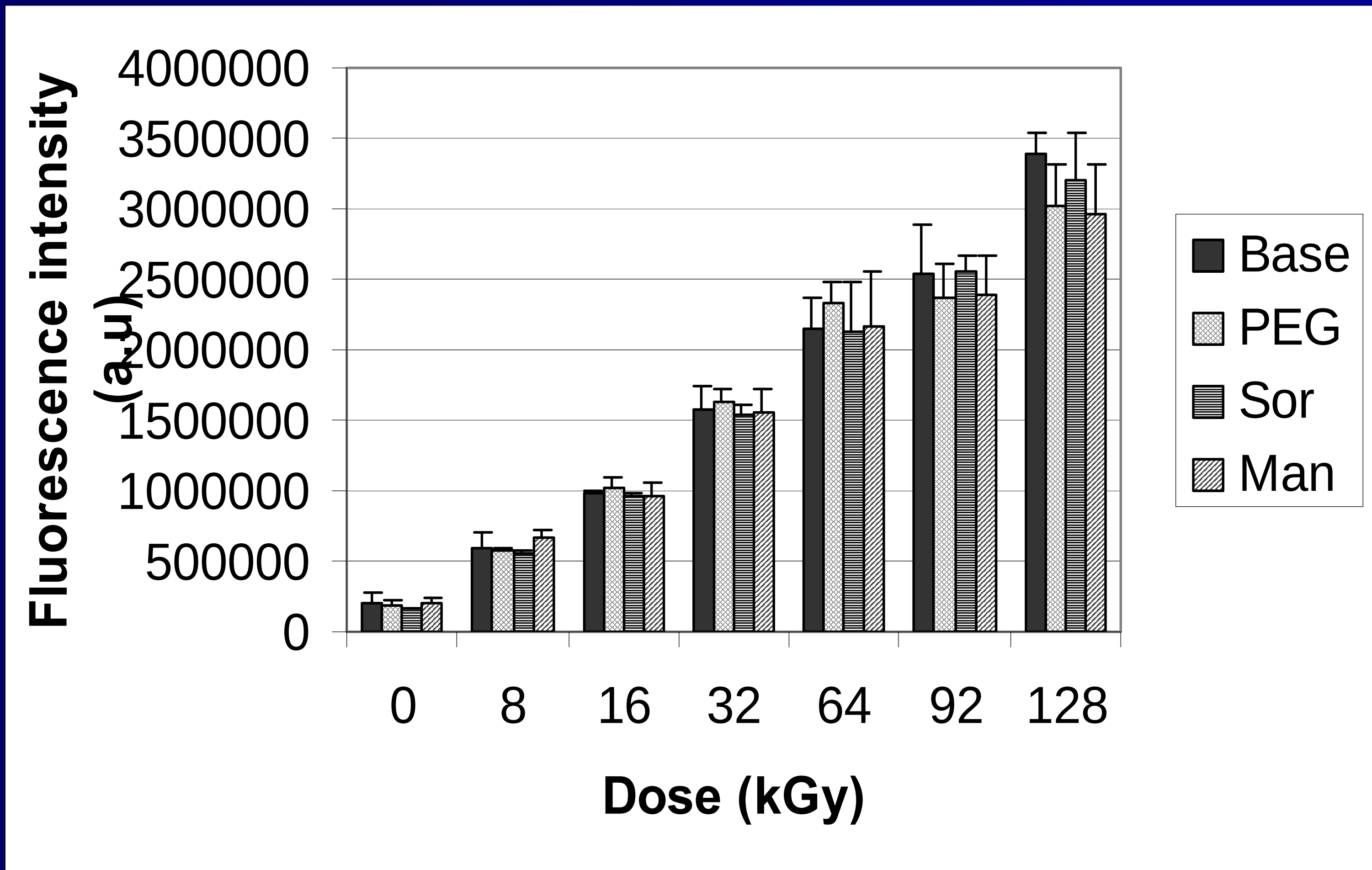
Objectives of the study

- Develop an active edible crosslinked coating and packaging containing natural antimicrobials.
- Use irradiation in combined treatments in order to increase the bacterial radiosensitization and the the shelf life of foods.

Film preparation

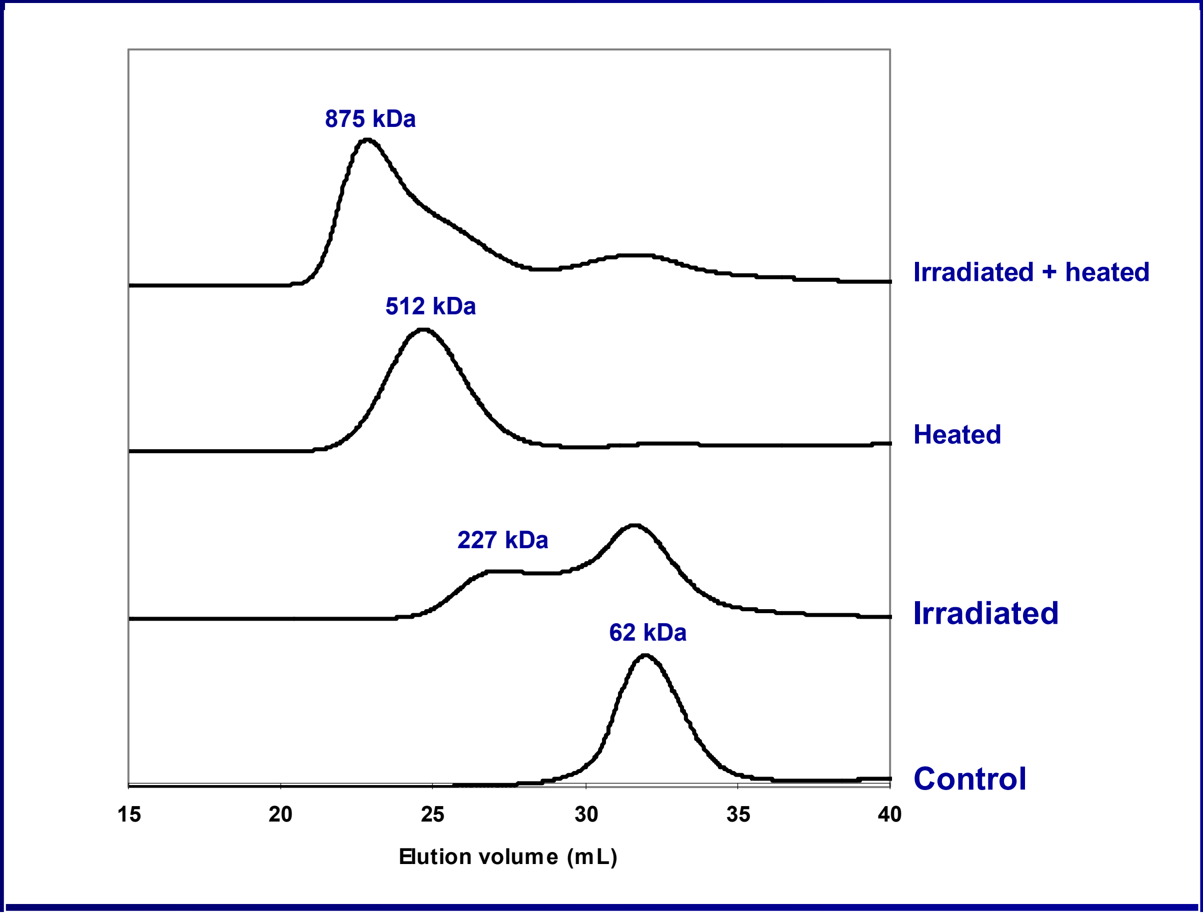


Formation of bityrosine in calcium caseinate films as a function of irradiation dose

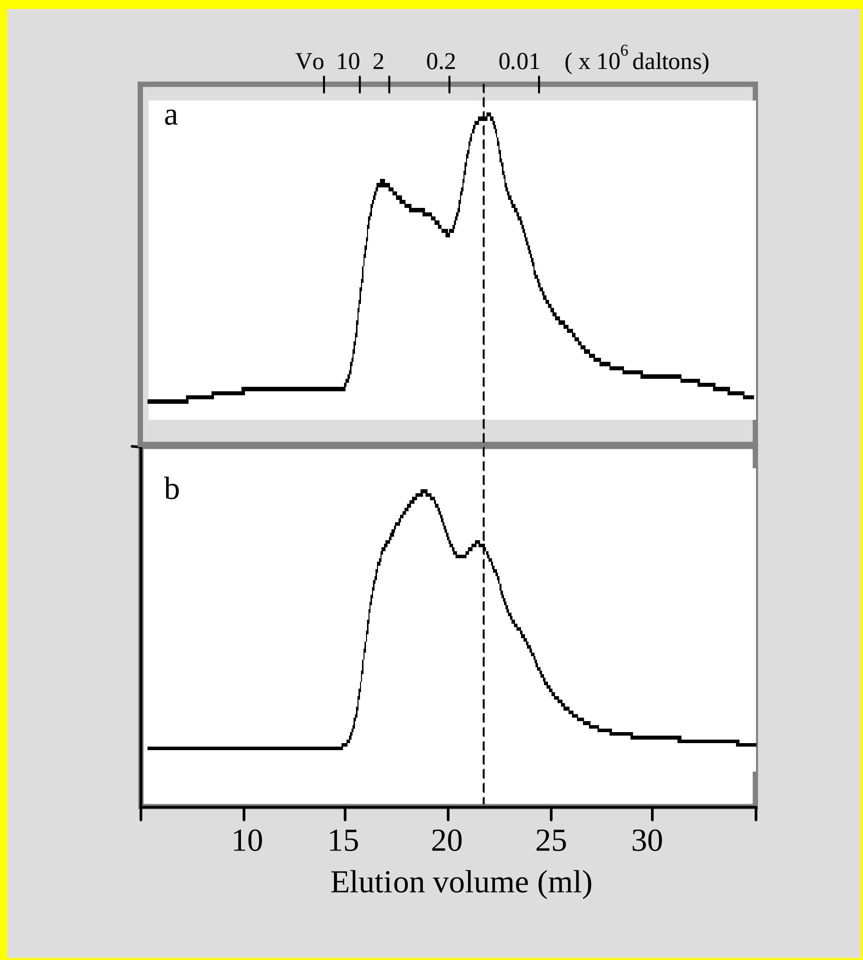


Size-exclusion chromatography

Absorbance at 280 nm



SE - HPLC elution curves for soy protein isolate (SPI): a) native; b) heated at 90°C and irradiated at 32 kGy



Result of isothermal calorimetry showing the effect of γ- irradiation on ΔH interaction of protein-water

Formulation	Heated (H)	H + Irradiated
CC : WPI	$-64.2 \pm 3.2^{a,1}$	$-56.2 \pm 1.6^{a,2}$
CC : WPI : Glyc	$-23.4 \pm 0.4^{b,1}$	$-20.1 \pm 1.0^{b,2}$
CC:WPI:Glyc:CMC	$-16.5 \pm 0.1^{cd,1}$	$-14.7 \pm 0.3^{c,2}$
CC:WPI:Glyc:CMC: pectin	$-19.5 \pm 0.5^{c,1}$	$-12.2 \pm 0.2^{d,2}$
CC:WPI:Glyc:CMC: pectin:Agar	$-15.1 \pm 0.2^{d,1}$	$-13.1 \pm 0.5^{cd,2}$

