

Development of Active Chitosan-based Films for Sustainable Food Packaging Applications

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Doctorate School Coordinator: **Prof. Dr. Alessandro Ulrici**



2016-2019

THE STONE AGE



>3000 B.C.



the Bronze Age

3000 – 1200 B.C.



IRON AGE

<1200 B.C.

PLASTIC AGE

1907 – until now



STONE
AGE



IRON
AGE



PLASTIC
AGE

Sluka2019
Gatis
Sluka



19TH CENTURY



21ST CENTURY

PLASTICS are NOT BIODEGRADABLE

Biopolymers: why CHITOSAN?



CHITOSAN is the **second most abundant natural polymer** after cellulose

Strategies for the improvement of properties of chitosan-based films

- Chemical cross-linking
- Enzyme treatment
- Graft copolymerization
- Complexation
- Surface coating
- Fillers incorporation
- High-energy irradiation
- **Blending with other biopolymers**

OUTLINE

- **Chapter 1: Recent advances of chitosan-based blend films for food packaging applications – a review**
- **Chapter 2: Comparative analysis of blend and bilayer films based on chitosan and gelatin enriched with Ethyl Lauroyl Arginate (LAE) with antimicrobial activity for food packaging applications**
- **Chapter 3: Comprehensive characterization of active chitosan-gelatin blend films enriched with different essential oils**
- **Chapter 4: Development of antimicrobial films based on chitosan-polyvinyl alcohol blend enriched with Ethyl Lauroyl Arginate (LAE) for food packaging applications**
- **Chapter 5: Conclusions**

Web of Science InCites Journal Citation

 **Clarivate**
Analytics

WEB OF SCIENCE™

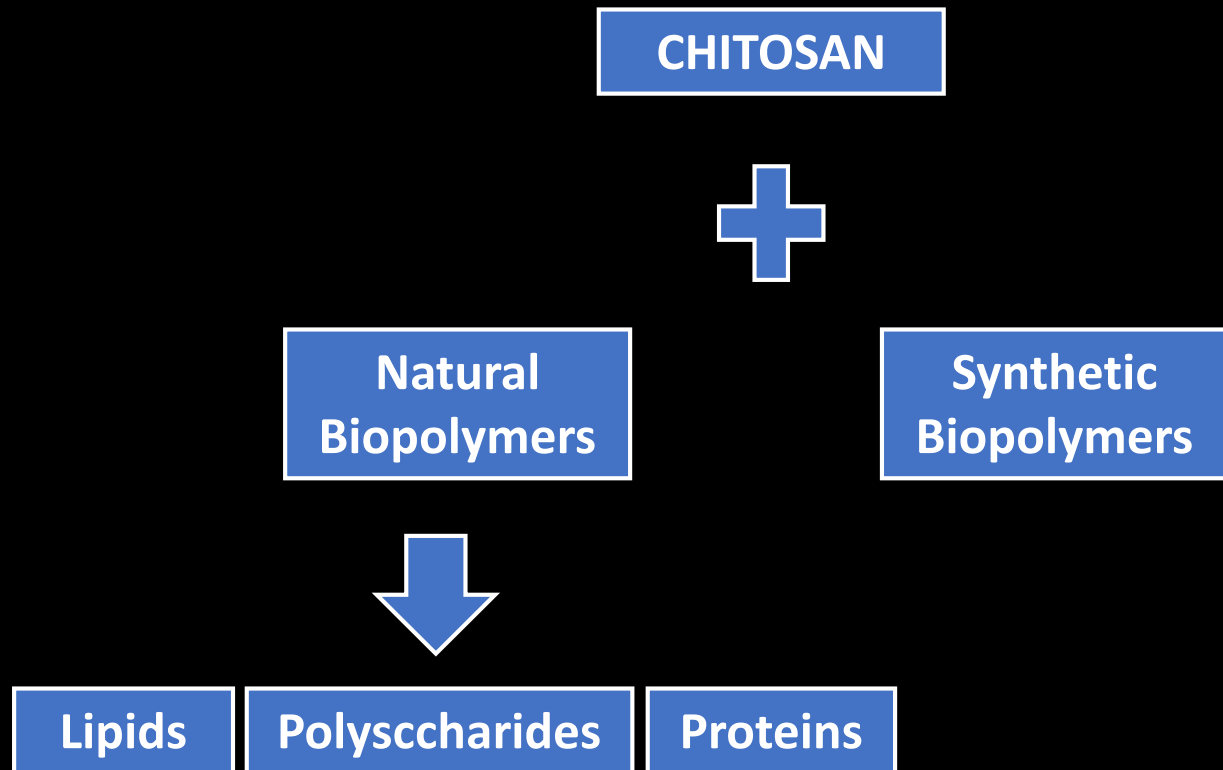
Results **164**
(from Web of Science Core Collection)

You searched for: TOPIC:
(chitosan, film, food packaging,
blend)

Timespan: Last 5 years.

Indexes: SCI-EXPANDED, SSCI,
A&HCI, CPCI-S, CPCI-SSH, ESCI.

