Engineered Biodegradable Coatings on Cellulosic and Biopolymeric Substrates for Active, High Barrier Packaging Solutions

Luciano Di Maio

Dipartimento di Ingegneria Industriale **Università di Salerno**









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Conference

"Finished product and new formulations of varnishes, inks, adhesives and various types of coatings in response to the European directives on sustainable food packaging"

October 22nd 2024





Food packaging means:



- Food safety
- Easy transport and handling
- Presentation and information





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- Food packaging constitutes the main volumetric fraction of municipal solid waste.
- 40% is made up of plastic



Sustainable packaging

The value chain of plastic packaging needs a **deep transformation** in the perspective of sustainability and of the Circular Economy principles, in order to stop the environmental pollution caused by the huge quantities of waste produced by this sector all over the world.

CIRCULAR ECONOMY: Plastic never becomes waste



The strategies

- Effectiveness of
 - packaging systems
- Competitiveness
- Reduction of food waste

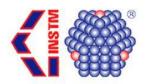
SUSTAINABILITY

 Nanotechnologies
 Active/Intelligent Packaging
 Replacement of multi-material with single-material solutions
 Active and Passive Coatings

INNOVATION

- Raw materials from renewable sources
- Implementing mono-material packaging solutions
- Recycled raw materials
- Thickness/mass reduction







Which are the CONSTRAINS ?

INDUSTRIAL FEASIBILITY

Use of conventional production technologies that are easily scalable at industrial level

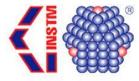
SAFETY AND SUITABILITY FOR FOOD CONTACT

Use of additives and materials approved by the FDA and EFSA for food contact; Verification of compliance with the requirements of the European regulation for materials intended for food contact (EU No 1935/2004 and subsequent).



Food packaging critical key points

seal ability
 oxygen and vapor barrier properties
 antimicrobial and/or oxygen scavenging properties
 printability





BIODEGRADABLE POLYMERS AND CELLULOSIC SUBSTRATES

PROS

- Good mechanical, optical and rheological properties;
- Low toxicity of degradation products
- Rapid degradation rate after use
- Consumer attractive

CONS

- Scarce gas barrier properties
- Brittleness
- Limited processability
- Low thermal resistance;
- Scarce impact resistance

Some functional properties are not fully satisfactory, limiting their applications to foods with a short shelf-life.





FEATURED APPROACHES





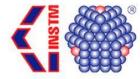




Nanocomposites, Blends, Multilayers films, Active phases, Coatings

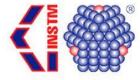






COATING TECHNOLOGY





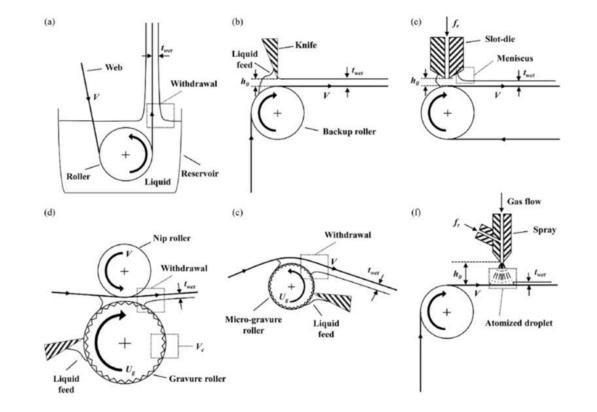
COATING TECHNOLOGY

Process scalability Process flexibility Materials choices Low cost

...







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Coating technology for realization of biodegradable multilayer films with enhanced functionalities for food packaging

Sustainability

- 100% biodegradable materials;
- Easy layer separation in post-consumer phase

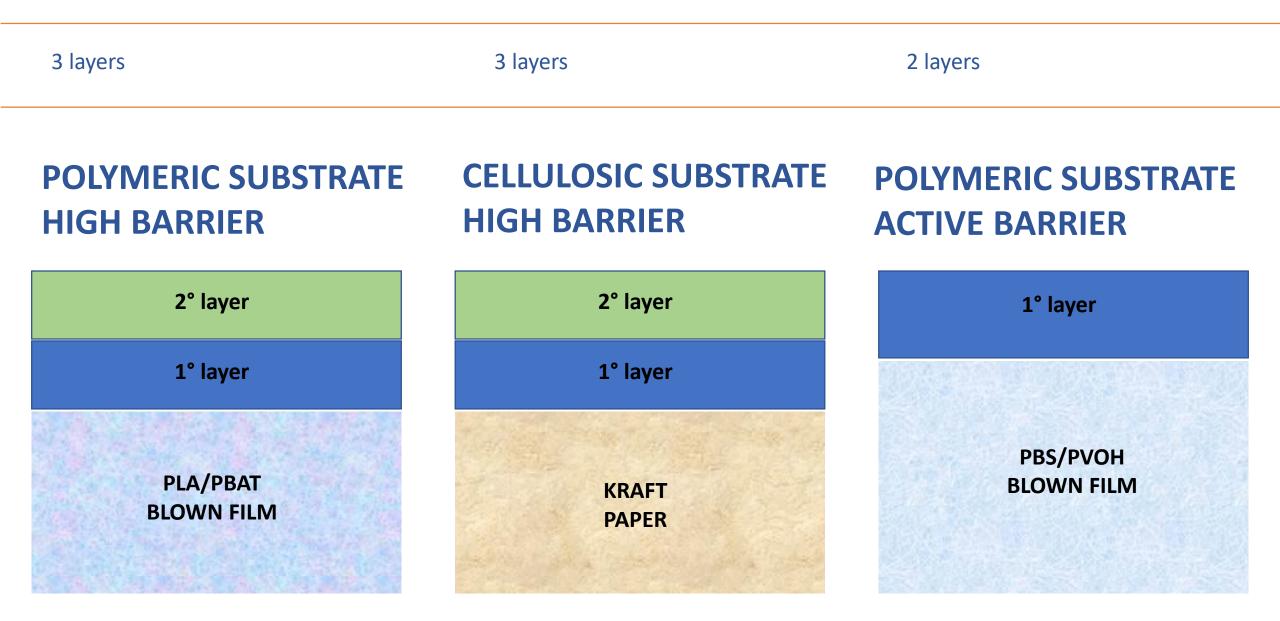
Applicability in food packaging field

- Materials approved for food contact;
- Multiple functional properties (structural, barrier, sealability, water resistance).

Industrial feasibility

 Films produced by film blowing and coating process, conventional technologies easy scalable at industrial level;

100% biodegradable multi-layers films

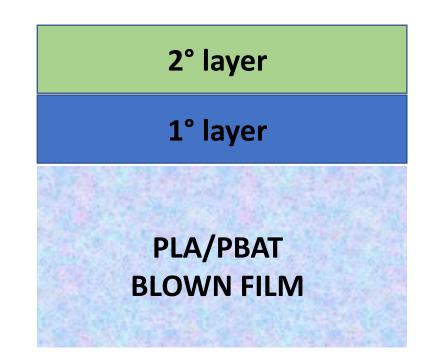






POLYMERIC SUBSTRATE HIGH BARRIER

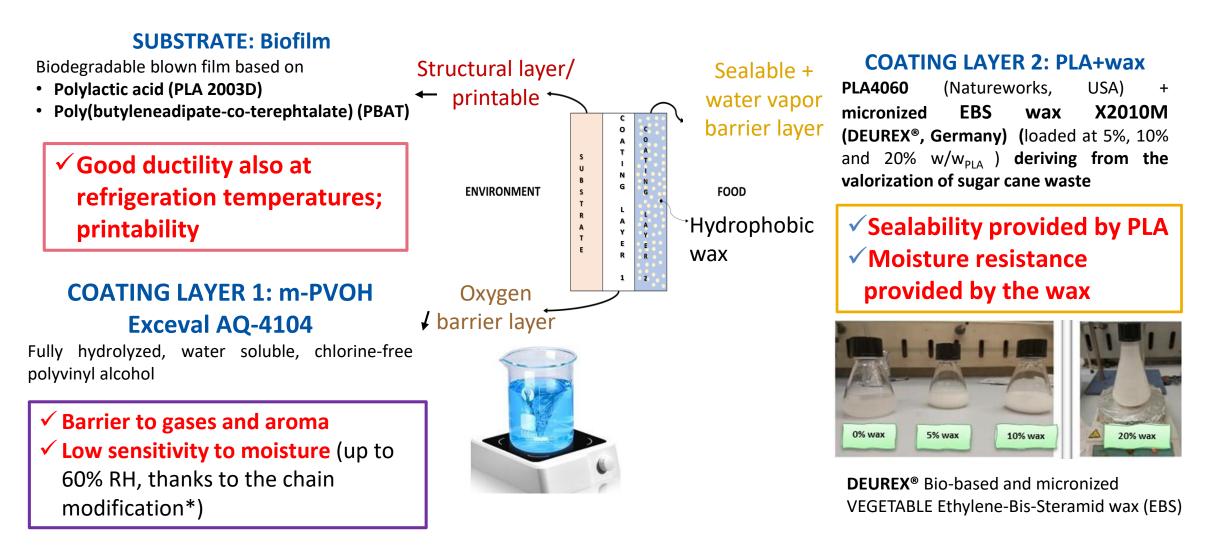
PLA-PBAT blown films COATED WITH PVOH and WAX