In the same raw, means followed by the same number are not significantly differen

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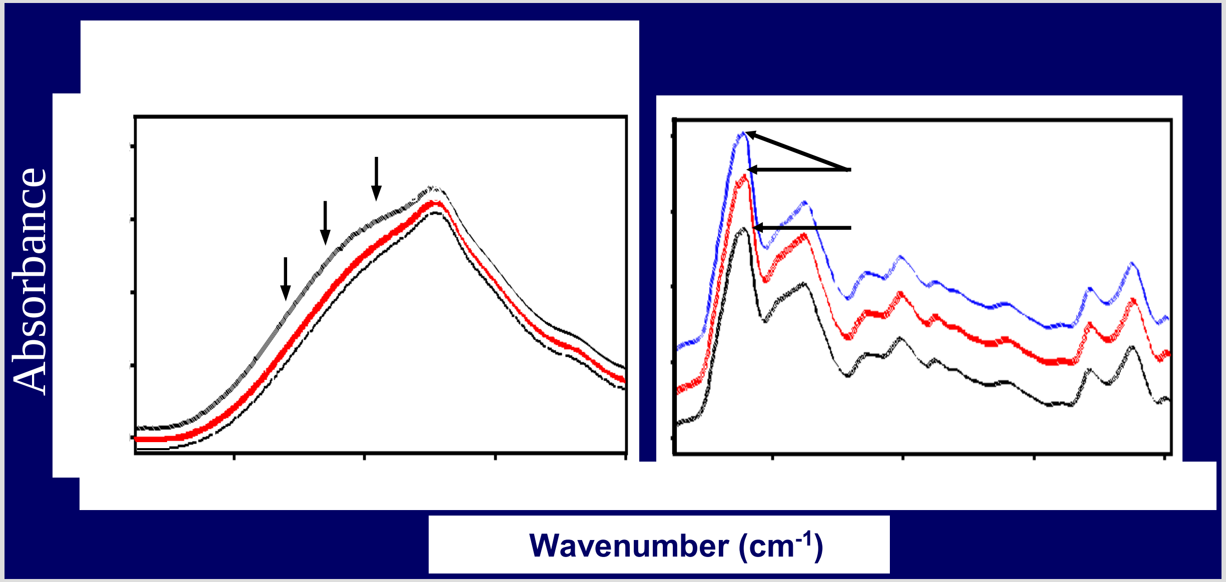
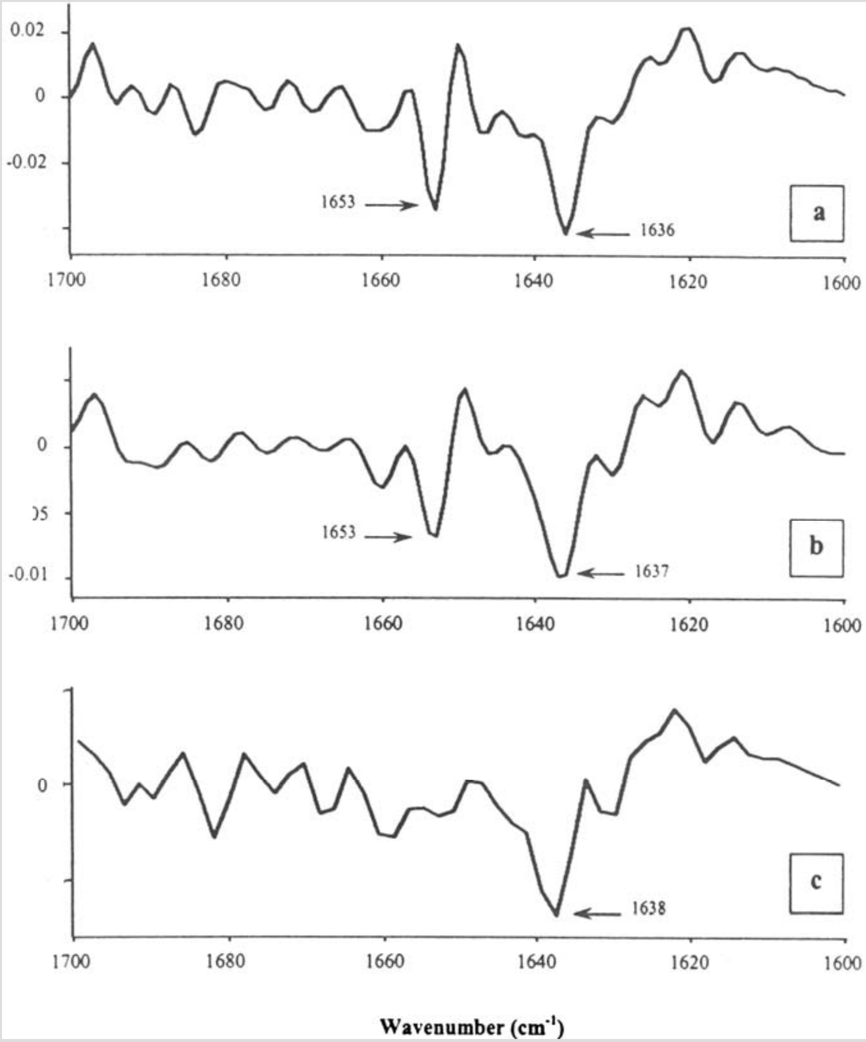
FT-IR spectra of whey protein film



a) Spectra regions 3600-3000 cm^{-1} (upper curve: control film; middle curve: heated film; lower curve: irradiated film); b) Spectra regions 1700-1000 cm^{-1} (lower curve: control film; middle curve: heated film; upper curve: irradiated film.

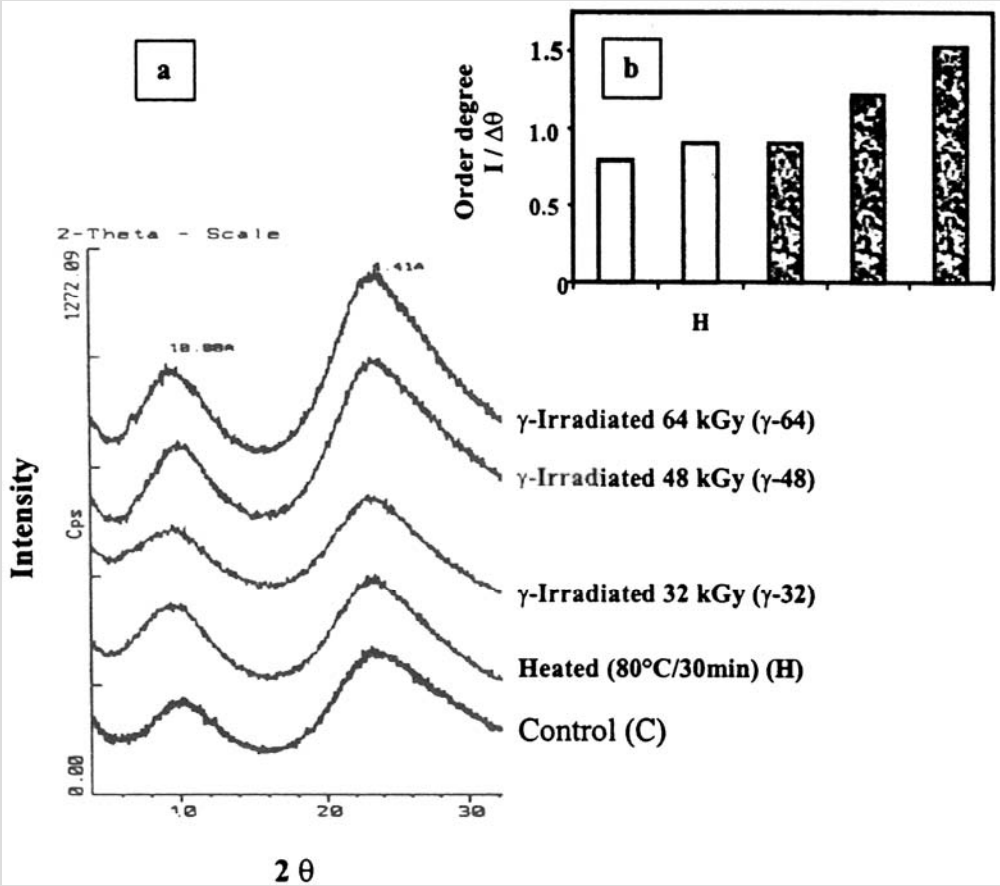
Second derivative of the FT-IR spectra of whey protein films



Mean Frequency Assignment (cm-1)
1623 ± 3 β-Structure
1630 ± 4 β-Structure
1637 ± 3 β-Structure
1645 ± 4 Unordered
1653 ± 4 α-Helix

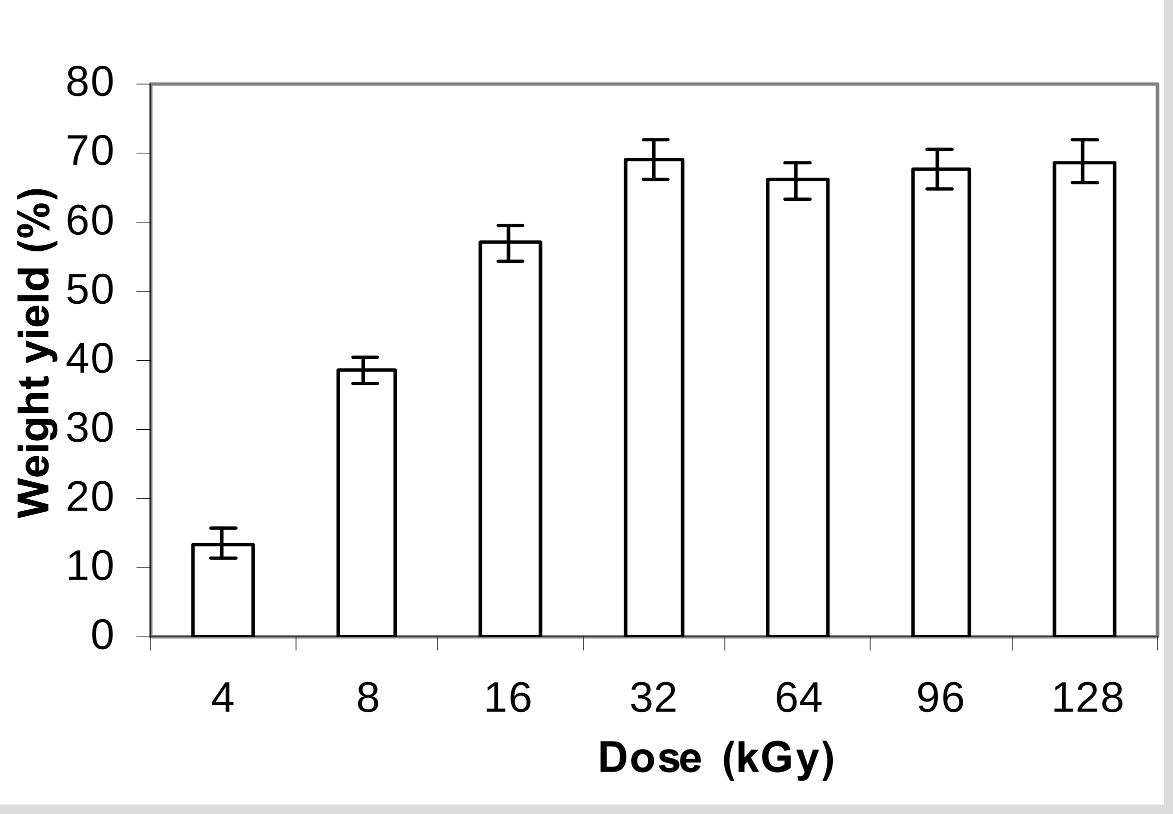
a) control film; b) heated film; c) irradiated film. Assignment of main frequencies (insert) is based on spectras data from 17 proteins (including β-lactoglobulin and α-lactalbumin) according to *Byler and Susi* (1988).

