2nd Annual Meeting "Sustainable Food Packaging"

"Rivestimenti, prodotti e materiali che assicurano la massima sicurezza di protezione e conservazione degli alimenti per il packaging flessibile. Tecnologie innovative per il processo produttivo"

May 27, 2025 Fiera Rho - Milano

Surface treatments and functionalization via coating of biodegradable substrates for high-barrier packaging

Annalisa Apicella

Department of Industrial Engineering, University of Salerno

Biodegradable plastics for sustainable packaging

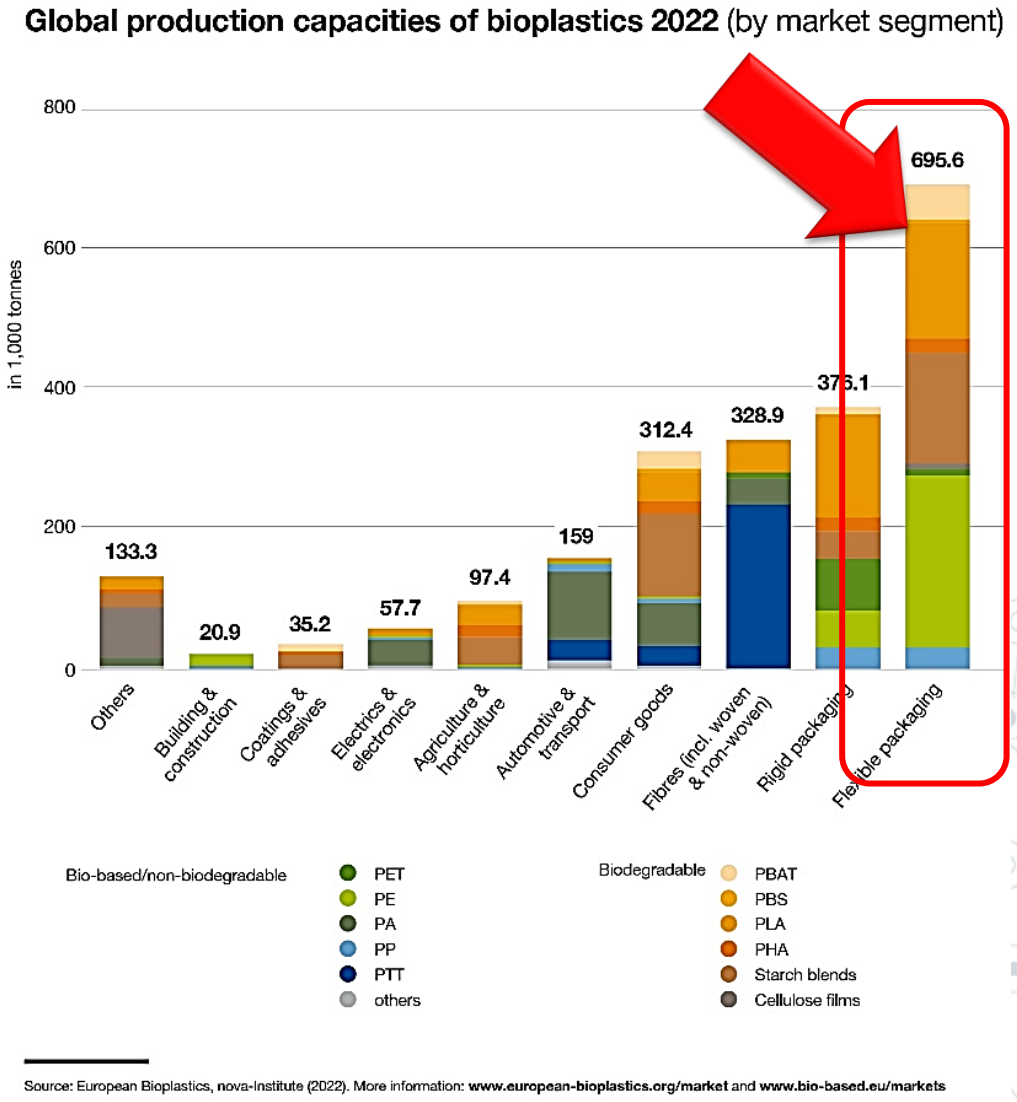
Biodegradable polymers represent a sustainable alternative to traditional, fossil-based plastics to reduce environmental pollution.