...Less



Synopsis of research published between 2015-2019 addressing chitosan-polysaccharide blend films for food packaging applications

Biopolymer	Additives	Key findings	Reference
- Potato starch (4% w/v) - Chitosan (1.5% w/v)	Citric acid (5, 10, 15 and 20% w/w on a dry biopolymer basis)	- Citric acid addition to the biopolymers blend showed a crosslinking and plasticizing effect. - Composite films exhibited a homogenous and denser structure with higher surface roughness and enhanced water resistance, mechanical and antimicrobial properties compared with non-crosslinked films.	(H. Wu et al., 2019)
- Hemicellulose (2% w/v) - Chitosan (2% w/v)	Cellulose nanofiber (5, 10, 15 and 20% w/w of biopolymers)	- The tensile strength of the film increased by adding 5% cellulose nanofiber. - The films containing 10–40% plasticizers (glycerol, xylitol, sorbitol) showed slightly higher water vapor permeability, oxygen permeability, transparency, solubility, and lower contact angle.	(J. Xu, Xia, Zheng, Yuan, & Sun, 2019)
- Carboxy methyl chitosan (1% w/v) - Chitosan (2% w/v)	Nisin (1000 and 6000 IU/mL of film forming solution).	- Carboxymethyl chitosan had a plasticizing effect and decreased thermal stability. - Antibacterial activity against <i>L. monocytogenes</i>.	(Zimet et al., 2019)
- Starch (1.5% w/v) - Chitosan (1.5% w/v)	- Clove essential oil (3%, 6%, 9% and 12% w/w) - Nano titanium dioxide (1%, 3%, 5% and 7% w/w)	- The incorporation of Nano titanium dioxide improved the compactness of the film, increased tensile strength and antioxidant activity, and decreased water vapor permeability. - The incorporation of clove essential oil decreased tensile strength and increased hydrophobicity as well as water vapor barrier.	(W. Li et al., 2019)

CHITOSAN



**Natural
Biopolymers**

**Synthetic
Biopolymers**



Lipids

Polysccharides

Proteins



Gelatin



Polyvinyl alcohol

Conclusion

- **Blending chitosan** with **natural** and **synthetic biopolymers** is a simple and effective way to improve its functional properties and overcome its intrinsic shortcoming such as low water barrier properties and high price.

Haghighi H, Licciardello F, Fava P, Siesler HW, Pulvirenti A. Recent advances of chitosan-based films for sustainable food packaging applications – a review- Under revision.

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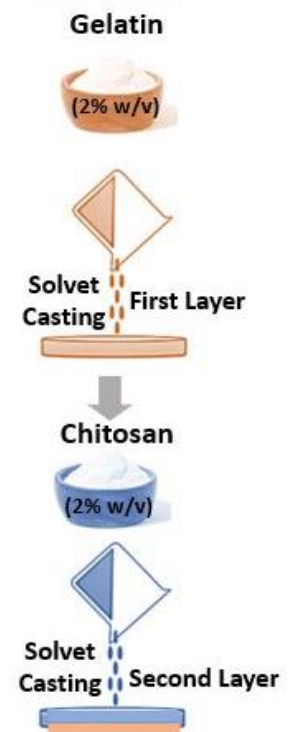
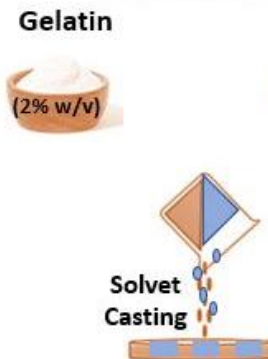
Schematic Overview

Gelatin

Chitosan

Blend

Bilayer



Characterization and Study of Different Properties for Food Packaging Applications

Physical Properties

Mechanical Properties

Antimicrobial Properties

Barrier Properties

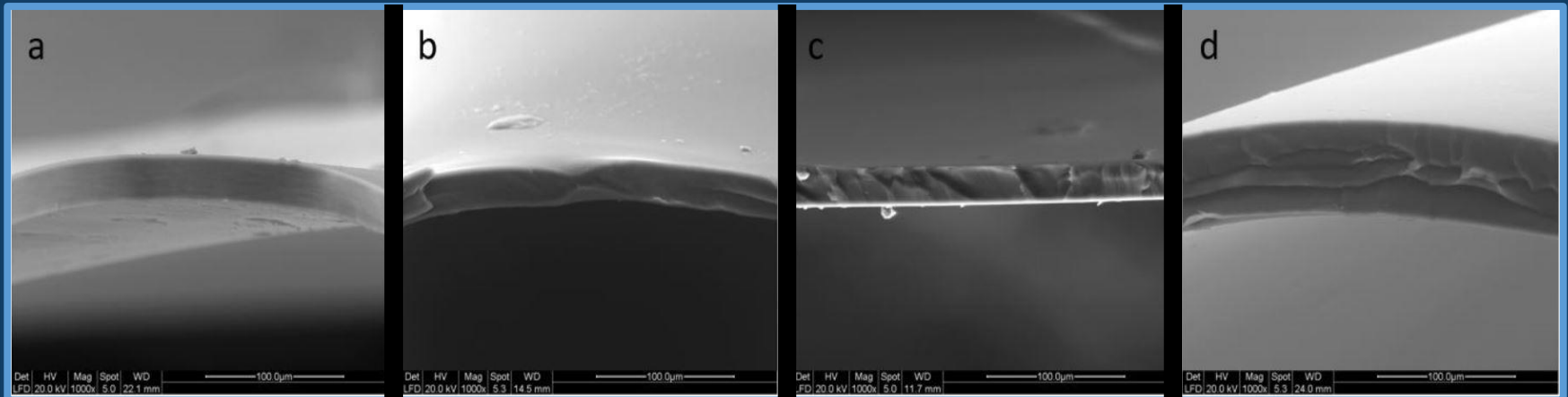
Scanning Electron Microscopy (SEM)