X-ray diffraction of whey protein films

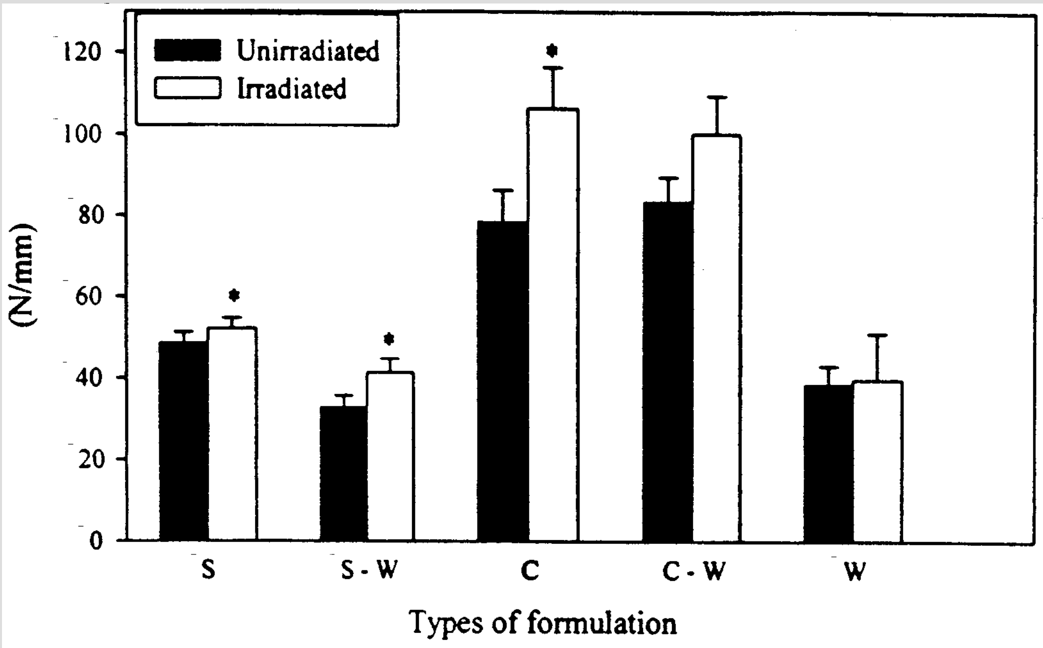


a) level of sharp angle (A/2δ, where A is the band intensity and δ is the half width at half height of the band) in function of different methods and irradiation doses.

Fraction of insoluble matter in function of the irradiation dose
Results are expressed as the percentage in solid yield after soaking the films 24 hours in water



Effect of gamma irradiation on the puncture strength of protein-based edible films



S = soy protein isolate; W = whey protein isolate; C = calcium caseinate

(*) Significant difference compared to corresponding unirradiated films

Mechanical Properties
Puncture strength (N/mm)

Formulation	NI[1] Films	I[1] films
Proteins/Glyc	56.48 b	67.22 b*
Proteins/Gly/MC	73.00 d	80.89 c*
Proteins/Gly/CMC	23.97 a	49.33 a*
Proteins/Gly/ALG	61.64 c	69.73 b*

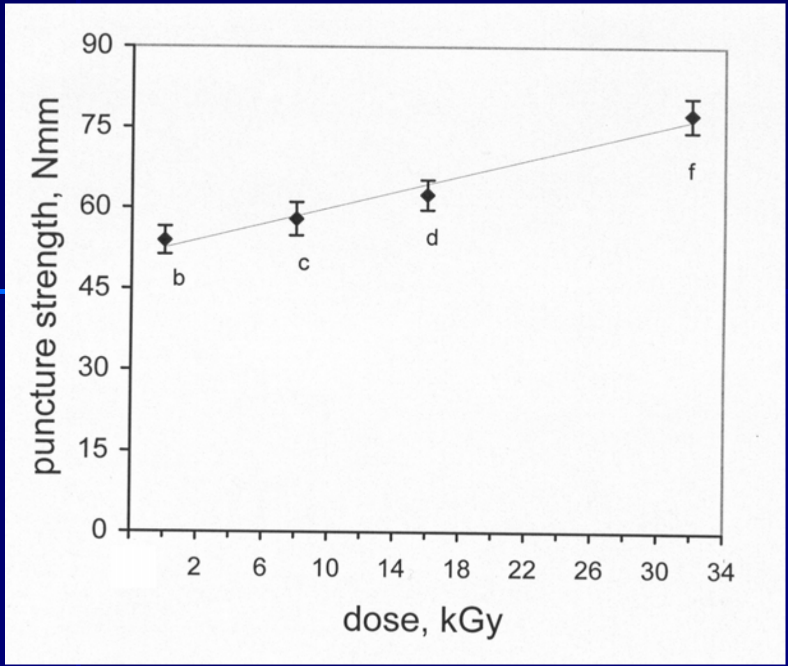
[1] I: irradiated NI: Non irradiated

Column: lower case raw: *

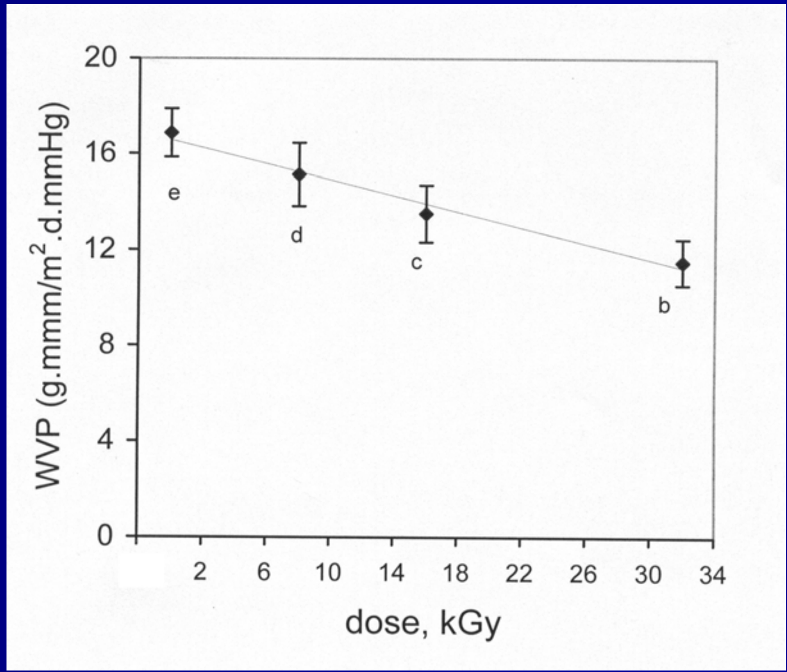
Mechanical Properties puncture deformation (mm)

Formulation	NI[1] (mm)	I[1] (mm)
Proteins/Glyc	4.02 c	3.70 c
Proteins/Gly/MC	3.50 b	3.34 b
Proteins/Gly/CMC	2.23 a	2.14 a
Proteins/Gly/ALG	3.67 b	3.44 b

1 NI: Non irradiated I: Irradiated   Column: lower case



Caseinate:WPI:Glycerol (1:1:0.1)