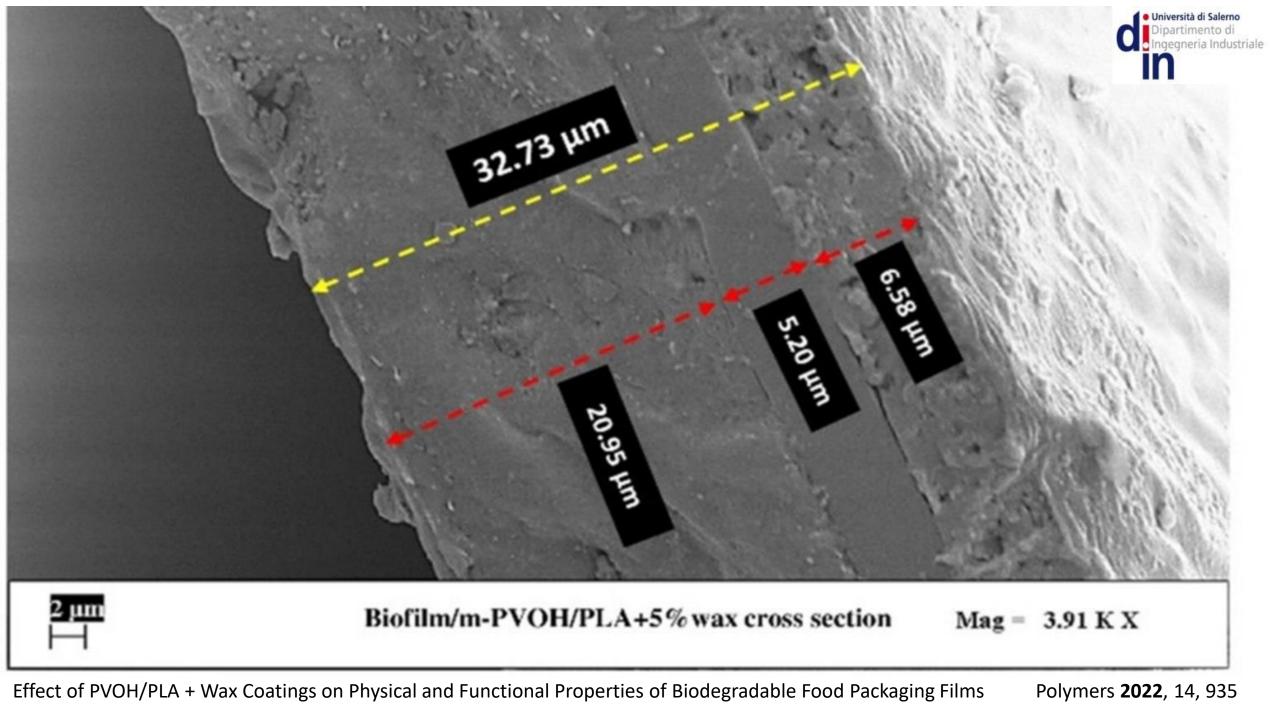




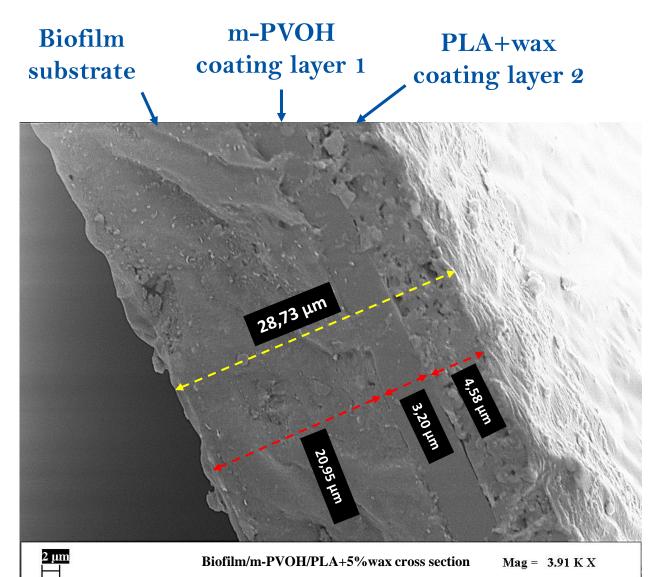
2° layer COATING	PLA + IDROPHOBIC WAX - H ₂ O Barrier Barrier/Sealable
1° layer	M-PVOH coating - O ₂ Barrier
COATING	Exceval AQ-4104. Water soluble: easy to be removed in post consumer phase, High barrier properties, Reduced moisture sensitivity due to chemical modification
PLA/PBAT BLOWN FILM	blown film based on blends of PLA/PBAT











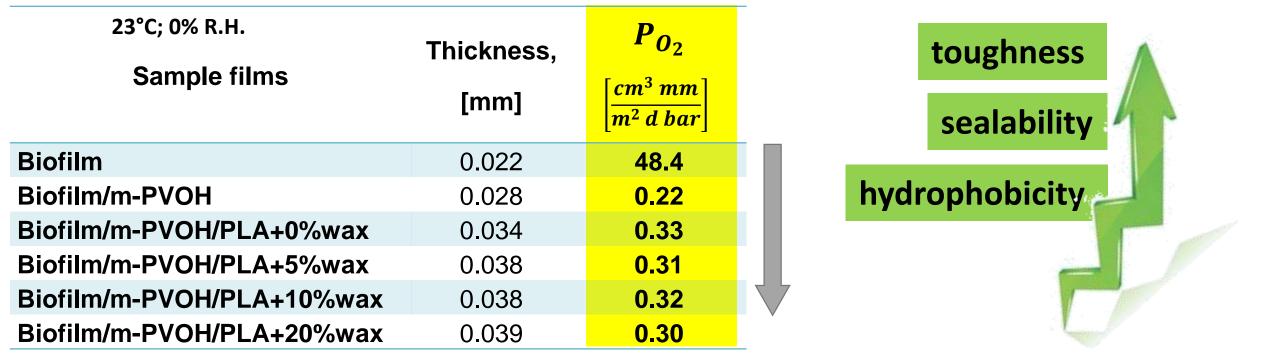
Films morphology and quality of interlayer adhesion

- Good interlayer adhesion for both the m-PVOH and PLA coating layers, with no boundary lines or voids in the whole cross-sectional area of the investigated films;
- **Good control** of the layers thickness during the coating process.
- No delamination occurred by increasing wax content

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OXYGEN BARRIER PROPERTIES



The proper design/combination of supports and coatings allows to keep the toughness of PLA/PBAT system with the barrier properties of m-PVOH and with the seal ability and hydrophobicity provided by the PLA layer with natural wax.