Chitosan

Gelatin

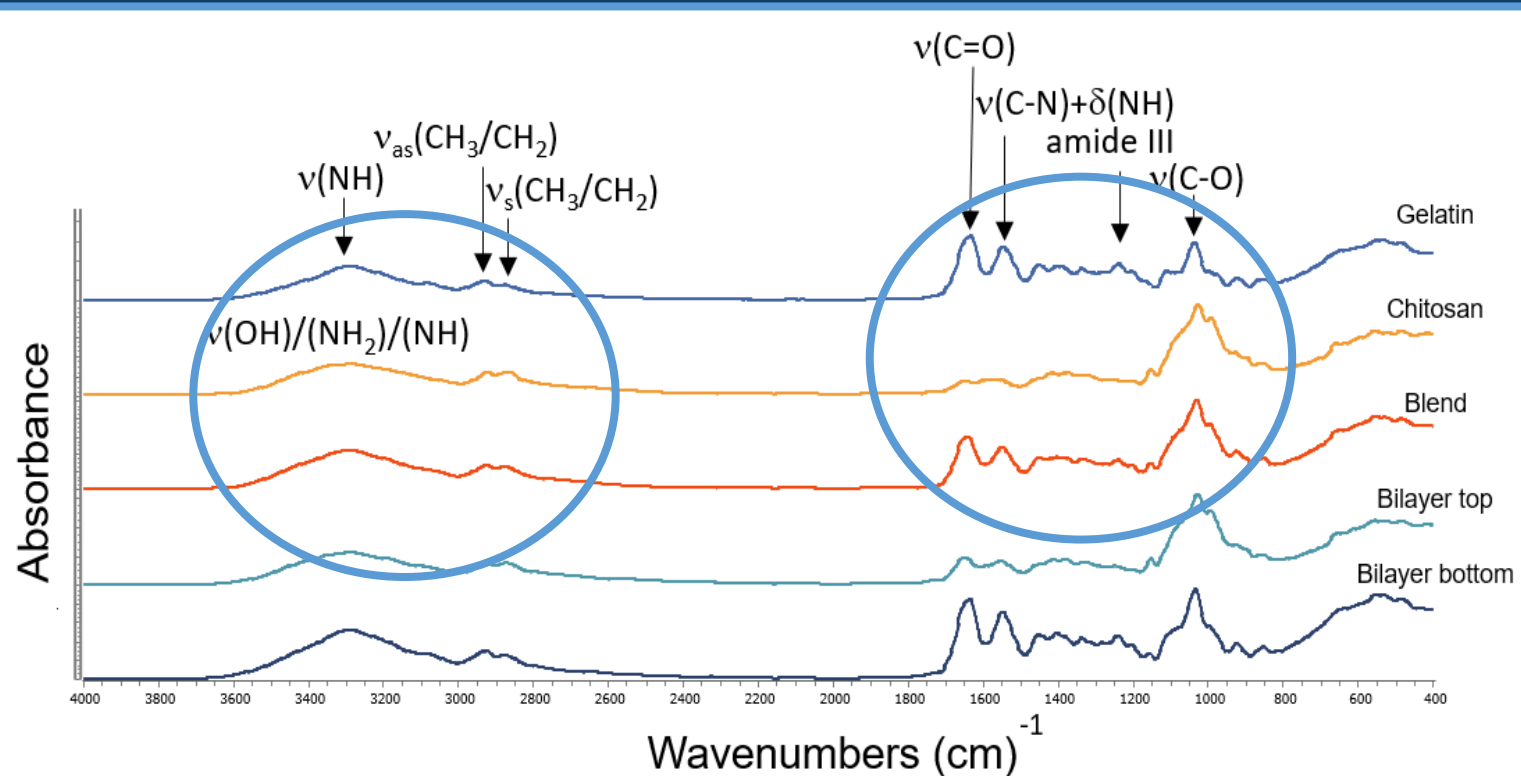
Blend

Bilayer



- Blend and bilayer films based on chitosan-gelatin showed homegenous surface.
- Blend films showed compact cross-section while bilayer films showed stacked layers.

Fourier Transform – Infra Red (FT-IR)



- FT-IR spectra indicated that interactions existed between chitosan and gelatin mainly due to **electrostatic interactions** and **hydrogen bond formation**.