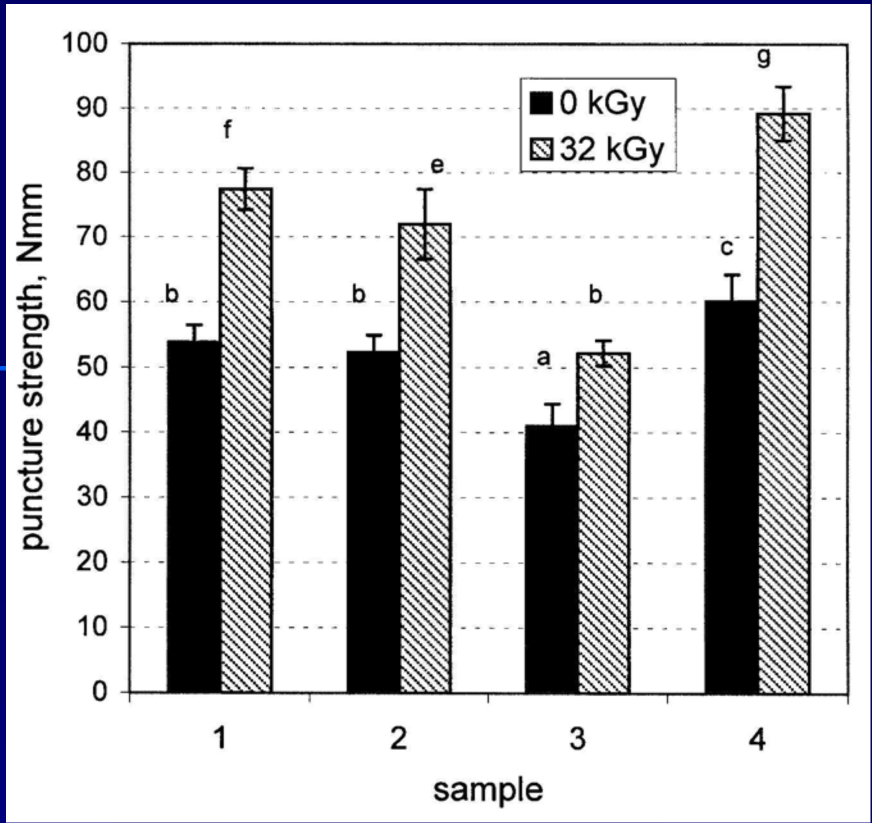


Water vapor permeability g.mm/m^2.day.mmHg

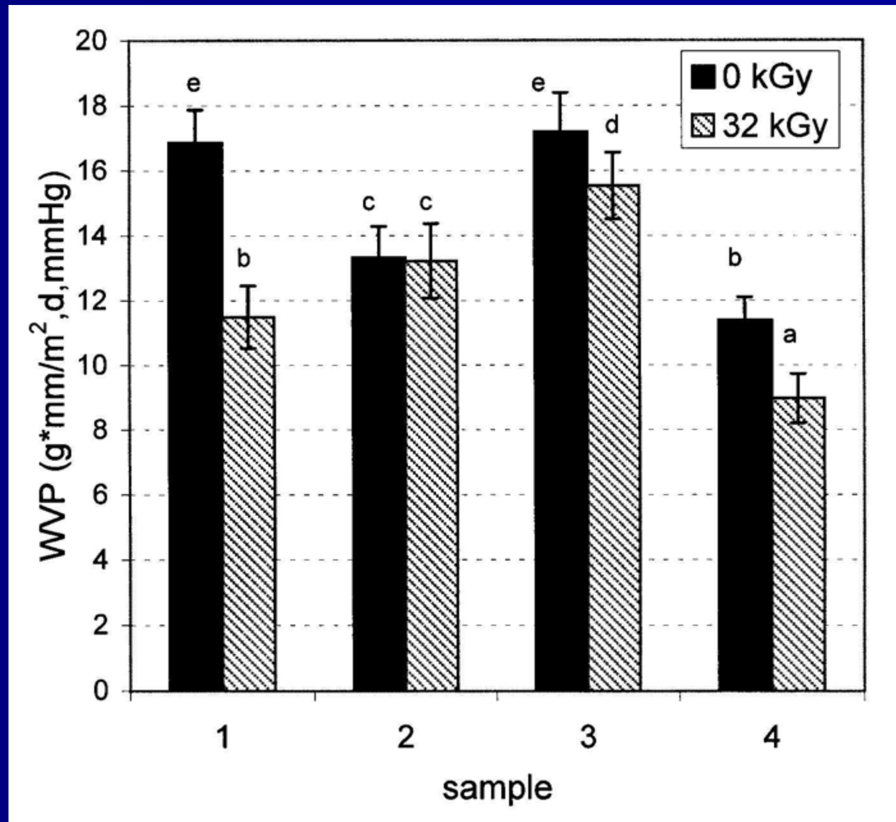
Formulation	NI[1]	I[1]
Proteins/Glyc	2.03 bB	1.75 bA
Proteins/Gly/MC	1.73 aA	1.71 abA
Proteins/Gly/CMC	1.78 aB	1.53 aA
Proteins/Gly/ALG	1.73 aA	1.71 abA

1 NI: Non irradiated I: Irradiated

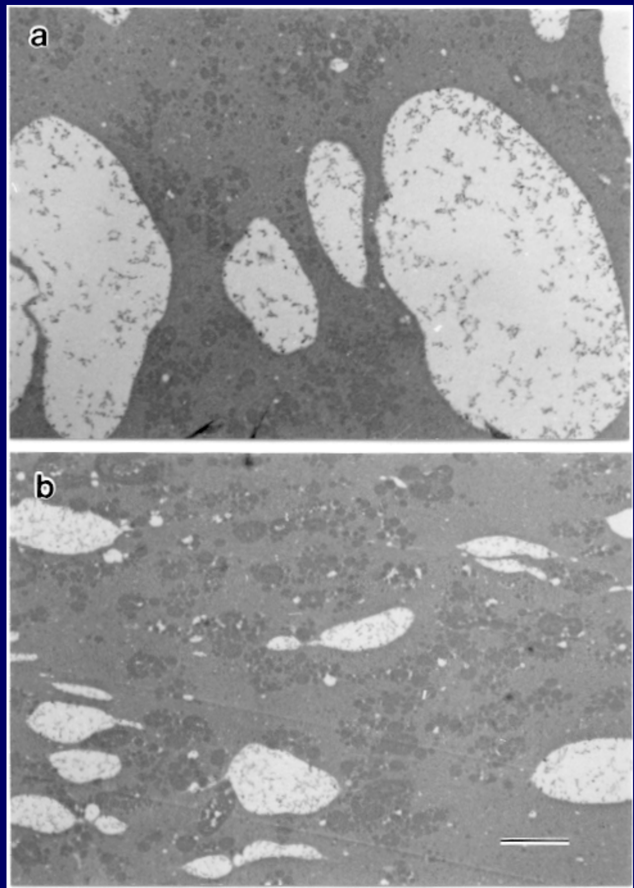
Column:lower case raw:upper case



1: CC-WPI
2: CC-WPI-PS
3: CC-WPI-SPS
4: CC-WPI-Alginate

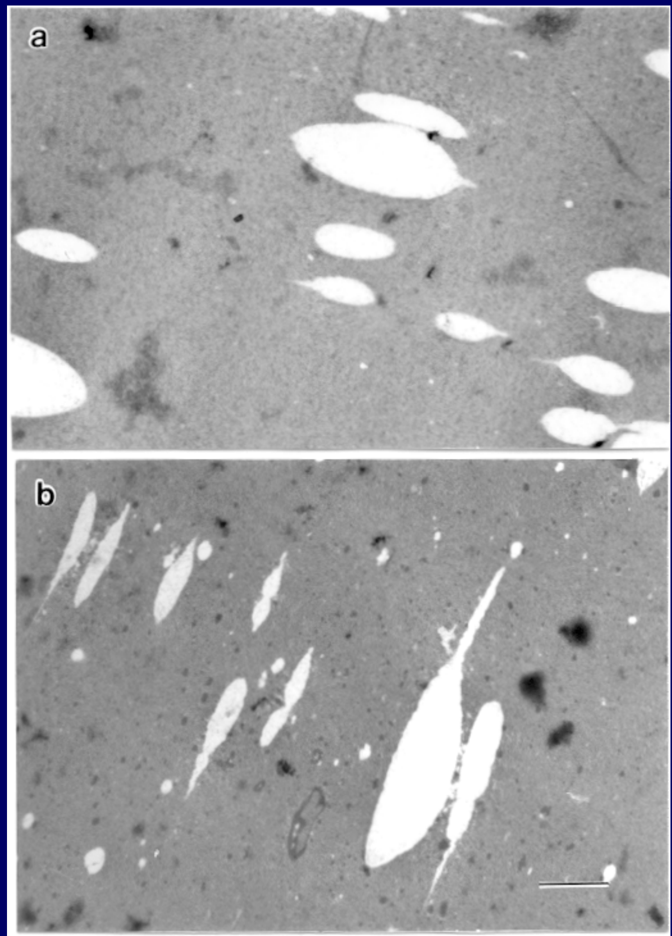


Cross section of calcium caseinate films
a) heated at 90°C for 30 min; b) irradiated (32 kGy)
(9 mm bar = 3 μm)

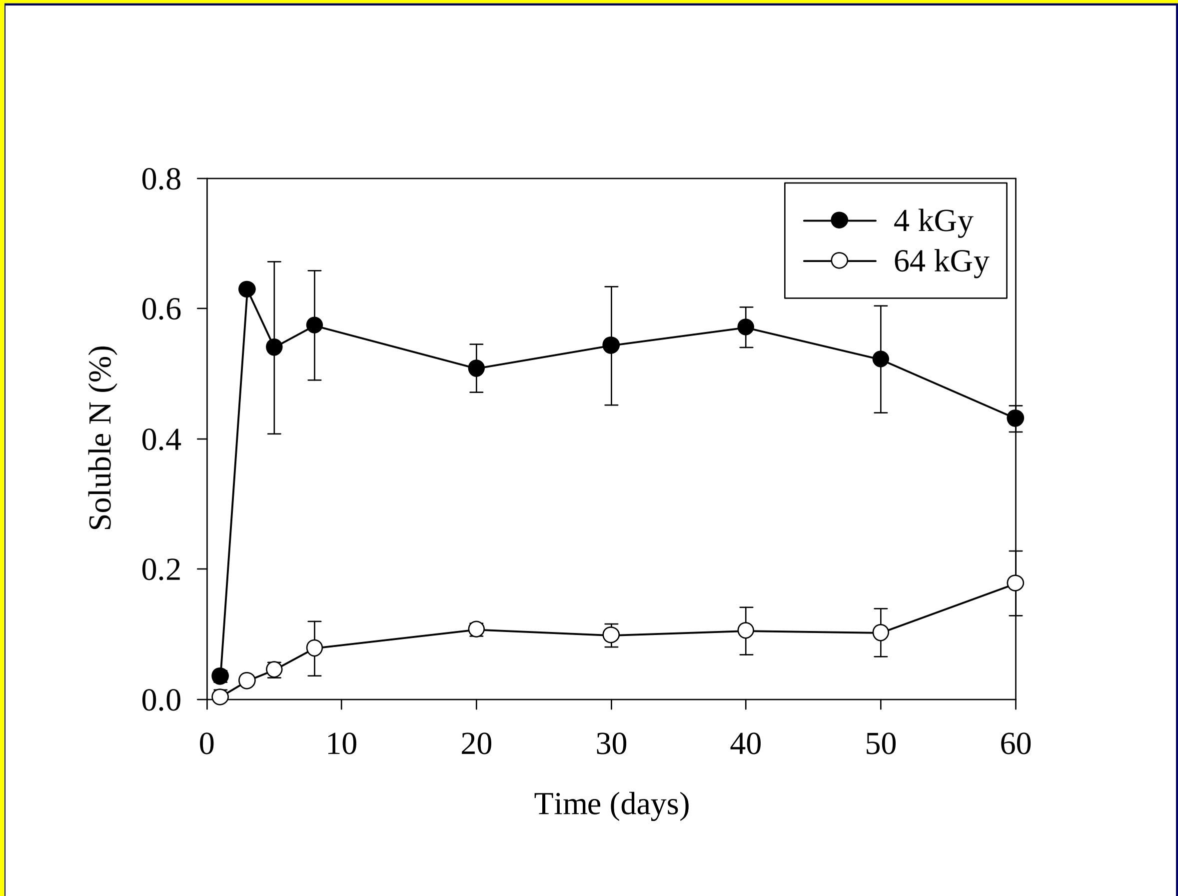


Cross section of WPI-calcium caseinate films

a) heated at 90°C for 30 min; b) heated at 90°C and irradiated at 32 kGy. (9 mm bar =3μm)