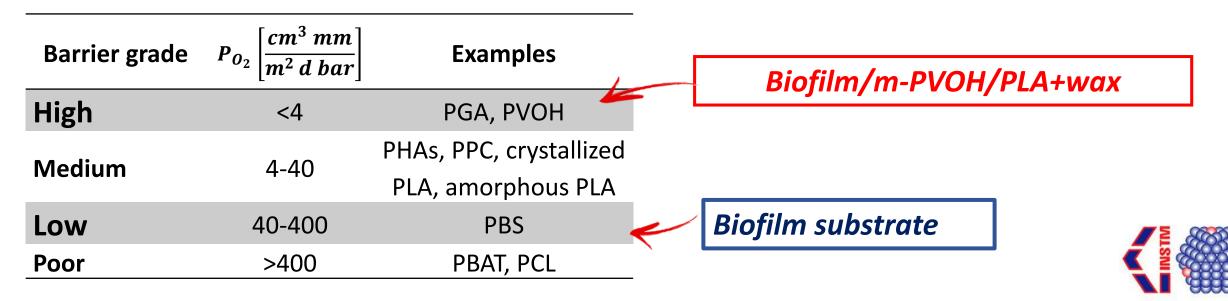
Multilayer films with wax are classified as <u>HIGH</u> oxygen barrier grade

23°C; 0% R.H.	Thickness,	$\frac{P_{O_2}}{\left[\frac{cm^3 mm}{m^2 d bar}\right]}$	
Sample films	[mm]		
Biofilm	0.022	48.4	
Biofilm/m-PVOH	0.028	0.22	
Biofilm/m-PVOH/PLA+0%wax	0.034	0.33	
Biofilm/m-PVOH/PLA+5%wax	0.038	0.31	
Biofilm/m-PVOH/PLA+10%wax	0.038	0.32	
Biofilm/m-PVOH/PLA+20%wax	0.039	0.30	

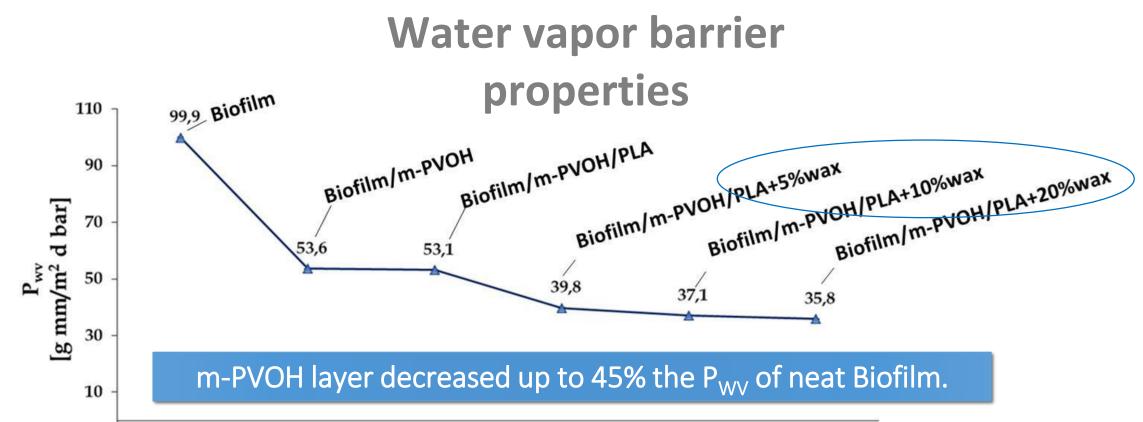
OXYGEN BARRIER PROPERTIES

P₀₂ decrease of up to 2 o.o.m.

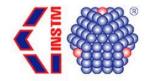
Classification of the biodegradable polymers depending on barrier perfomance (J. Wang et al.,2018)





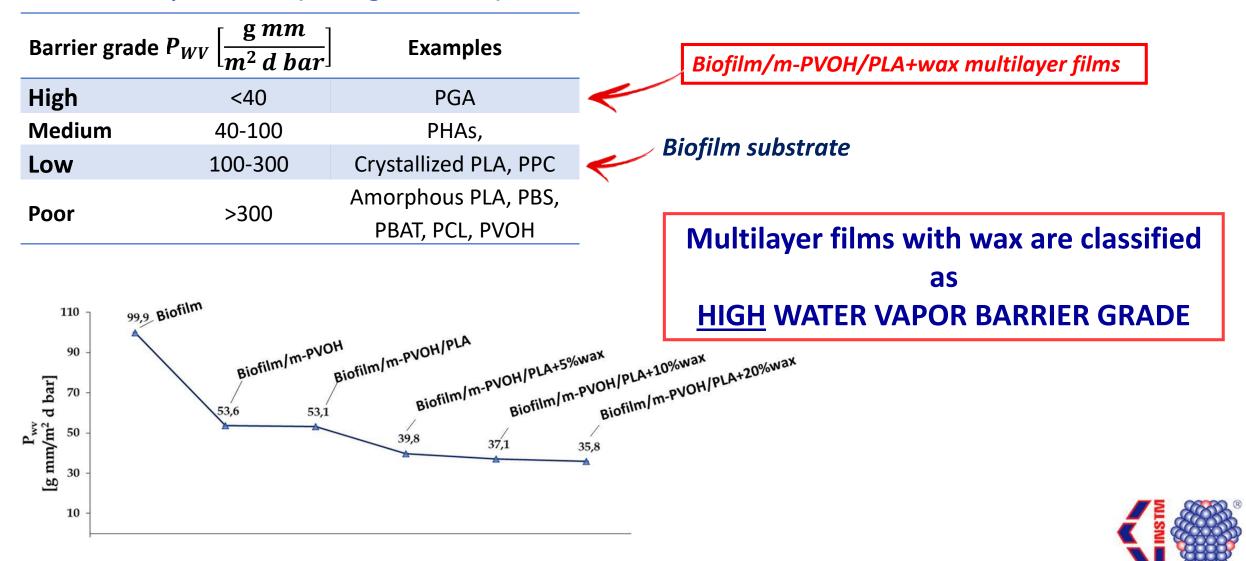


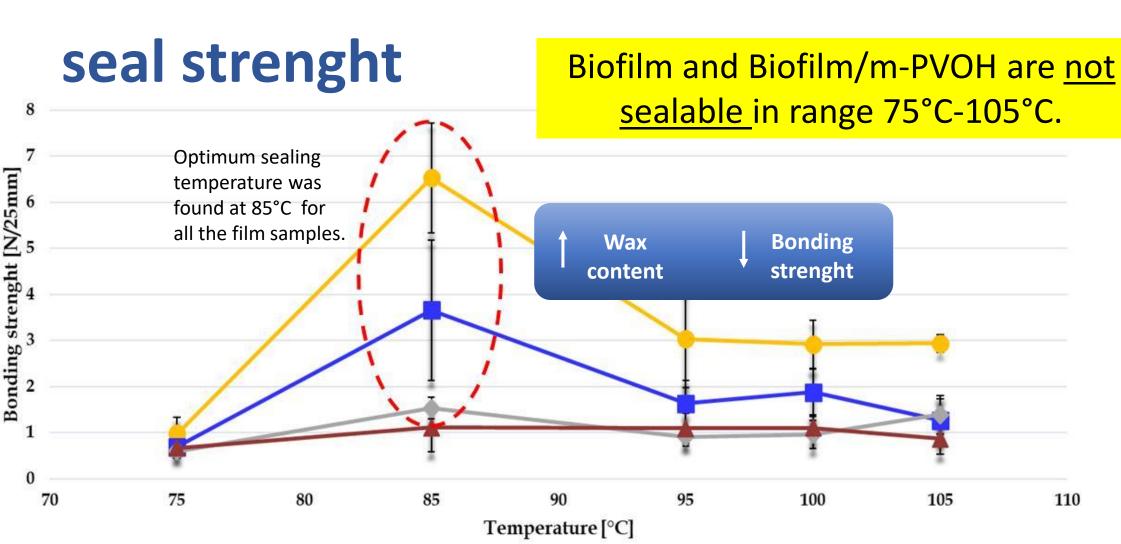
Wax addition in PLA effectively hinders the vapor permeation into multilayer structure further improving water vapor barrier and protecting m-PVOH against moisture.