Mechanical Properties

Film Sample	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus (Mpa)
Chitosan	22.8 ± 0.6 ^b	28.9 ± 0.5 ^a	565.2 ± 23.7 ^c
Gelatin	09.3 ± 0.1 ^a	29.4 ± 1.8 ^a	361.3 ± 08.9 ^a
Blend	31.9 ± 1.7^c	28.7 ± 0.5 ^a	534.6 ± 06.4^c
Bilayer	24.3 ± 3.2 ^b	31.6 ± 0.6 ^a	462.6 ± 10.2 ^b

Values are given as mean ± standard deviation.

Different lowercase letters in the same column indicate significant differences ($p < 0.05$).

- Blending chitosan and gelatin showed **improvement in tensile strength and elastic modulus** ($p < 0.05$).

Water Barrier Property

Film Sample	Water Solubility (%)	Water Vapor Transmission Rate (g/day m)	Water Vapor Permeability (gr mm/kP day m2)
Chitosan/LAE	17 ± 0.6 ^a	3795.7 ± 34.00 ^b	0.024 ± 0.00021 ^b
Gelatin/LAE	100 ± 0.0 ^c	4262.5 ± 53.60 ^c	0.022 ± 0.00028 ^b
Blend/LAE	26 ± 0.6 ^b	3202.0 ± 53.73 ^a	0.018 ± 0.00031^a
Bilayer/LAE	26 ± 0.7 ^b	3690.4 ± 32.87 ^b	0.040 ± 0.00145 ^c

Values are given as mean± standard deviation.

Different lowercase letters in the same column indicate significant differences ($p<0.05$).

- Despite the hydrophilic nature of chitosan and gelatin, blending chitosan and gelatin showed **improvement in water barrier property** ($p<0.05$).

Conclusion

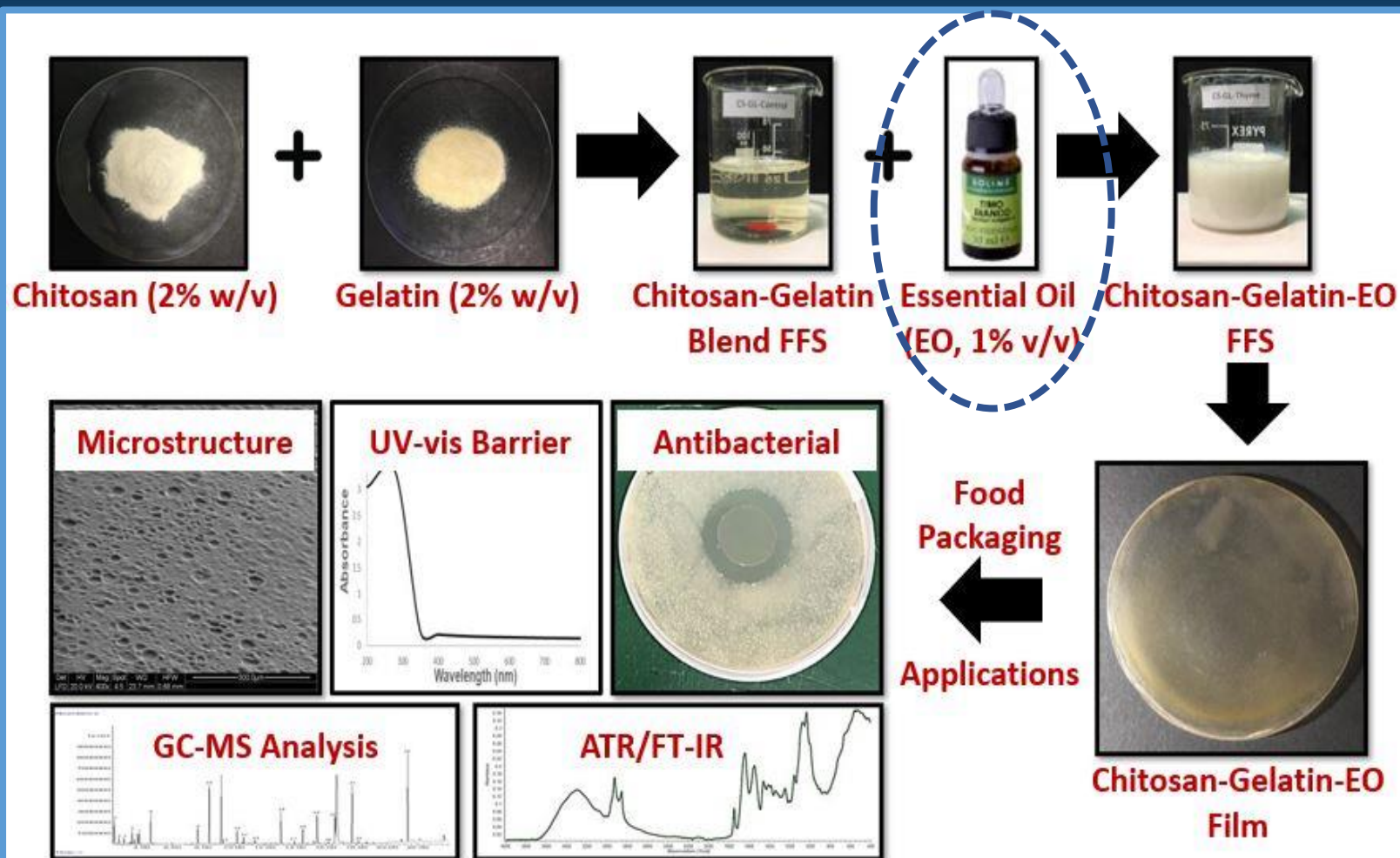
- Development of Blend and bilayer films based on chitosan and gelatin.
- Blending caused improvement in mechanical and water barrier properties.