PROS

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

CONS

- **Scarce gas barrier properties**
- Low surface energy
- **Poor printability and adhesion**
- Low thermal resistance and impact resistance



Challenges in developing multi-functional biodegradable food packaging

The **correct design** plays a crucial role to obtain **truly effective structures, competitive on the market** and which constitute a real added value for the reduction of food waste.

Sustainability and Eco-design

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

Industrial feasibility

- Films produced by **conventional technologies** **easy scalable** at industrial level;

Applicability in food packaging field

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

Functionalization strategies for biodegradable food packaging

It is fundamental to apply **functionalization strategies** to **improve and modulate bioplastics performances** with the aim of **expanding their commercial uptake in the food packaging field.**

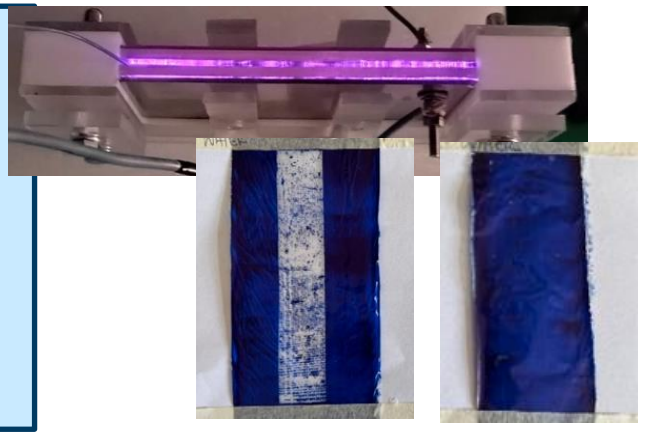
- Surface treatments,
- Coatings,
- Nanocomposites,
- Blends,
- Multilayer films,
- Active technologies

Università di Salerno
Dipartimento di Ingegneria Industriale

UNISA CASE STUDIES

CASE STUDY 1:

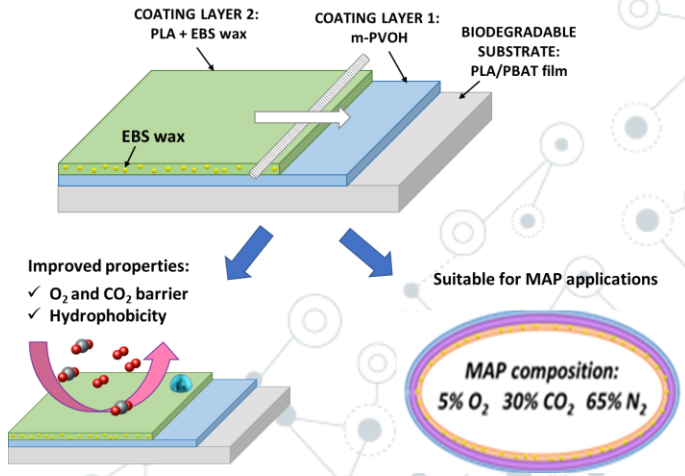
Study of the effects of cold-plasma treatment on blown films based on biodegradable PBS/PLA blends, and optimization of processing parameters to improve adhesion and printability.