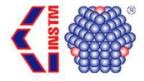


Classification of the biodegradable polymers depending on barrier perfomance (J. Wang et al., 2018)

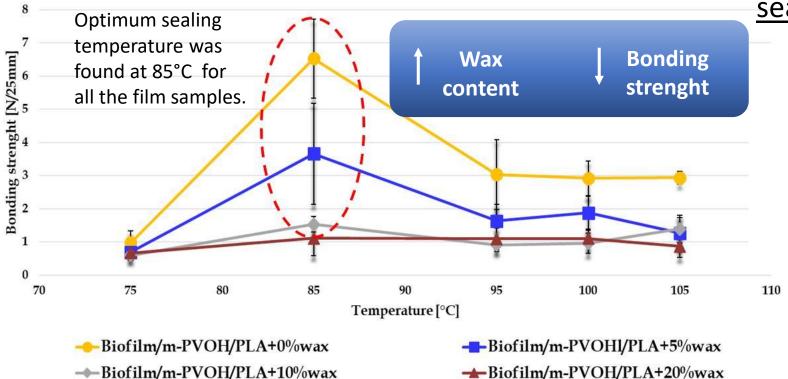




---Biofilm/m-PVOH/PLA+0%wax ---Biofilm/m-PVOH/PLA+10%wax ---Biofilm/m-PVOHI/PLA+5%wax ---Biofilm/m-PVOH/PLA+20%wax



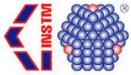
seal strenght



Biofilm and Biofilm/m-PVOH are <u>not</u> <u>sealable</u> in range 75°C-105°C.

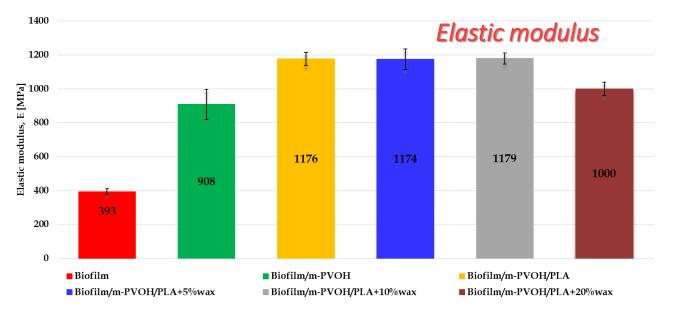
> The PLA coating layer provided additional sealability function to the multilayer films

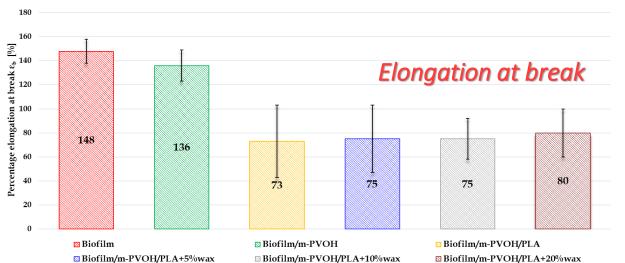
• In all cases, seal adhesion remained still acceptable for the films application in food packaging (Bamps et al., 2022; Iwasaki et al., 2015)





good balance between stiffness and ductility

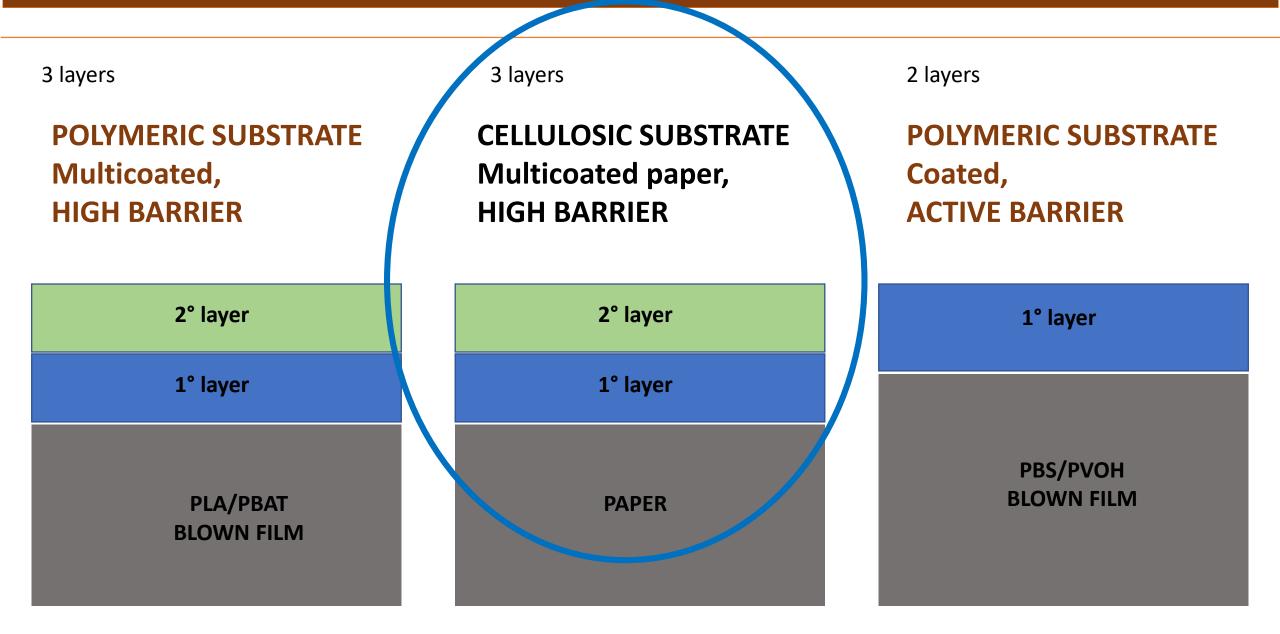




- Good ductility of Biofilm
- Consistent increase of its elastic modulus after the deposition of both the m-PVOH and PLA layers, up to a maximum equal to 1179 MPa.
- PLA coating layer decreases the films ductility which remain still acceptable around 73%-80%.
- No marked effects with wax incorporation are noticeable: increasing EBS wax percentage elastic modulus and elongation at break are not affected

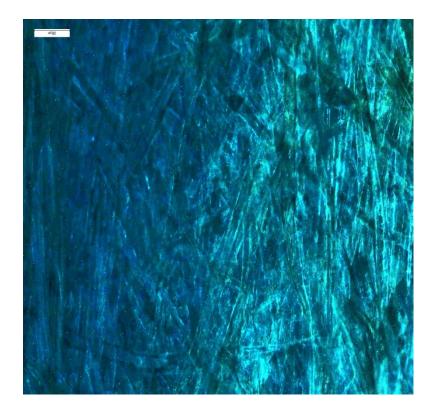


100% biodegradable multi-layers films

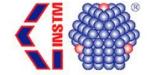




Multicoated paper



KRAFT PAPER COATED WITH m-PVOH and CARNAUBA WAX



Main limitations in the use of paper in the food packaging sector:

- High permeability
- Low resistance to oils and fats
- Hydrophilicity
- Non-sealable material

Proposed approach deposition of a m-PVOH coating layer on the kraft paper substrate

- Barrier properties
- Resistance to oils and greases

additional layer of coating of wax/polymer blend

- Sealing properties
- Hydrophobization



MATERIALS

High-quality KRAFT PAPER with a grammage of 100 g/m2;

Kraft paper Good mechanical strength;

Greater moisture resistance with respect other types of paper (richer in lignin).

m-PVOH Exceval AQ-4104. Water soluble: easy to be removed in post consumer phase, High barrier properties, Reduced moisture sensitivity due to chemical modification

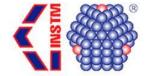
Mater Bi (EF05B)

- Flexible polymer matrix
- Excellent sealing properties (designed for shopper production)
- Hydrophilic

Carnauba wax

- Natural wax
- Highly hydrophobic
- Approved for use in contact with foodstuffs (cosmetics etc.)
- Odourless. tasteless
- Antioxidant properties are reported in literature