Haghighi H, Del Leo R, Bedin E, Pfeifer F, Siesler HW, Pulvirenti A (2019) Comparative analysis of blend and bilayer films based on chitosan and gelatin enriched with LAE (Lauroyl Arginate Ethyl) with antimicrobial activity for food packaging applications. Food Packaging and Shelf Life.19: 31-39.

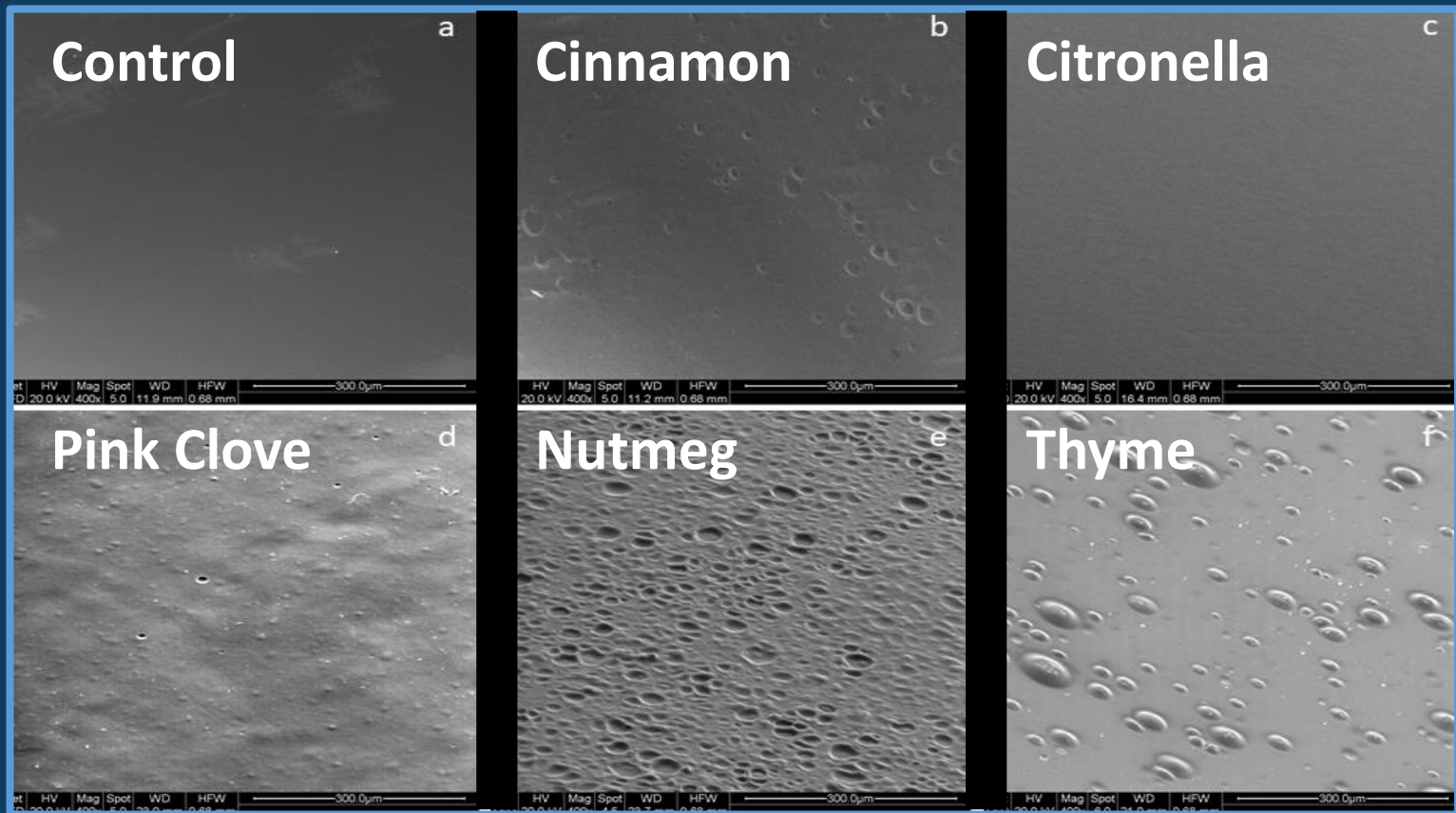
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Schematic Overview