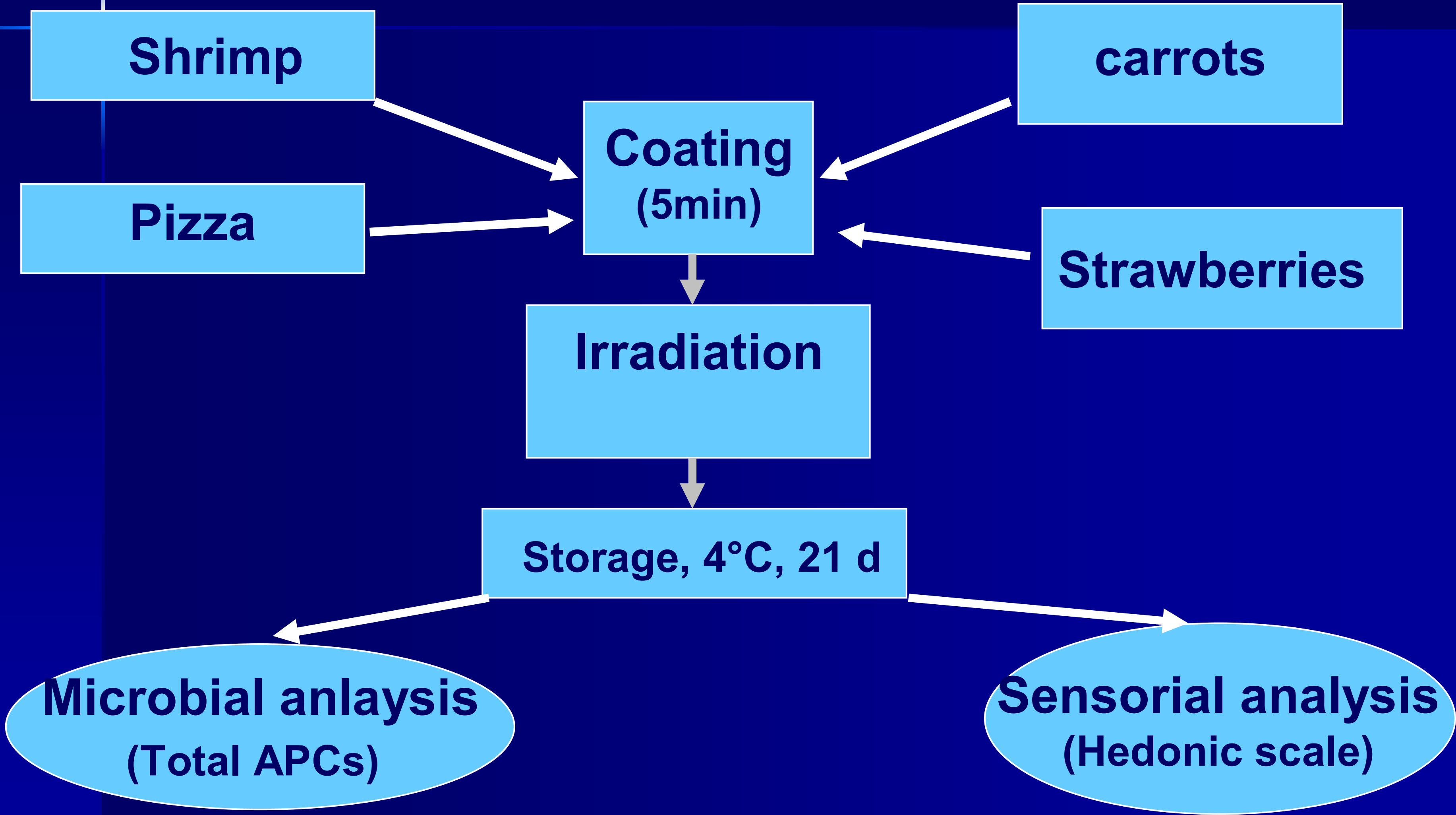
Percentage of nitrogen from calcium caseinate films converted to soluble N (% ± S.D) by *Pseudomonas aeroginosa* in standard stock solutions



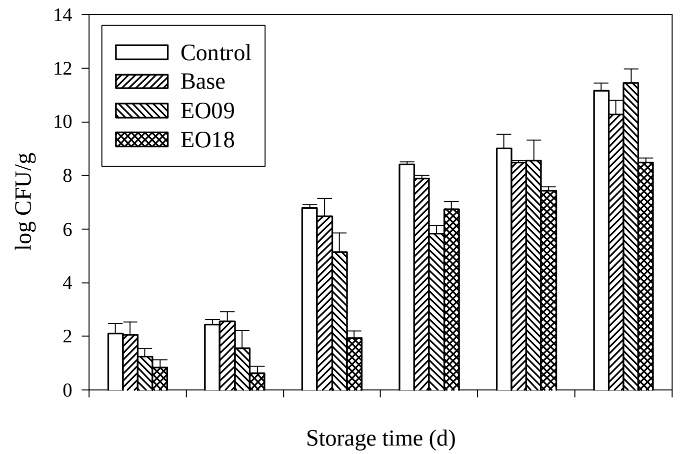
Application in food systems

Bioactive coating and packaging in combination with irradiation

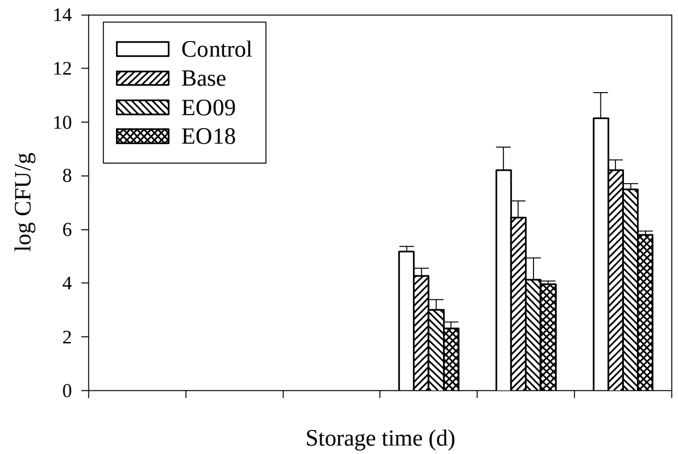
Procedure for antimicrobial and shelf life tests on irradiated coated convenience foods



Counts of bacterial population (APCs) in precooked shrimp during storage at 4°C



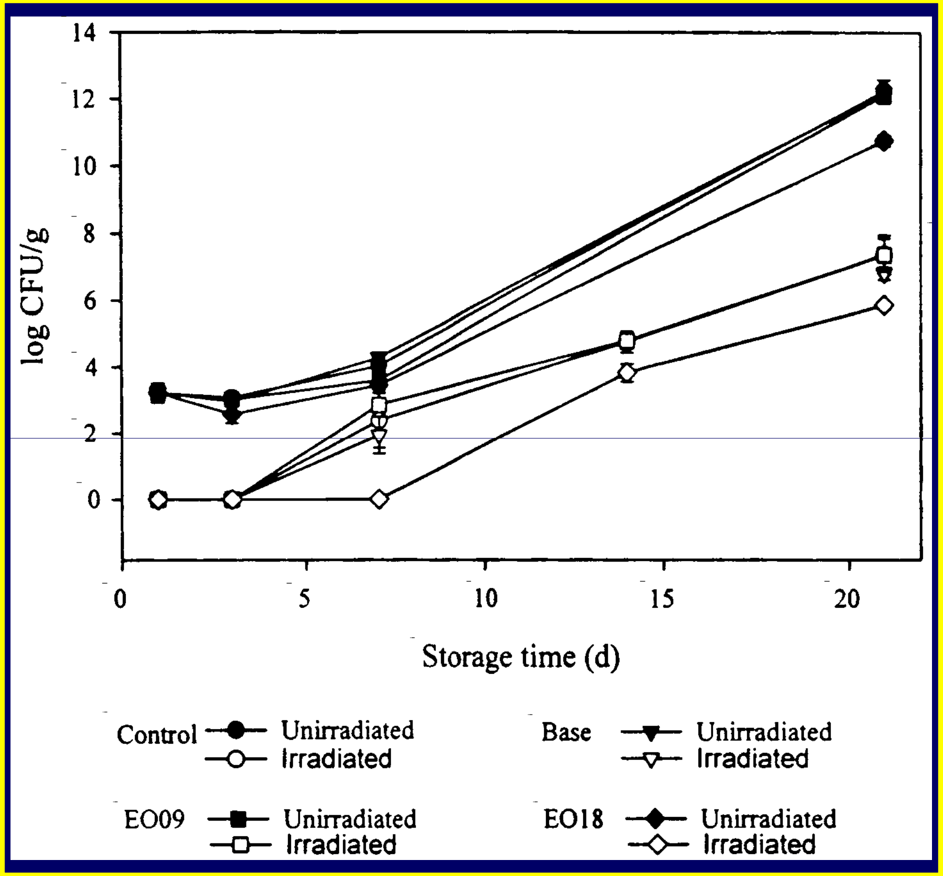
Unirradiated



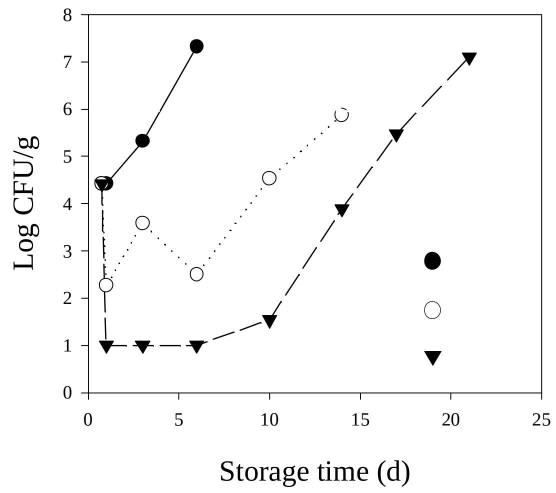
Irradiated (3 kGy)

For a given storage time, bars with different letters are significantly different ($p \leq 0.05$).

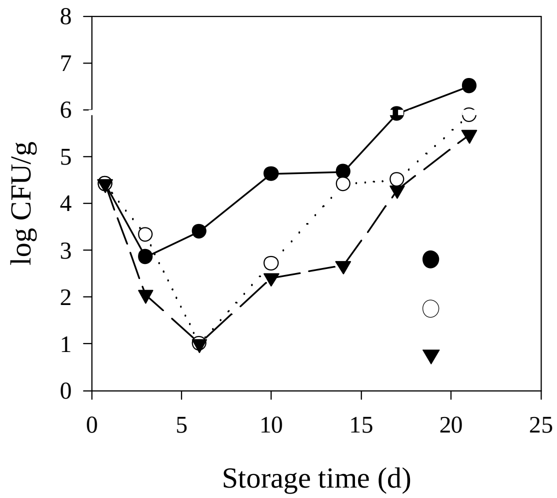
Effect of gamma irradiation and edible coating on the growth of *Pseudomonas putida* in precooked shrimp



Counts of bacterial population in refrigerated pizzas as affected by gamma irradiation and edible coating