SAMPLES KP/m-PVOH KP/m-PVOH/MB KP/m-PVOH/MB+10%CW KP/m-PVOH/MB+20%CW



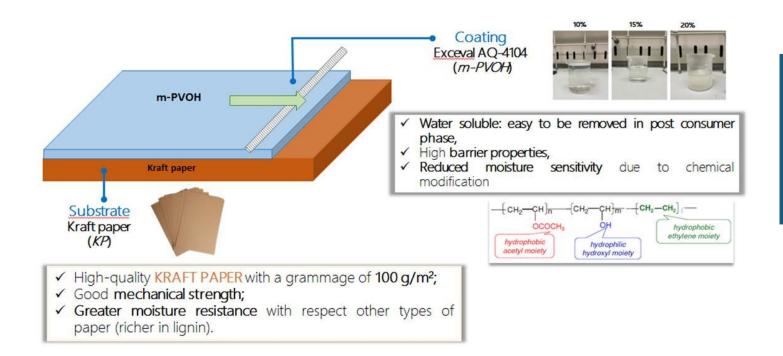


2° layer	Carnauba wax in Mater-Bi
1° layer	Exceval AQ-4104. Water soluble: easy to be removed in post consumer phase, High barrier properties, Reduced moisture sensitivity due to chemical modification
KRAFT PAPER	High-quality KRAFT PAPER with a grammage of 100 g/m2; Good mechanical strength; Greater moisture resistance with respect other types of paper (richer in lignin).
Angles Angles	



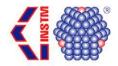
DESIGN AND REALIZATION OF THE COATED PAPER

The structures were realized through the deposition of water-based solutions having different percentages of PVOH (10%, 15%, 20% wt/wt) on the Kraft paper substate.

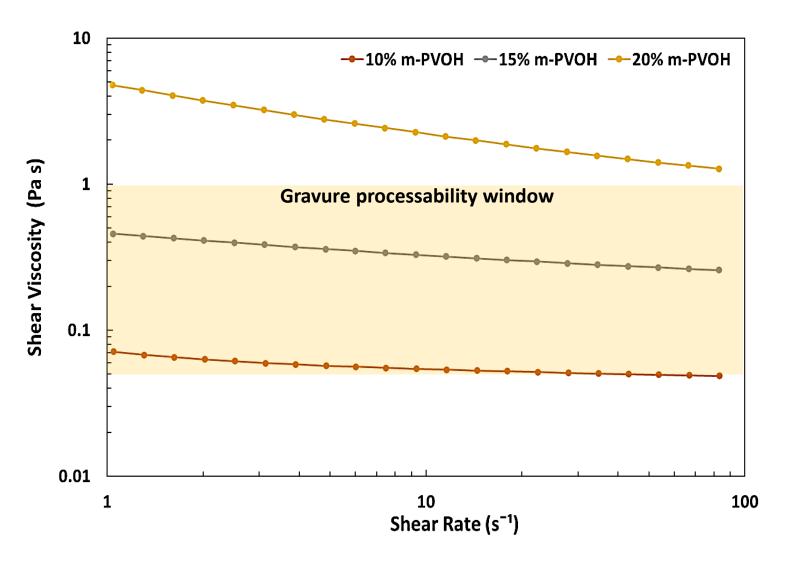


Produced samples:

Sample	m-PV0H conc. [%w/w]	Grammage [g/m²]	Thickness [µm]
KP	-	104.3±0.8	151.3±2.8
KP/10% m-PV0H	10	113.2±1.5	158.3±3.6
KP/15% m-PV0H	15	116.0±1.8	159.6±1.7
KP/20% m-PV0H	20	121.3±2	162.0±2.2



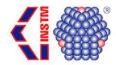




Why 15% m-PVOH?

- Is completely within the viscosity range of the process that we can reproduce with the hand coater (gravure).
- The overall properties of the KP/15% mPVOH sample are balanced .

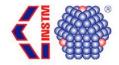
Printing method	Viscosity range (Pa s)
Piezo Inkjet	0.005-0.03
Gravure	0.05-1.5
Flexography	0.05-0.5
Screen	1-10
Offset	40-100



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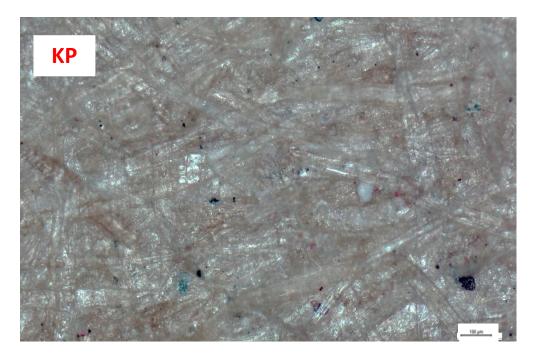
Sample list: coating weights and thicknesses

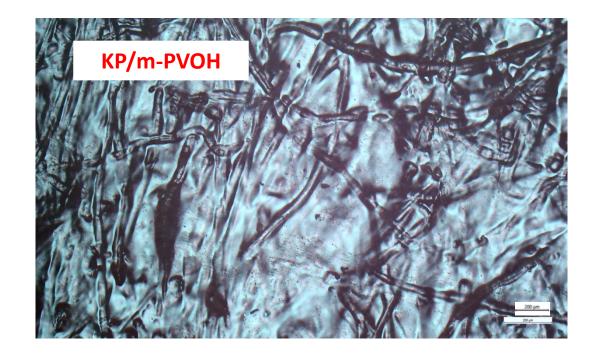
Sample	C. Wax conc. [%w/w]	Grammage of the first coating [g/m ²]	Thickness of the first coating [μm]	Grammage of the second coating [g/m ²]	Thickness of the second coating [μm]
KP/m-PVOH	-	EXC 11.7±1.8	EXCEVAL	-	C. WAX -
KP/m-PVOH/MB	-			19.5±2.5	8.4±2.2
KP/m- PVOH/MB+10%CW	10			20.7±2.8	12.7±1.5
KP/m- PVOH/MB+20%CW	20			22.0±2.7	13.1±4.8
KP/m- PVOH/MB+30%CW	30			25.6±4.3	14.7±2.2