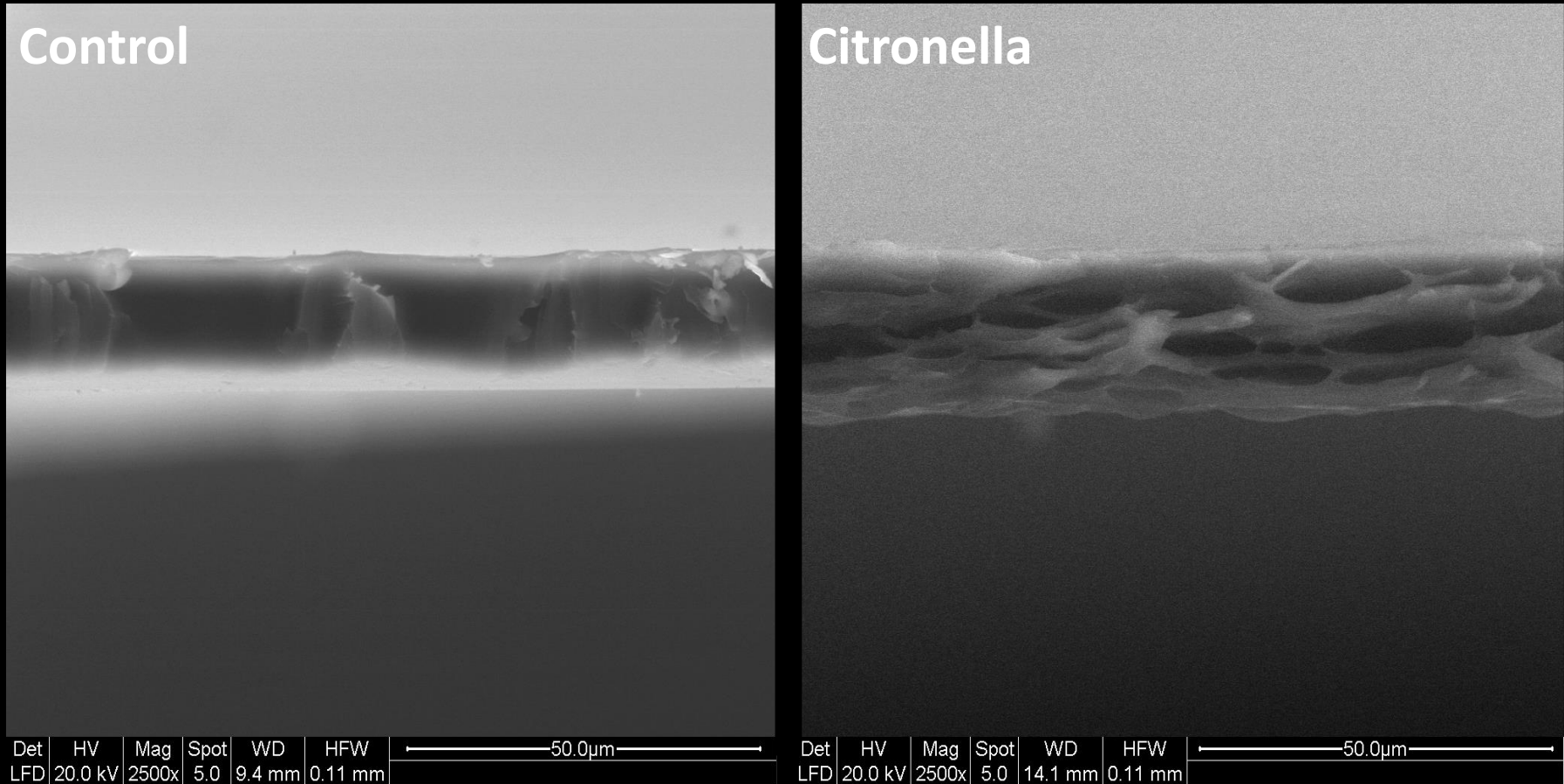


SEM: surface



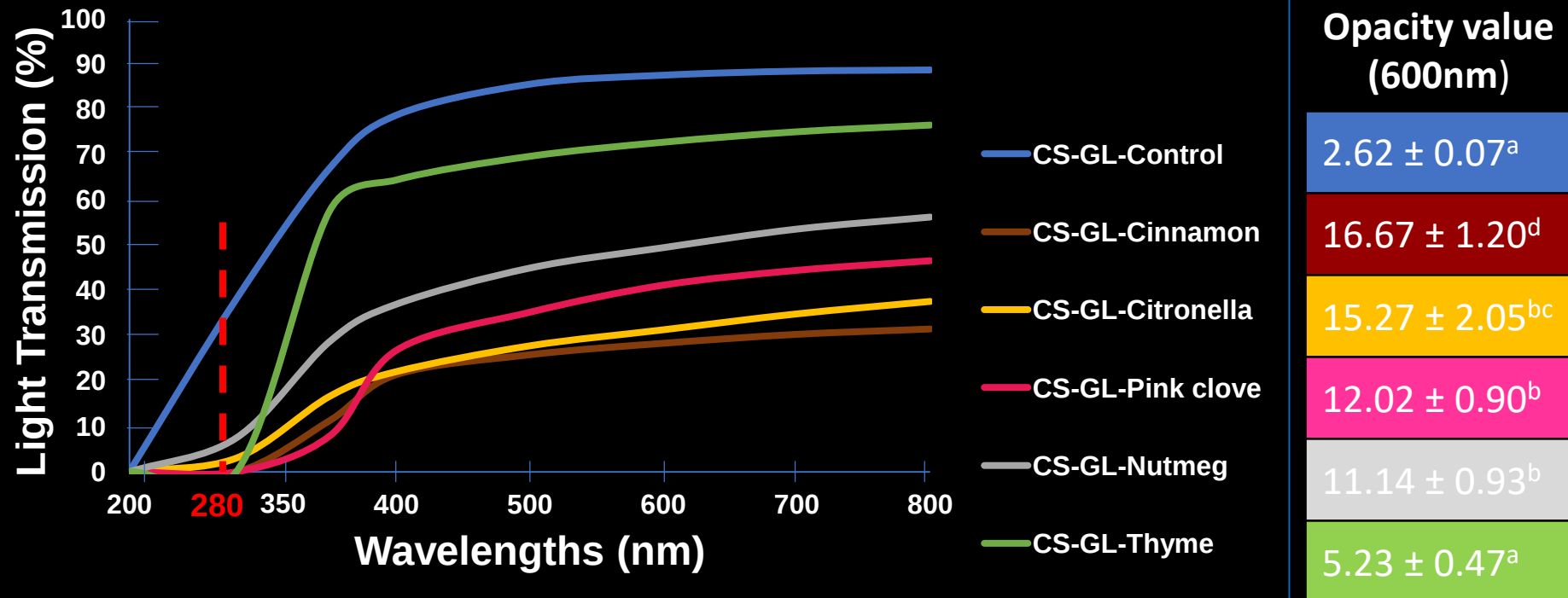
- Active films containing cinnamon, nutmeg and thyme showed **remarkable pores** on the surface.

SEM: cross-section



- Addition of EO caused the **disruption** and **restructuring** of **intermolecular interactions** in chitosan and gelatin film network.

UV-Vis Light Barrier Properties



- Essential oils effectively inhibited the UV light.
- Transparency decreased with the addition of essential oils.

Antibacterial Properties

Film sample	<i>C. jejuni</i>	<i>E. coli</i>	<i>L. monocytogenes</i>	<i>S. typhimurium</i>
CS-GL-Control	N. D.	N. D.	N. D.	N. D.
CS-GL-Cinnamon	5.3 ± 0.9 ^{bB}	2.6 ± 0.5 ^{aA}	2.0 ± 0.5 ^{aA}	1.0 ± 0.1 ^{aA}
CS-GL-Citronella	4.3 ± 1.9 ^{abA}	2.8 ± 0.7 ^{aA}	2.3 ± 0.5 ^{aA}	2.8 ± 0.7 ^{aA}
CS-GL-Pink clove	5.3 ± 0.9 ^{bB}	3.5 ± 0.2 ^{aAB}	2.4 ± 0.3 ^{aA}	3.0 ± 0.1 ^{aA}
CS-GL-Nutmeg	0.4 ± 0.1 ^{aA}	2.7 ± 0.3 ^{aC}	2.3 ± 0.5 ^{aBC}	1.0 ± 0.5 ^{aAB}
CS-GL-Thyme	11.3 ± 0.9^{cC}	5.7 ± 0.5^{bB}	3.0 ± 0.1^{aA}	6.2 ± 0.7^{bB}

Values are given as mean ± standard deviation. N.D means as not detected.

Different lowercase letters in the same column indicate significant differences ($p < 0.05$).