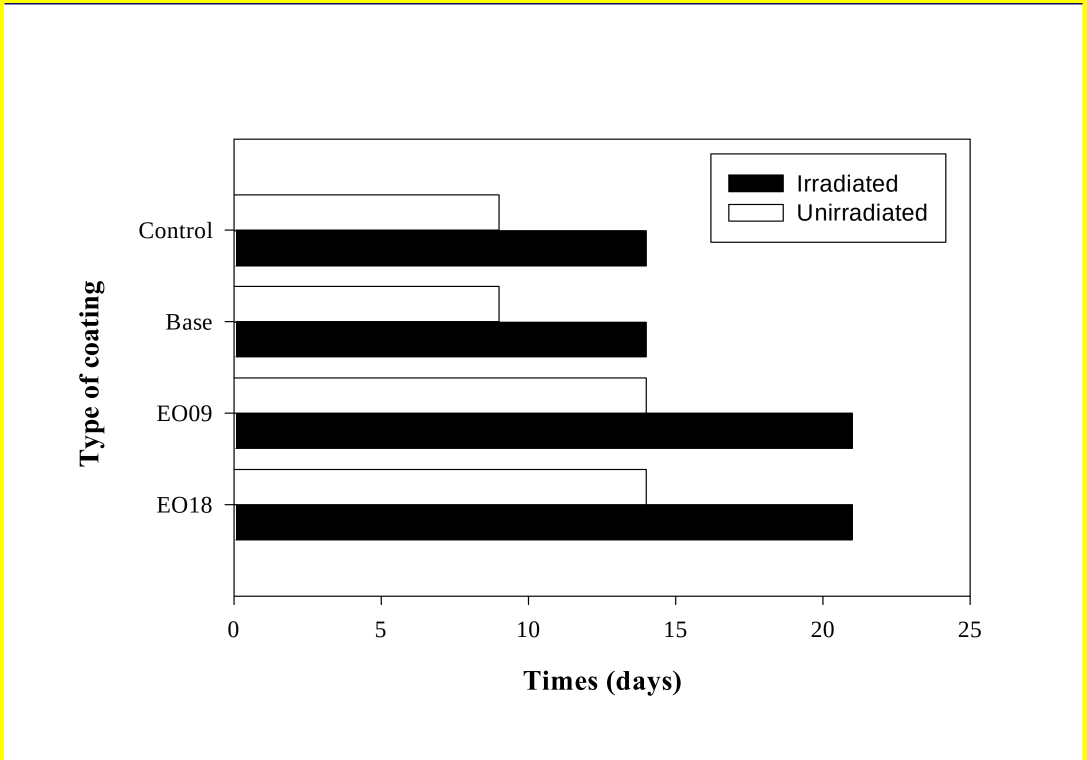


Irradiation alone



Irradiation + edible coating

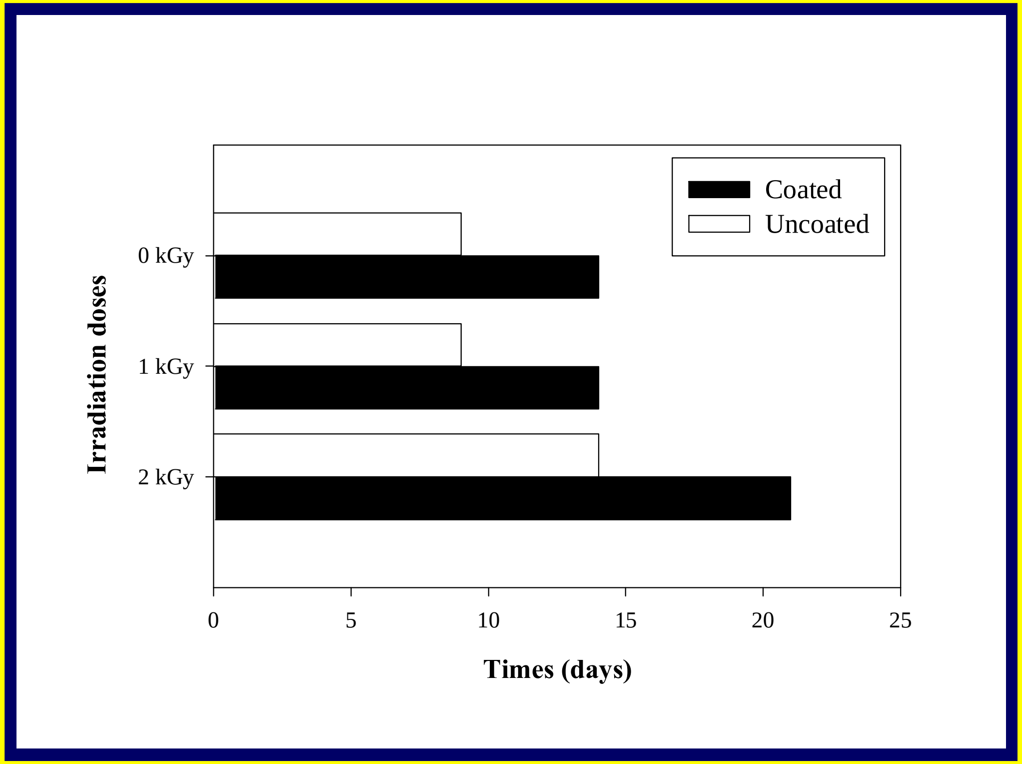
Shelf life periods of precooked shrimp during refrigeration as affected by gamma irradiation and edible coating



Results are expressed in terms of time to reach the onset of spoilage (10^7 CFU/g)

(*) The onset of spoilage was not reached at the end of the experiment period (21 d)

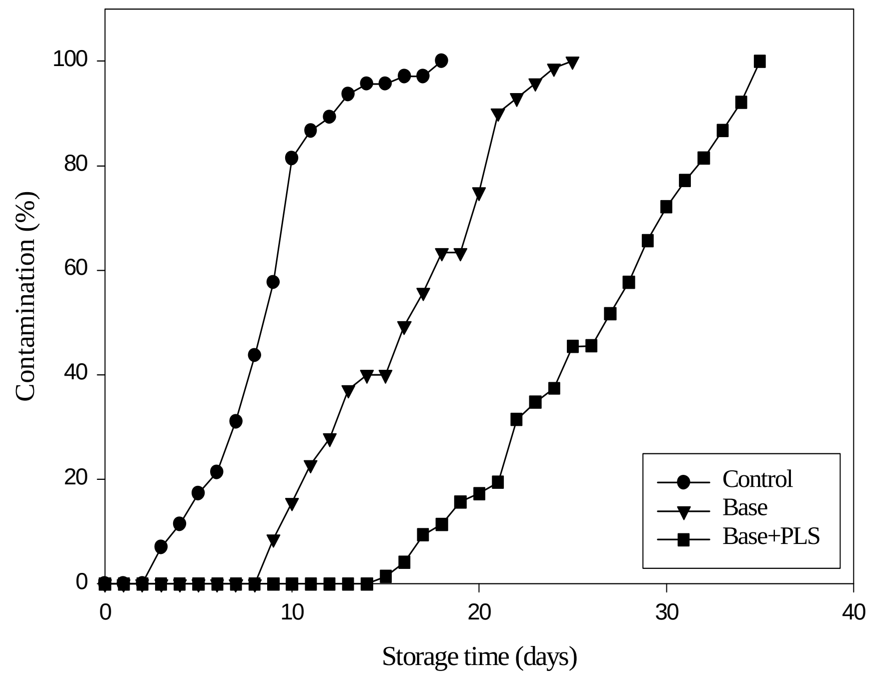
Shelf life periods of pizza during refrigeration as affected by gamma irradiation and edible coating



Results are expressed in terms of time to reach the onset of spoilage (10^6 CFU/g)

(*) The onset of spoilage was not reached at the end of the experiment period (21 d)

Application of coating for mold growth on strawberries

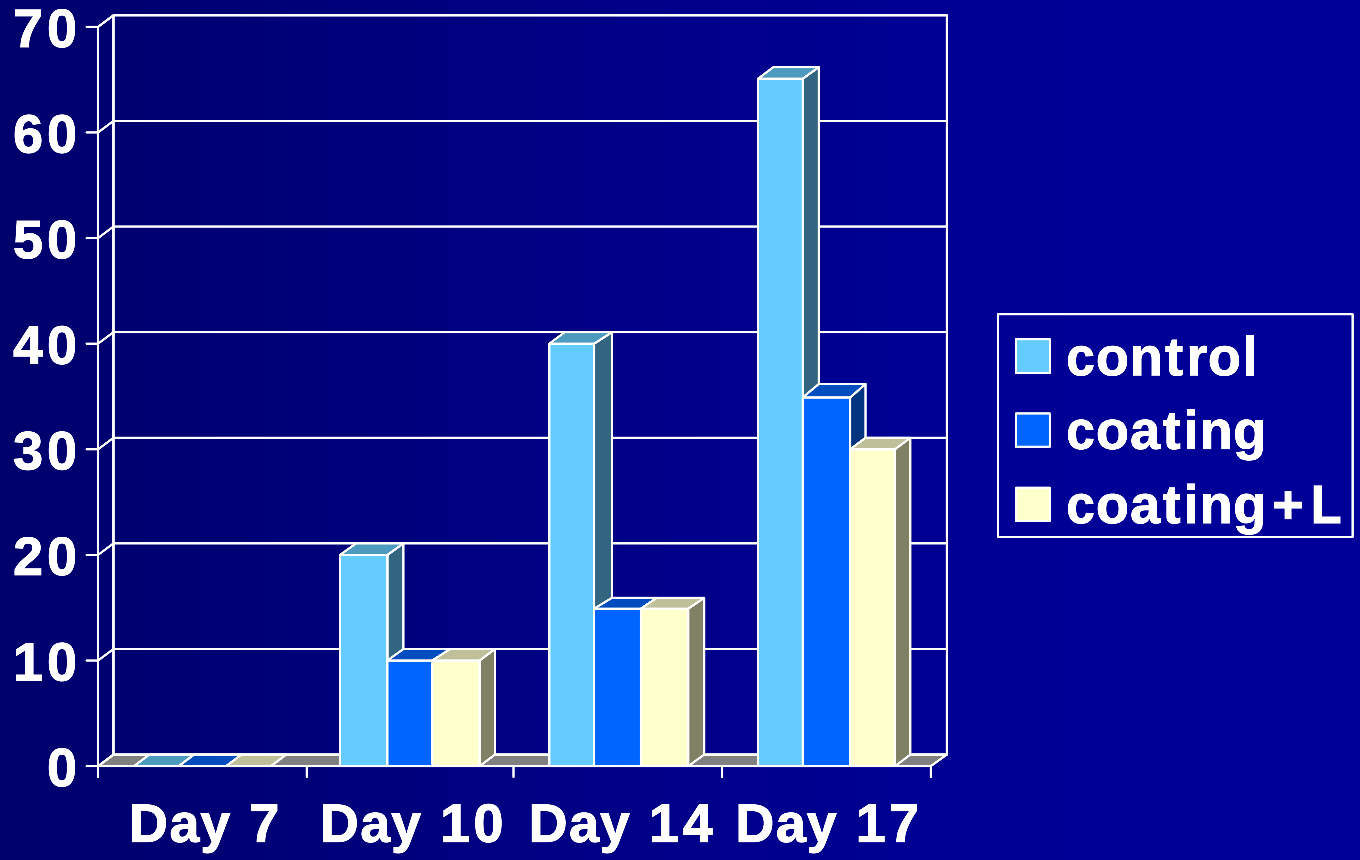


Irradiation and coating effect on moulds growth on strawberries (%)

Day	Control	Control coated with NIF**	Control coated with IF*	Irradiated	Irradiated coated with NIF	Irradiated coated with IF
3	7	11	5	0	1	0
9	68	40	30	22	23	20
11	85	65	44	38	47	40
12	90	75	56	44	56	45
13	93	85	68	51	58	54
17	97	97	89	79	81	84

* IF: Irradiated coating films at 32 kGy ** NIF: Non irradiated films

Effect of crosslinked coating on rotting fruits (%) during storage at 4 ºC



The influence of antimicrobial compounds and MAP on radiation sensitivity of *Listeria monocytogenes* present in ready-to-use carrots and strawberries

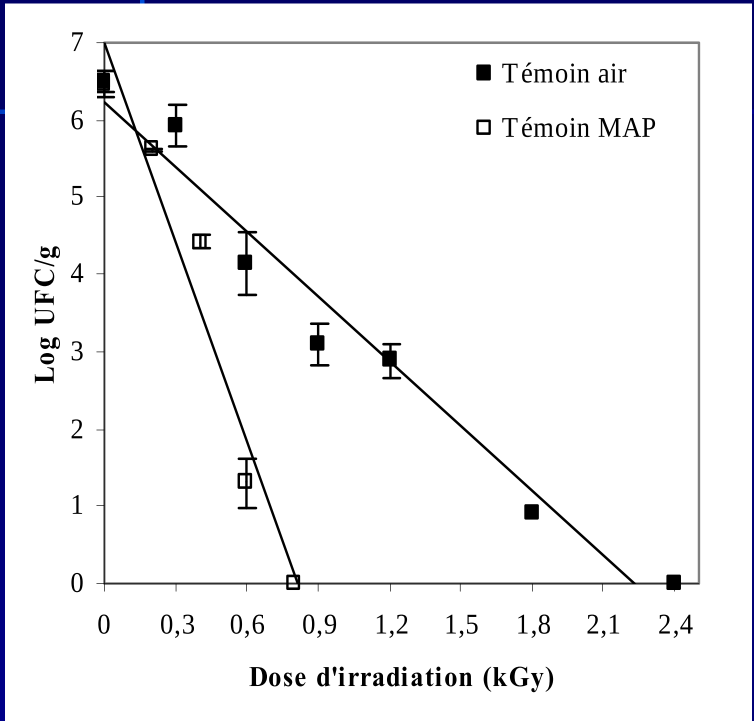
Four compounds were evaluated:

- *trans*-cinnamaldehyde (from cinnamon)
- Spanish oregano, winter savory and
- Chinese cinnamon essential oils and limonene

Relative radiation sensitivity (D_{10}) were evaluated in presence of the compound or essential oil under air or under MAP (60% O2, 30% CO2, and 10% N2).