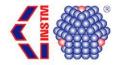


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Optical microscopy

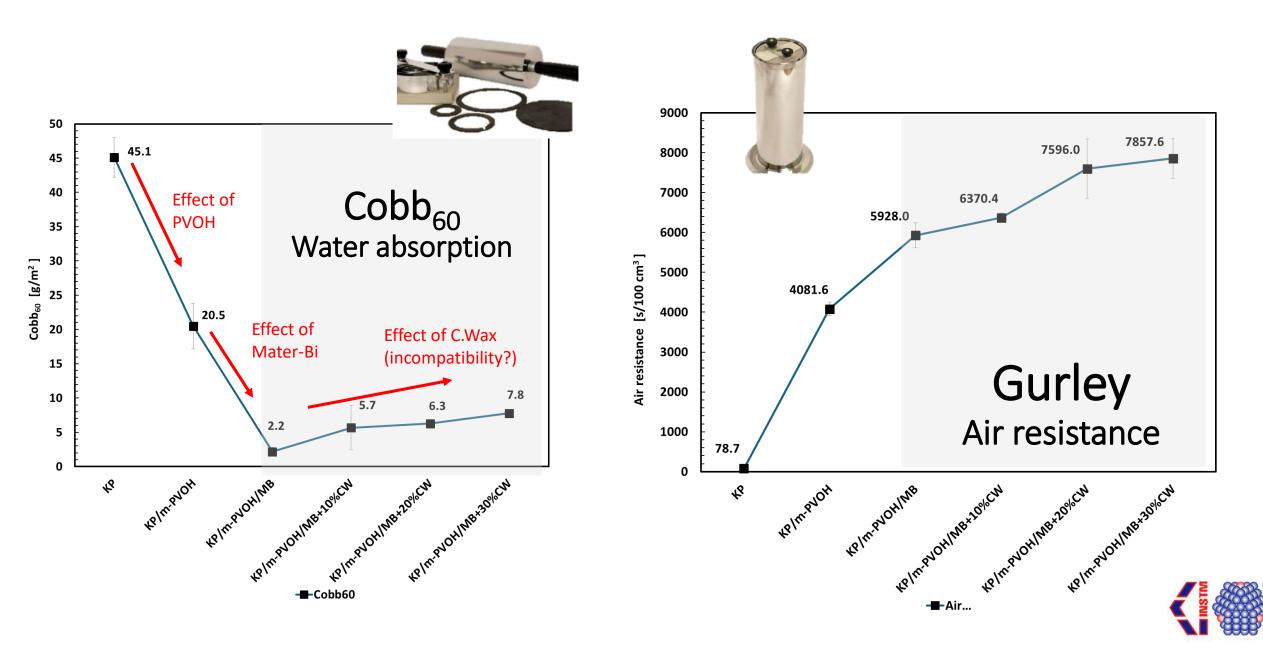






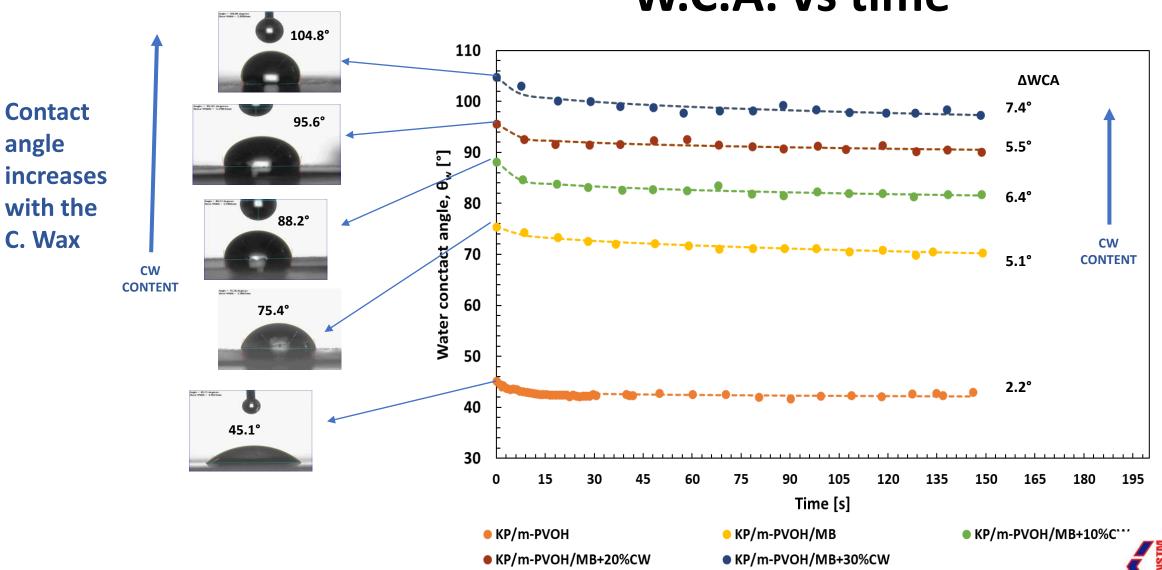
KRAFT PAPER COATED WITH m-PVOH and POLYMER/CARNAUBA WAX





KRAFT PAPER COATED WITH m-PVOH and POLYMER/CARNAUBA WAX





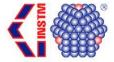
W.C.A. vs time



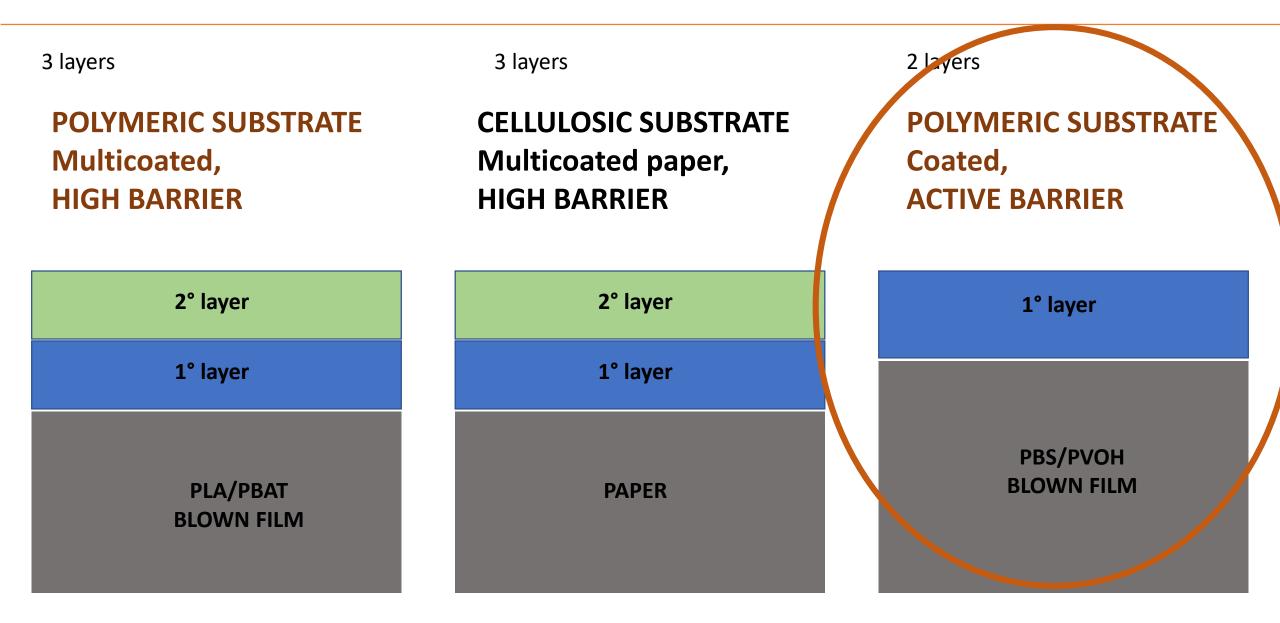
Tensile in MD

Sample	Tensile strength [kN/m]	Elongation at break [%]	Tensile Energy Absorption. TEA [J/m ²]
KP/m-PVOH	10.8±0.3	2.4±0.2	158.5 ± 9.9
KP/m-PVOH/MB	<mark>11.7±0.7</mark>	<mark>2.8±0.2</mark>	<mark>202.2±27.3</mark>
KP/m- PVOH/MB+10%CW	11.4±0.7	2.8±0.2	199.1 ± 27.0
KP/m- PVOH/MB+20%CW	11.3±0.9	2.7±0.2	187.4±28.9
KP/m- PVOH/MB+30%CW	11.3±0.8	2.6±0.2	180.0±23.4

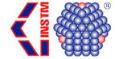
- MATER-BI improves mechanical properties: TS and elongation increase as does TEA
- The introduction of wax does not change the properties, which remain good and superior to the KP/mPVOH



100% biodegradable multi-layers films



Biodegradable packaging with quercetin-based antioxidant coatings for fresh-cut preservation



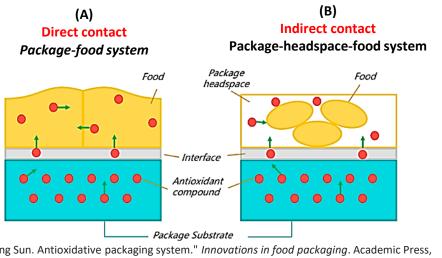




An **active food antioxidant packaging** system is able to :

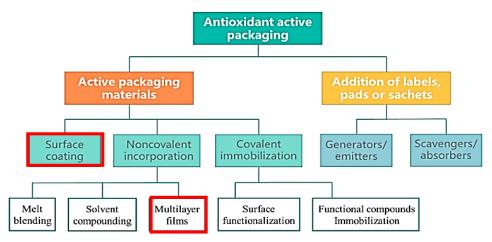
- Protect against oxidative damages the food item,
- Extend shelf-life of sensitive foods,
- **Reduce food waste** avoiding economic losses.

Release of antioxidant molecules can be achieved through two methods:



Lee, Dong Sun. Antioxidative packaging system." Innovations in food packaging. Academic Press, 2014.111-131.