Different capital letters in the same row indicate significant differences ($p < 0.05$).

- Active films inhibited the growth of four major bacterial pathogens.
- Film containing thyme essential oil was the most effective ($p < 0.05$).

Conclusion

- Incorporation of essential oils notably **improved the UV-barrier** properties of chitosan-gelatin blend film.
- Active films showed **antimicrobial activity** against common food bacterial pathogens.

Haghighi H, Biard S, Bigi F, De Leo R, Bedin E, Pfeifer F, Siesler HW, Licciardello F, Pulvirenti A (2019) Comprehensive characterization of active chitosan-gelatin blend films enriched with different essential oils. Food Hydrocolloids. 95: 33-42.

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Schematic Overview



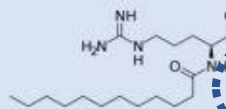
Chitosan (CS)
(1% w/v)



Polyvinyl Alcohol (PVA)
(5% w/v)



CS-PVA Blend FFS
(1:1)



Lauroyl Arginate Ethyl (LAE)
(1, 2.5, 5 and 10 % w/w)

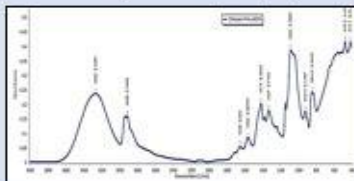
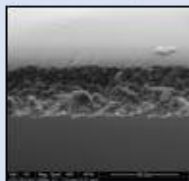


CS-PVA-LAE Film



Characterization for Food Packaging Applications

(Microstructure, FT-IR, Thickness, Mechanical, Optical, Water Barrier and Antimicrobial Properties)