NON-TREATED TREATED

CASE STUDY 2:

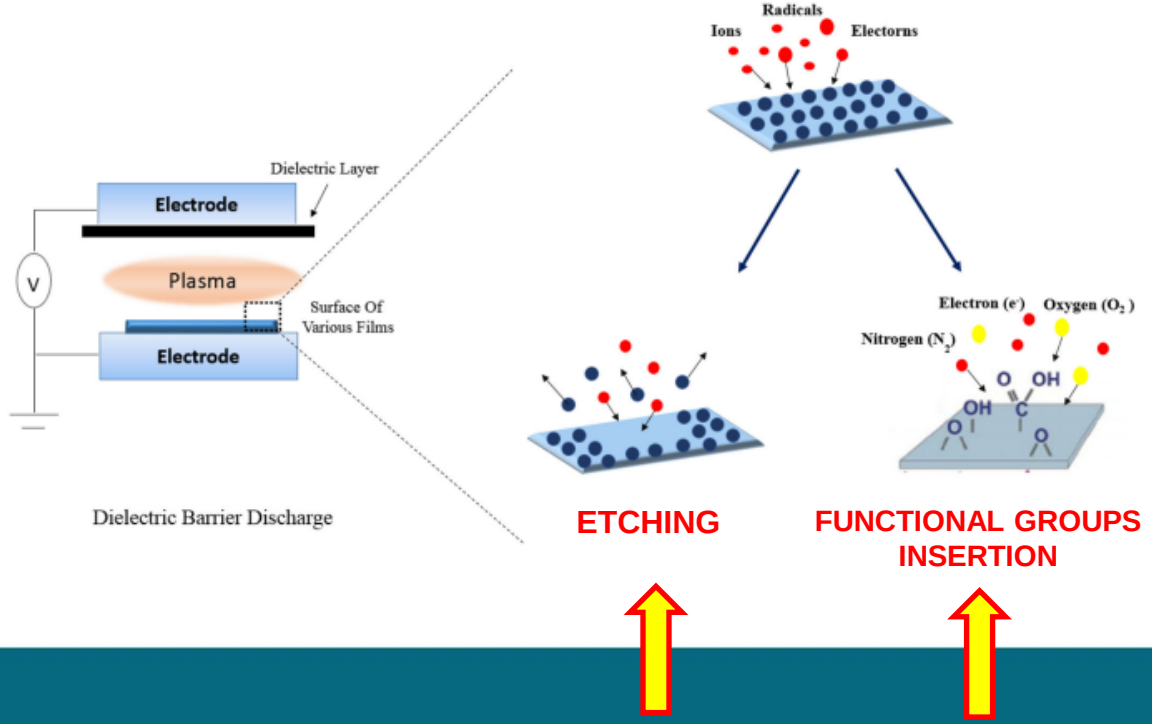
Plasma treated biodegradable substrates functionalized by PVOH/PLA + wax double coatings with high barrier properties for food packaging applications



Cold-plasma for surface functionalization of biopolymer films

ADVANTAGES:

- Cold plasma treatment allows to increase surface wettability of polymer films**, enhancing their ability to adhere to other materials, to be printed, coated, or laminated.**
- Simple, fast, solvent-free, and does not produce toxic waste.
- Cold-plasma enables **low-temperature treatments,** suitable for biopolymeric substrates.



CHALLENGES:

Plasma treatment is applied at an industrial level mainly on conventional films.

- Few studies on the optimization of process parameters: applied voltage, treatment time, and gas flow rate.
- Lack of studies on the chemical-physical effects of plasma treatment on films based on biodegradable blends, especially in the long term.

UNISA CASE STUDY 1: Surface functionalization of PBS/PLA biodegradable films by cold plasma treatment

STEP 1: Realization of the biodegradable blown films

PLA 4032D, NatureWorks LLC (USA).

- High mechanical resistance
- Good processability
- Good optical properties and heat sealability (for amorphous grades)

PBS FZ91PM, Mitsubishi Gas Ch. Co., Thailand).