Antioxidant molecules can be added adopting different technological solutions:



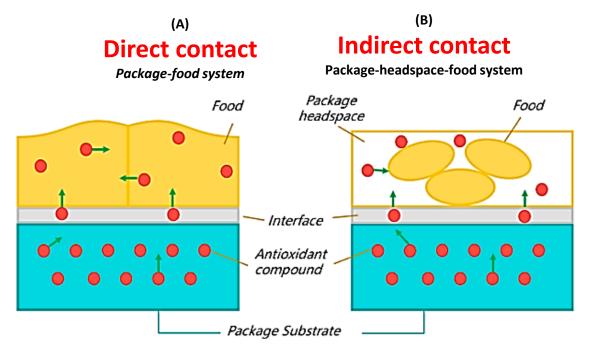
Kuai, Lingyun, et al. "Controlled release of antioxidants from active food packaging: A review." Food Hydrocolloids 120 (2021): 106992.

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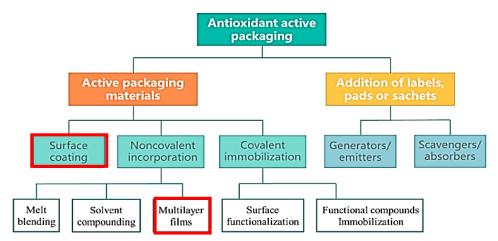


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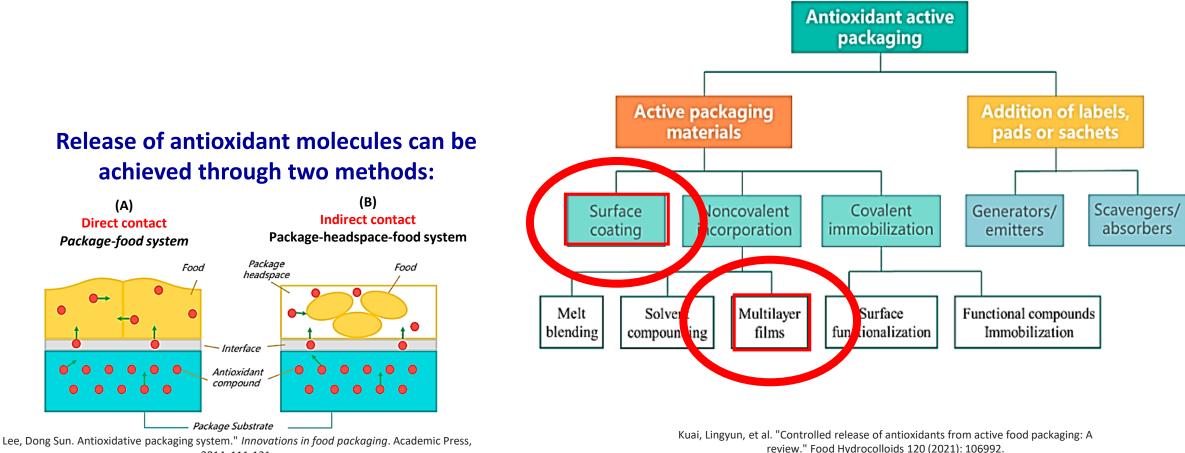


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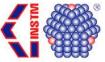
Antioxidant molecules can be added adopting different technological solutions:





2014. 111-131.

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Quercetin is a naturally occurring yellow-colored plant phenolic (flavonoid) compound widely found in onions (10-30 mg/100 g), blueberries (15 mg/100g), asparagus (15-20 mg/100g) and many other crops.

Quercetine main biological activities:



Source: Swarup Roy, Parya Ezati, Ajahar Khan & Jong-Whan Rhim (2023): New opportunities and advances in quercetin-added functional packaging films for sustainable packaging applications: a mini-review, Critical Reviews in Food Science and Nutrition,

1. Antioxidant activity

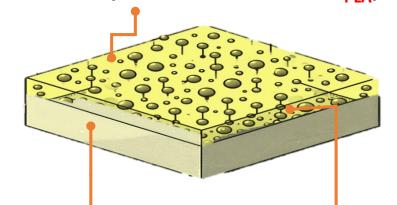
- Quercetin's antioxidant capability is six times that of commonly used Trolox (Wang et al., 2016).
- 2. Safety and approval
 - FDA-approved and GRAS (Generally Recognized As Safe) for food applications (Roy and Rhim, 2021).
- 3. Versatility and stability
 - Stable compound and easily incorporated into polymeric packages, mainly produced by solution casting and electrospinning (Roy et al., 2023)

Quercetin represents a good candidate for the development of functional food packaging films and/or coatings



MATERIALSA blown film (biodegradable substrate) was functionalized through
the application of an antioxidant coating layer carried by PLA

Antioxidant phase (QUE): Quercetine (0%, 3%, 5%, 7% w/w_{PLA})



Bio-substrate (BS): PBS/PVOH 80/20 wt% blown film

- ✓ Balanced mechanical and barrier properties
- ✓ Fully biodegradable
- ✓ Not sealable

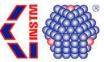
Coating layer: Amorphous PLA4060 + Tween 80 (1% w/w_{QUE}) SURFACTANT

- ✓ Sealable layer
- ✓ Easy soluble to be removed



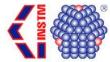
Film sample	Que conc. [%w/w _{PLA}]	Coating layer thick. [µm]	Total thick. [µm]
BS	-	-	35±3
BS/PLA	-	7±1	40±2
BS/PLA+3%QUE	3	6±2	39±3
BS/PLA+5%QUE	5	7±1	40±3
BS/PLA+7%QUE	7	8±1	41±2

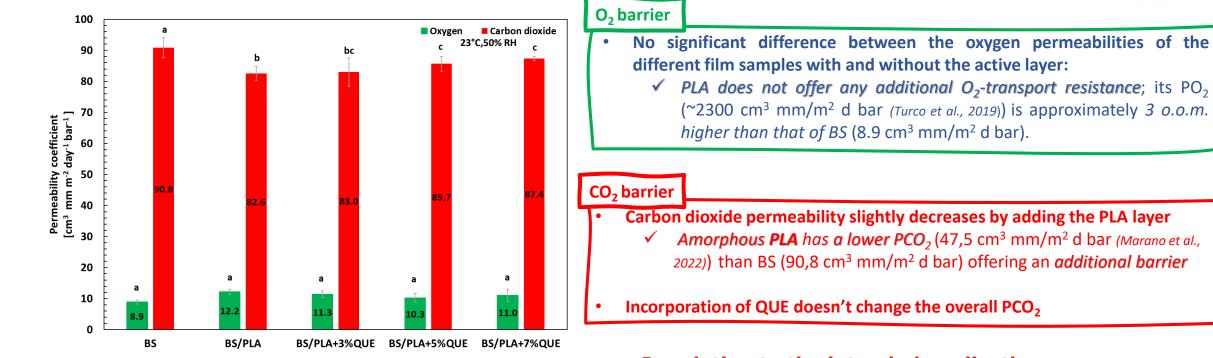






O₂/CO₂ barrier properties and perm-selectivity





In relation to the intended application:

Adequate O₂ and high CO₂ levels have been proved to effectively control enzymatic browning, firmness and decay of fresh-cut fruits and vegetables (Rojas-Graü et al., 2008)

The optimal CO_2/O_2 perm-selectivity ratio for fresh-cut produce packaging depend on the specific respiration characteristics and gas requirements of the product.

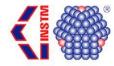
• A β value in the range 2.2-8.7 is typical for most films used in this application (Hussein et al., 2015).