SEM

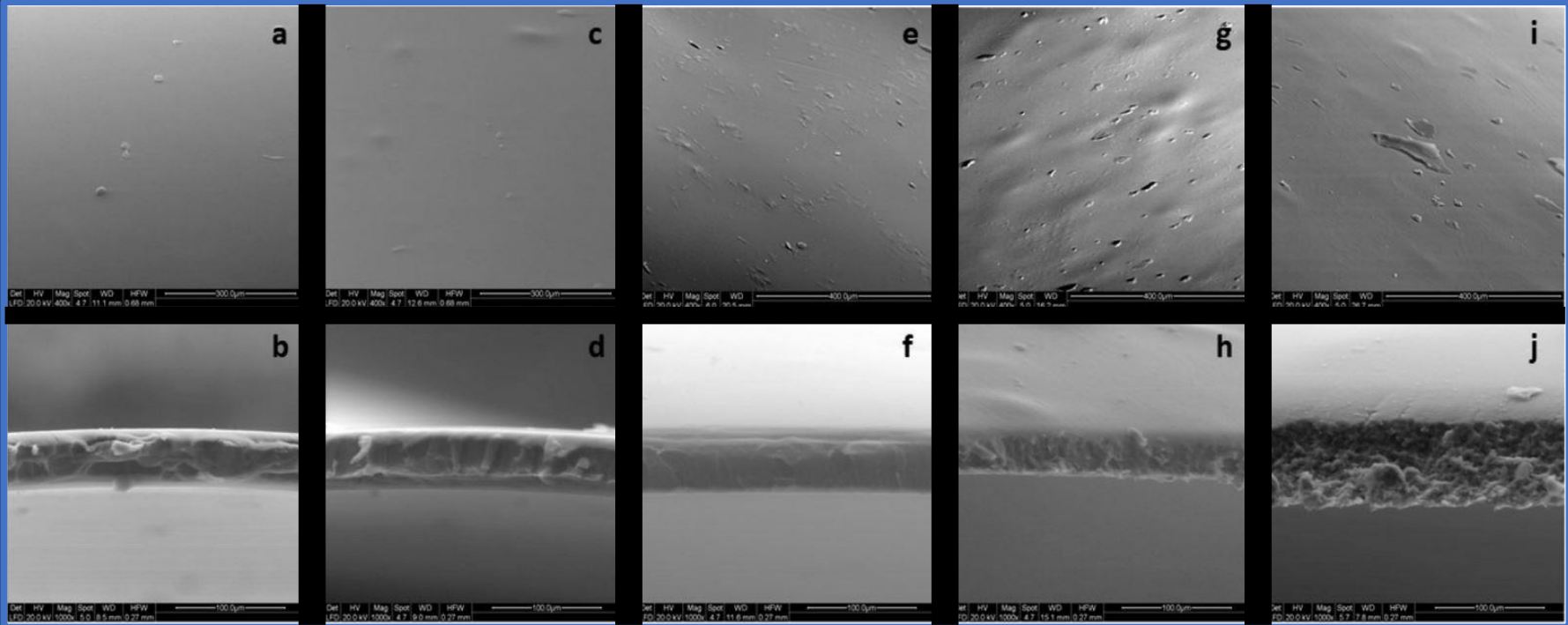
Control

LAE 1%

LAE 2.5%

LAE 5%

LAE 10%



- Active films containing 5 and 10% LAE showed **small particles and aggregations** at the surface of films.
- Active films containing 5 and 10% LAE showed **irregular and sponge shape structure**.

Mechanical Properties

Film Sample	Tensile Strength (Mpa)	Elongation at break (%)	Elastic modulus (Mpa)
Chitosan-PVA	42.5 ± 1.6 ^d	54.2 ± 2.0 ^d	1570.1 ± 139.0 ^d
Chitosan-PVA-LAE 1%	33.0 ± 2.4 ^c	38.9 ± 3.1 ^c	1153.1 ± 121.1 ^{bc}
Chitosan-PVA-LAE 2.5%	34.5 ± 4.2^c	39.0 ± 2.6^c	1287.3 ± 77.8^c
Chitosan-PVA-LAE 5%	22.2 ± 0.9 ^b	25.0 ± 2.8 ^b	1016.9 ± 90.8 ^b
Chitosan-PVA-LAE 10%	15.7 ± 1.2 ^a	14.3 ± 1.9 ^a	701.3 ± 53.8 ^a

Values are given as mean ± standard deviation.

Different lowercase letters in the same column indicate significant differences ($p < 0.05$).

- High LAE levels negatively affected mechanical properties.

Conclusion

- Development of films based on chitosan-PVA blend enriched with different concentration of LAE.
- High LAE levels **negatively** affected mechanical properties.
- Active films showed **antimicrobial activity** against common food bacterial pathogens.

Haghighi H, Kameni Leuguue S, Pfeifer F, Siesler HW, Licciardello F, Fava P, Pulvirenti A (2020) Development of antimicrobial films based on chitosan-polyvinyl alcohol blend enriched with ethyl lauroyl arginate (LAE) for food packaging applications. Food Hydrocolloids.

Life in PLASTIC is FANTASTIC!



99% of market belongs to synthetic plastics!

Thank you all!



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