$D_{10} = D_{10}$ (kGy) control samples / radiation *D*10 (kGy) samples treated in presence of antimicrobial compounds.

Radiosensitivity of *Listeria* during irradiation treatment of mini carrots



MAP: 60% O_2
30% CO_2
10% N_2

D_{10} (air) = 0.36 kGy

D_{10} (MAP) = 0.12 kGy

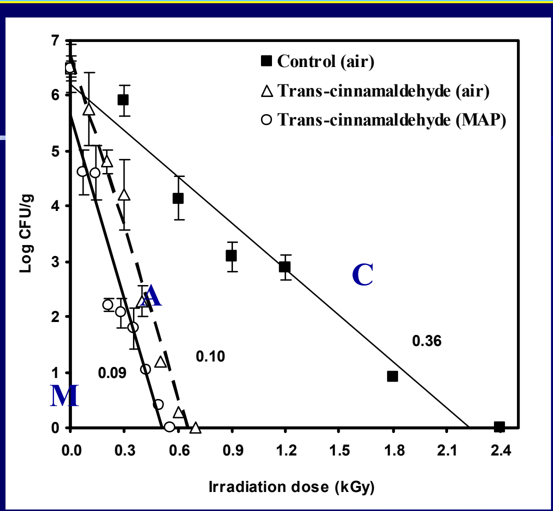
Increase of the Radiosensitivity by 3 time under MAP

D_{10} value = Irradiation dose required (kGy) to decrease 90% of the bacterial population

D_{10} determination of *L. monocytogenes* under air and MAP in presence of antimicrobial compounds

R_A=3.7

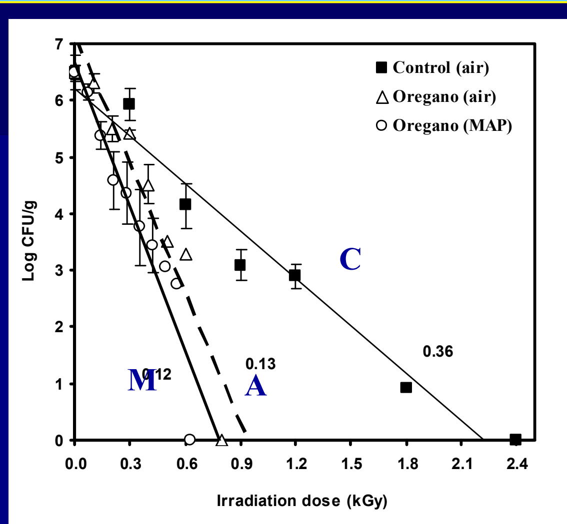
R_M= 4



A: *trans*-cinnamaldehyde

R_A= 2.8

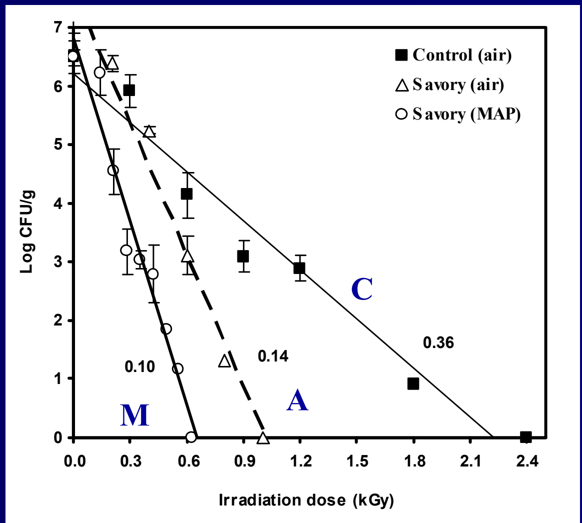
R_M= 3



B: Spanish oregano

R_A= 2.5

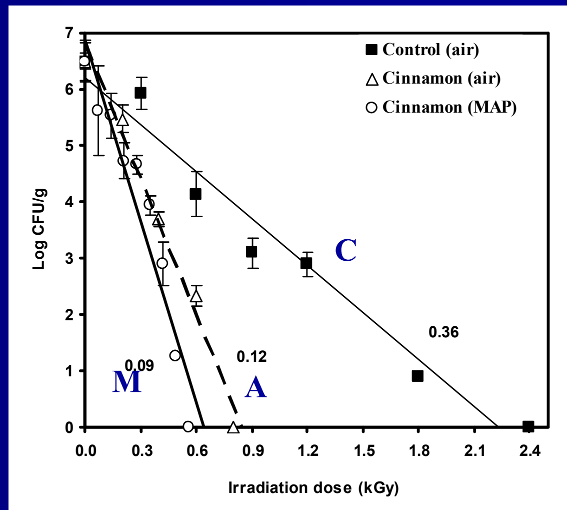
R_M=3.7



C: winter savory

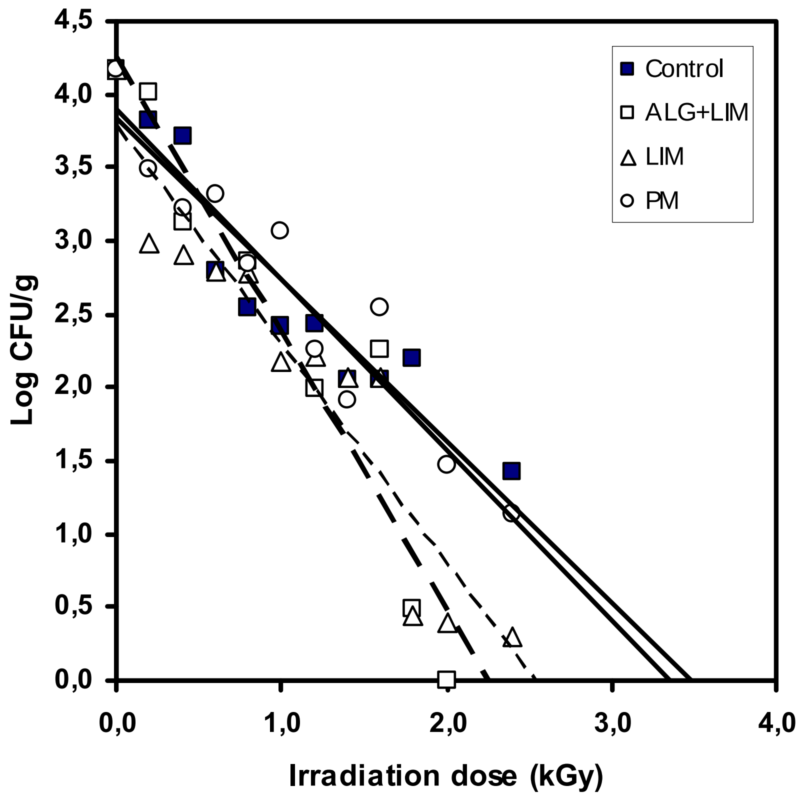
R_A= 2.9

R_M = 3.9



D: Chinese cinnamon

Radiosensitization of moulds on strawberries



radiosensitization

Lim : 1.35
Mod.Alg + Lim: 1.71
PM:1.05
Control: 1.00

Lethal dose

Mod.ALG+LIM: 2.2 kGy
LIM:2.5 kGy
Control:3.5kGy

Bioactives films

In order to carry:

Antioxydant and antimicrobial compounds

Scientific Challenge

Improve the physico-chemical properties

The water resistance

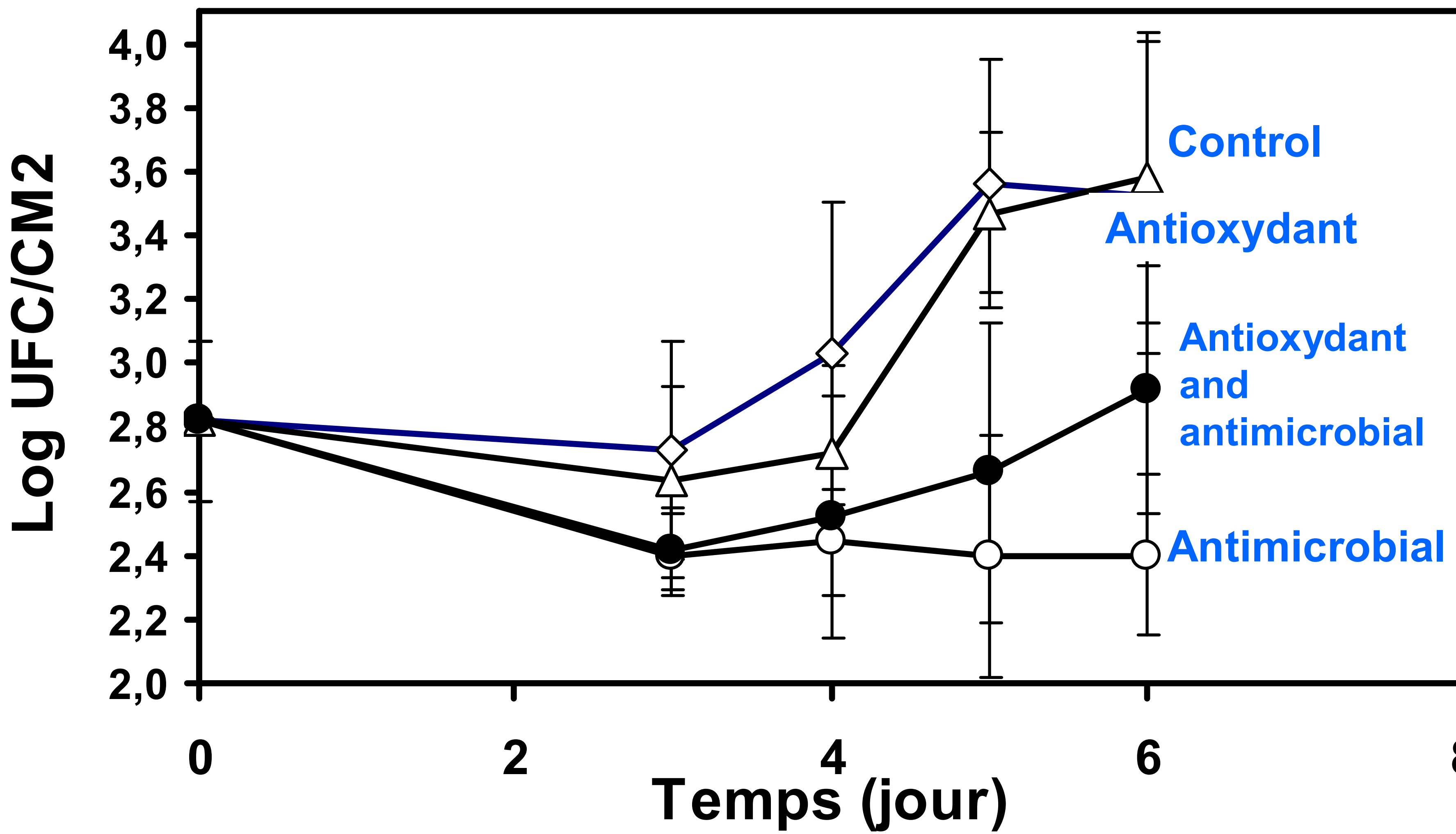
Polymers should be biodegradable

Irradiation should be applied in combination with other treatments like Chemical modification