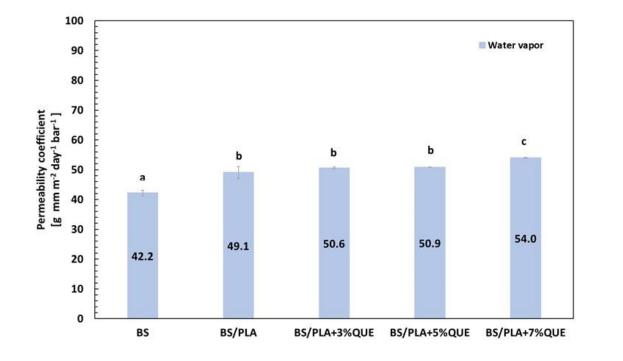


Permselectivity,
$$\beta = \frac{P_{CO_2}(23, °C 50\% RH)}{P_{O_2}(23, °C 50\% RH)}$$

Film sample	Perm-selectivity P _{CO2} /P _{O2} [-]
BS	10.2
BS/PLA	6.8
BS/PLA+3%QUE	7.3
BS/PLA+5%QUE	8.3
BS/PLA+7%QUE	7.9

Water vapor barrier properties





Classification of the biodegradable polymers depending on barrier perfomance (*J. Wang et al.,2018*)

Barrier grade	$P_{WV}\left[\frac{gmm}{m^2dbar}\right]$	Examples
High	<40	PGA
Medium	40-100	PHAs,
Low	100-300	Crystallized PLA, PPC
Poor	>300	Amorphous PLA, PBS, PBAT, PCL, PVOH

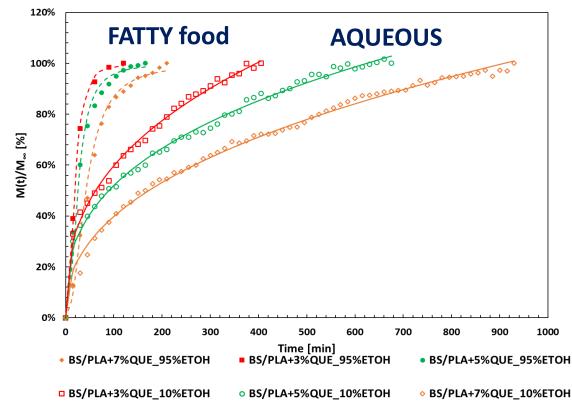
Water vapor barrier Pwv slightly increases by adding the PLA layer: *High solubility of water vapor in PLA* (Barbato et al., 2023). Gradual slight increase of Pwv by increasing QUE concentration; more pronounced for BS/PLA+7%QUE: *Quercetin's hydrophilicity attract water*, increasing water vapor transmission and enhancing film permeability as its content rises (Roy et al., 2023).

Developed multilayers are classified as <u>MEDIUM</u> water vapor barrier grade

In relation to the intended application: *Moderate water vapor transpiration is crucial to prevent moisture buildup, condensation, and microbial growth in the packaging* thereby preserving the freshness of cut produce.

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Release kinetics and antioxidant activity [1/2]



Test conditions:

- Release media: Ethanol 10% v/v (AQUEOUS SIMULANT) and ethanol 95% v/v (FATTY SIMULANT) V=100mL*
- Films Area: 1 dm²
- Stored in darkness at room temperature
- **Release kinetics by UV-Vis measurement** (λ=317 nm) and calibration curve
- Antioxidant activity by DPPH test on the release medium at release plateau

Sample	Exhaust. time [h]	Max amount released [mg/L]	DPPH scav. activity [%]
BS/PLA+3%QUE_95%ETOH	2	71.5	48.4
BS/PLA+5%QUE_95%ETOH	3	88.4	69.0
BS/PLA+7%QUE_95%ETOH	4	101.7	77.3
BS/PLA+3%QUE_10%ETOH	7	0.83	8.1
BS/PLA+5%QUE_10%ETOH	11	1.0	9.1
BS/PLA+7%QUE_10%ETOH	16	1.2	10.8

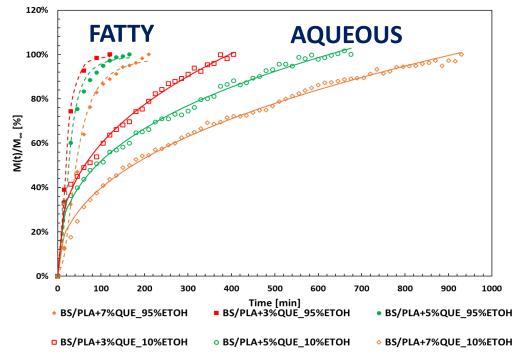
Effectiveness of antioxidant release in both food simulants.
 Release time and released amount depentent by QUE concentration

Tunable release kinetics by varying the food matrix characteristics and the film composition.



Release kinetics and antioxidant activity [2/2] <





POSSIBLE APPLICATION

Sensitive foods with:

- high respiration rates
- modest lipid content
- short-medium storage term

Sample	Exhaust. time [h]	Max amount released [mg/L]	DPPH scav. activity [%]
BS/PLA+3%QUE_95%ETOH	2	71.5	48.4
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BS/PLA+7%QUE_10%ETOH	16	1.2	10.8

IN FATTY FOOD SIMULANT:

- Faster release kinetic
- Higher antioxidant release (max. for BS/PLA+7%QUE: 101,7 mg/L)
- Higher antioxidant activity (max. for BS/PLA+7%QUE: 77%)

Greater affinity of quercetin for fatty foods



Fresh-cut avocado

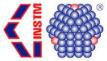
(Persea Americana)

15 g total lipids/ 100 g product*

*Dreher, M.L.; Cheng, F.W.; Ford, N.A. A Comprehensive Review of Hass Avocado Clinical Trials, Observational Studies, and Biological Mechanisms. Nutrients 2021, 13, 4376. https://doi.org/10.3390/nu13124376



Preliminary shelf life tests: Visual appearance





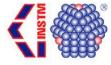
Experimental Setup

- Materials:
 - 15 x 15 cm² Bags made of BS/PLA and BS/PLA+7%QUE films
 - Unpackaged avocado slices (control samples)
- Sample configuration:
 - Each bag contains two/three avocado slices
 - Average weight per bag: 42.9 ± 3.8 g
- Storage conditions:
 - Temperature: 4 ± 2°C (refrigerated)
 - Duration: 9 days
- Analysis schedule:
 - Conducted on days 0, 1, 3, 6 and 9
 - Three package replicates tested at each time point

	•••				
	DAY 0	DAY 1	DAY 3	DAY 6	DAY 9
CONTROL					
BS/PLA					
BS/PLA+7%QUE				(((

- □ CONTROL GROUP: Rapid browning along storage period and visible loss of weight and texture.
- □ BS/PLA GROUP: Visible darkening at the edges from day 3, weight and texture loss more moderate.
- BS/PLA+7%QUE GROUP: Only small signs of browning on day 6. Change towards reddish on day 9. Texture and moisture almost preserved.



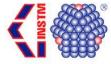


Engineered Biodegradable Coatings on Cellulosic and Biopolymeric Substrates for Active, High Barrier Packaging Solutions

Conclusive remarks

Sustainable multilayer film based on passive and active materials were successfully produced by coating technique on both polymeric or cellulosic substrates





Engineered Biodegradable Coatings on Cellulosic and Biopolymeric Substrates for Active, High Barrier Packaging Solutions

Conclusive remarks

It is possible to tailor both the substrate by using different biodegradable materials and the coatings, even in multiple steps, in order to achieve the requested performances.





Engineered Biodegradable Coatings on Cellulosic and Biopolymeric Substrates for Active, High Barrier Packaging Solutions

Conclusive remarks

- ✓ The use of a substrate based on polymeric blend allow to balance between ductility, and the stiffness, sealing ability
- ✓ Excellent oxygen barrier and water barrier properties provided by the m-PVOH and waxes
- Coating solutions: potential to serve as effective carriers for the controlled release of antioxidant agents in fruits with varying lipid concentrations.



Thank you for the kind attention

Luciano Di Maio

Dipartimento di Ingegneria Industriale Università di Salerno LDIMAIO@UNISA.IT

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COLLABORAZIONI

Le attività di formazione si svolgono in collaborazione con enti, università e aziende di rilievo internazionale, tra cui: PROPLAST, Istituto Superiore di Sanità, Swansea University -Welsh Centre for Printing and Coating. CONAI/COREPLA/COMIECO, CNR-IPCB

Prima fase: lezioni frontali erogate in modalità blended (in presenza, livestreaming, on-demand) Seconda fase: tirocini formativi presso le aziende partner

PLACEMENT

DIDATTICA



Dopo 6 mesi dal Master, il 90% deali iscritti è impiegato, con l'80% nel settore del packaging (il 60% nelle aziende partner) e il 20% in altri ambiti.

PERCORSO FORMATIVO

Info e contatti master.matespack@unisa.it f in Con il patrocinio di: AIMAT 🔍 🔼 comieco