- High ductility and toughness
- Excellent chemical, thermal and impact resistance

- Biopolymers approved for direct food contact
- PBS/PLA 70/30 wt% blend was realized by melt compounding, through a twin screw extruder (Collin ZK25, D=25 mm, L/D = 42)
- Films based on neat PLA, PBS and on the PBS/PLA 70/30 blend were produced by blown film extrusion (Gimac, D = 12 mm, L/D = 24)

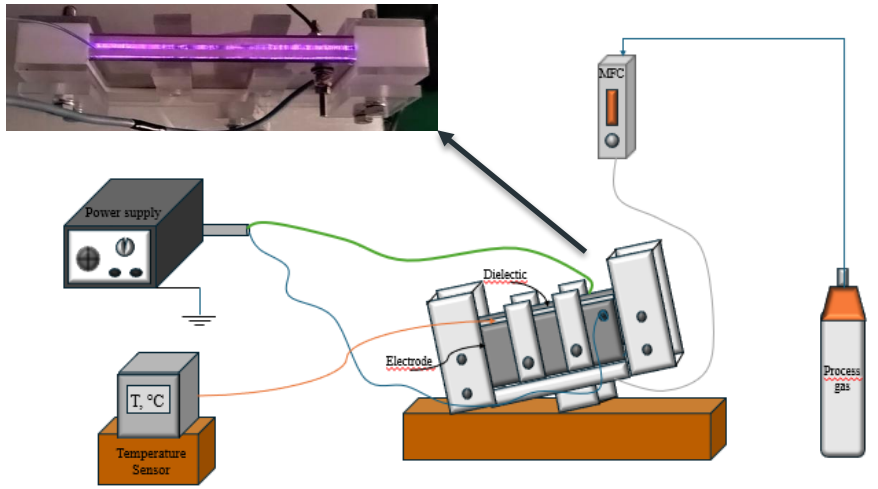
Average thickness of 40 ± 2 μm.

UNISA CASE STUDY 1: Surface functionalization of PBS/PLA biodegradable films by cold plasma treatment

STEP 2: Cold plasma treatment and optimization of processing parameters

Reactor configuration: DBD **(Dielectric Barrier Discharge) with parallel electrodes:**

- Stable,
- Easy scalable
- Atmospheric pressure: easy to integrate on roll-to-roll lines
- Equipped with fiber optic probes for temperature measurements



Optimization of the processing parameters was carried out:

- Type of gas: air
- Voltage applied to the electrodes: from 0 kV to 30 kV.
- Gas flow rate: from 0 to 1 L/min.
- Treatment time: from 0 s to 80 s.

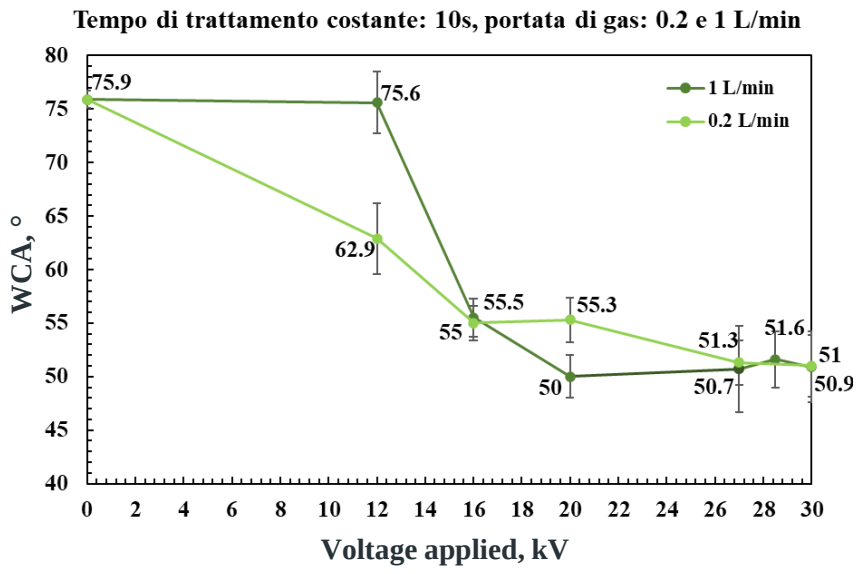
GOAL:
Minimization of the water contact angle (WCA)