or

development of new formulations should be done

Bioactive films and control of *E.coli* 0157:H7 on beef slices

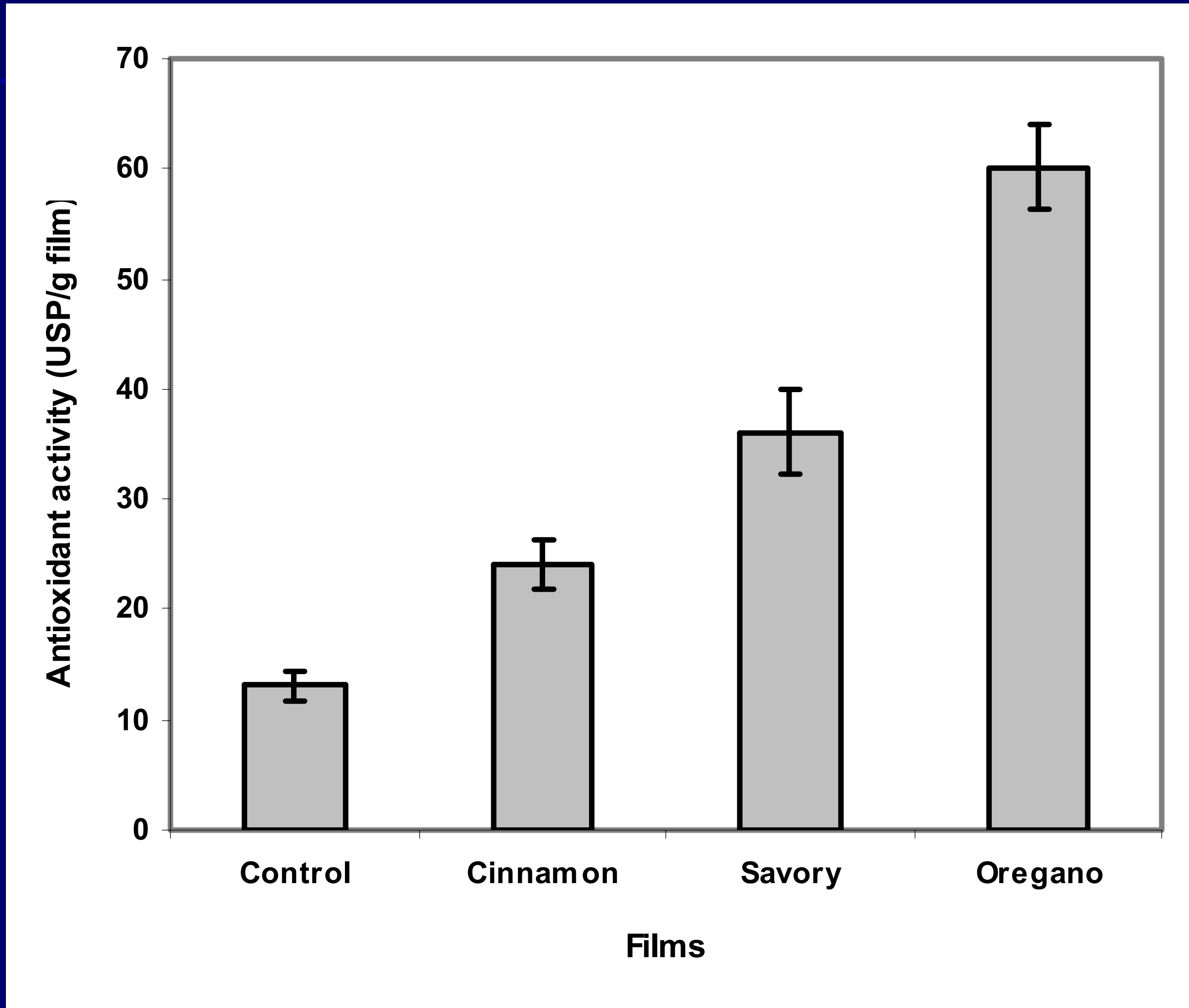


Release rate (%) of active compounds during storage of bologna at 4°C

Treatment	Day 2	Day 3	Day 4	**Day 5**
Origano	17 $\pm$ 3b	63 $\pm$ 6c	66 $\pm$ 3c	**72 $\pm$ 1c**
Cinnamon	62 $\pm$ 4a	84 $\pm$ 1a	78 $\pm$ 2a	**96 $\pm$ 0.3a**
Savory	20 $\pm$ 3b	72 $\pm$ 3b	84 $\pm$ 2b	**89 $\pm$ 0.3b**

Mean in the same column bearing the same letters are not significantly different ($P \leq 0.05$)

Antioxydant properties of films



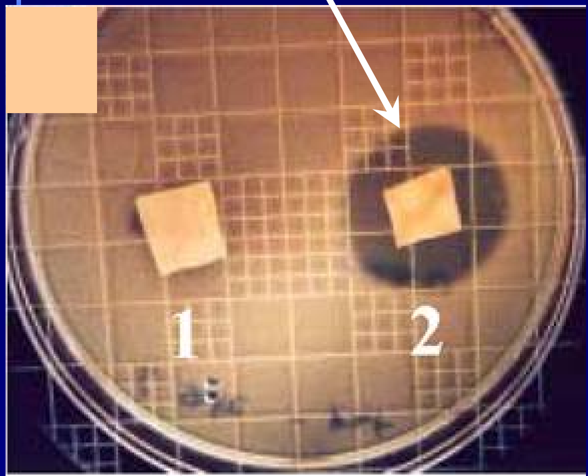
Mechanical properties of films

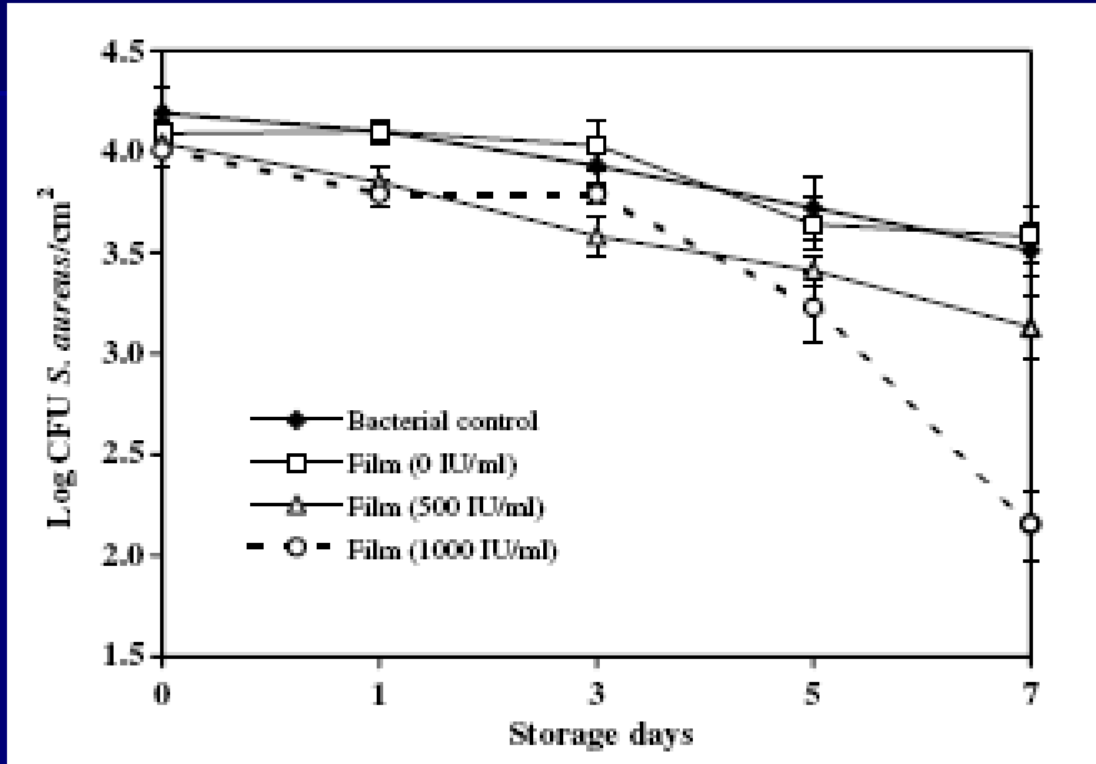
Type of film	Thickness (μm)	Puncture strength ($N.mm^{-1}$)	Puncture deformation (mm)	Viscoelasticity Coefficient (%)
Control	104 ± 6 a	80 ± 4 d	6.1 ± 0.3a	49 ± 0.3 ab
Origano	126 ± 6 b	58 ± 4 b	6.2 ± 0.3 a	52 ± 1.5 b
Savory	100 ± 7a	68 ± 9 c	5.8 ± 0.5 a	52 ± 3b
Cinnamon	127 ± 5 b	49 ± 5 a	6.1 ± 0.6a	48 ± 3a

Mean followed by the same letter between treatments are not significantly different ($P \leq 0.05$)

Bacteriocins immobilization

Inhibition area





Antimicrobial activity of bioactive film containing nisin against *S. aureus* (1: control; 2: 1000 UI/mL of nisine).

Inhibition of *S. aureus* inoculated on beef slice.

Conclusion

Gamma irradiation induced

- Increase of bityrosine production
- Increase of puncture strength
- Modification of protein structure
  (structure are more ordered and
  more stable)
- Reduction of pore size distribution in films (correlation with
  puncture strength)

crosslinking of natural polymers for the development of edible and biodegradable packaging.

Plasticizers decreased puncture strength
Sorbitol had the greatest plasticizing effect)

Thank you

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