Optimization of the processing parameters

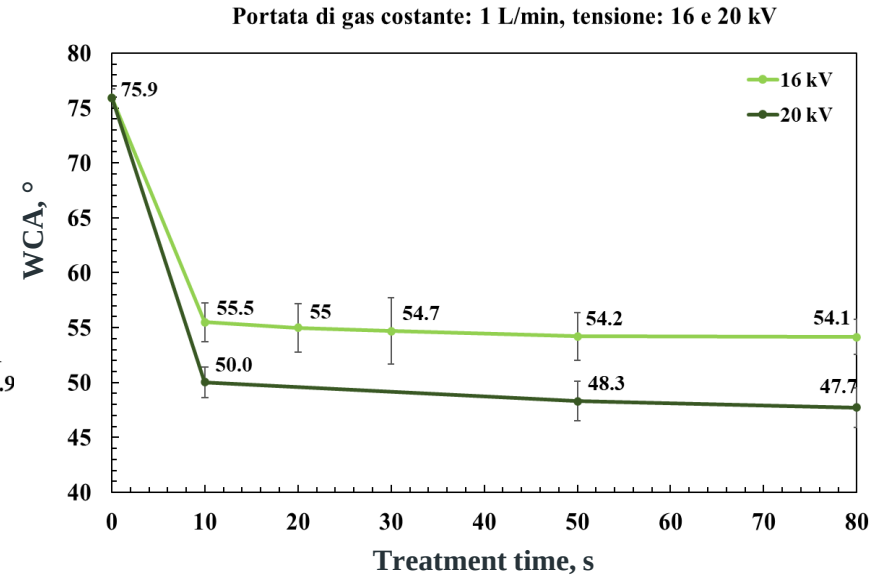
Reference film: PBS/PLA 70/30 (Initial WCA: 74.9°)

Maximum T measured = 60 °C

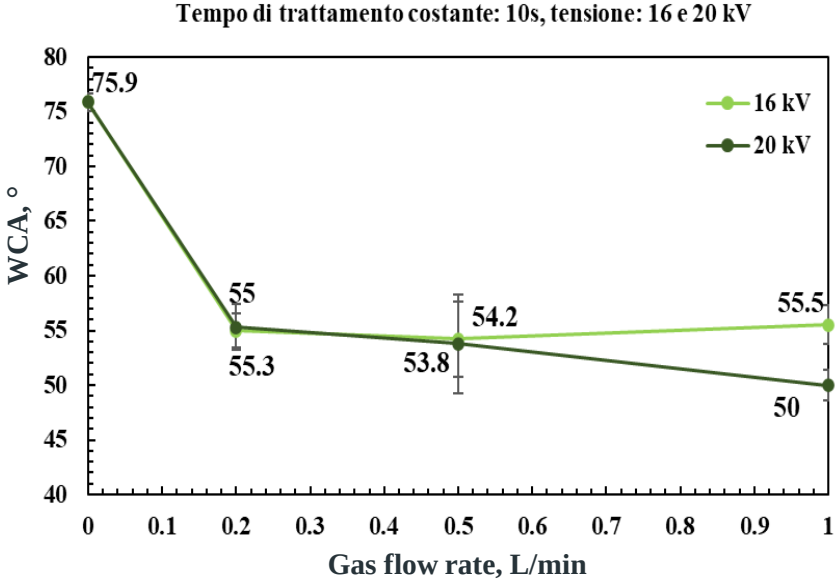
Effect of Voltage : 0-30 kV



Effect of Treatment time : 0-80s



Effect of Gas flow rate : 0-1 L/min



- A treatment time of **10 seconds is already sufficient to generate all the radical species** that can be formed regardless of gas flow rate and applied voltage.
- The number of ionizing molecules and radical species generated in the system depends on a **combined effect of voltage and flow rate.**

Optimization of the processing parameters

Treatment conditions with air plasma that allowed the maximum reduction of the WCA for PBS/PLA 70/30:

Condition	Voltage [kV]	Gas flow rate [L/min]	Treatment time [s]	WCA [°]
1	20	1	10	50.0±1.4
2	16	0.2	50	50.6±1.1

Foir both conditions, the calculated gas volume delivered during the process (flow rate * time) is the same (0.17 L).

A key difference between the two conditions could therefore be the **treatment time**: assuming the treatment is to be carried out in-line after film production, **a shorter time (10 s) allows for greater industrial applicability**, making condition 1 the optimal solution.

Optimal parameters:
Voltage=20 kV, Time=10s, Gas flow rate=1 L/min.

UNISA CASE STUDY 1: Surface functionalization of PBS/PLA biodegradable films by cold plasma treatment

STEP 3: Evaluation of the effects of plasma treatment on the films properties

Characterization tecnhiques

- FTIR-ATR
- Wettability, Surface Energy and Stability during time
- O2 permeability
- Water vapor permeability
- Mechanical tensile tests
- Printability and tape tests

Effect on wettability and Stability during time

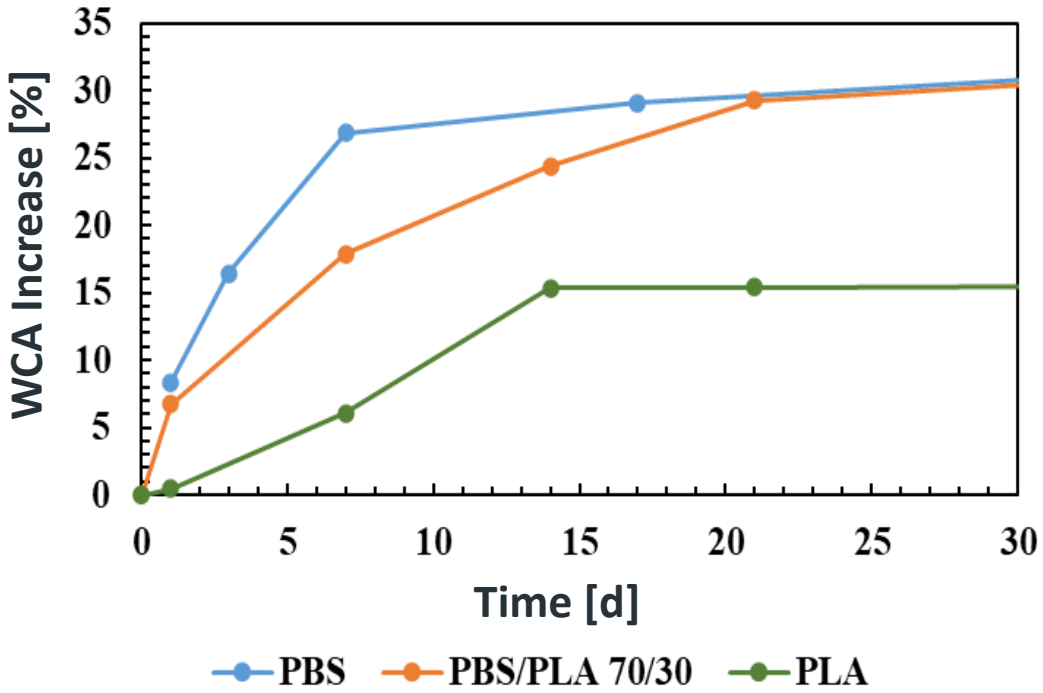
Sample film	Initial WCA [°]	Final WCA [°]	WCA Decrease [%]
PBS	79.6±2.6	49.9 ±0.4	37.3
PBS/PLA 70/30	75.9±0.8	50.0 ±1.4	34.1
PLA	74.5±2.1	57.3 ±2.5	23.1

The PBS film showed a more significant WCA decrease compared to PLA. This behavior is related to the chemical structure differences between the two polymers:

- **PBS**, with a Tg of about –30 °C, has a **more rubbery and mobile amorphous phase** → interactions with plasma radical species are favored.
- **PLA** is more rigid → it has **lower molecular mobility** → it is less susceptible to cleavage phenomena and insertion of polar functional groups.
- The blend showed **intermediate behavior**.

Effect on wettability and Stability during time

Hydrophobic recovery → the surface wettability modification induced by plasma activation is not permanent, as the surface gradually tends to return to its initial condition.



- **PBS showed the highest hydrophobic recovery during the time.**
- Hydrophobic recovery not higher than 30%

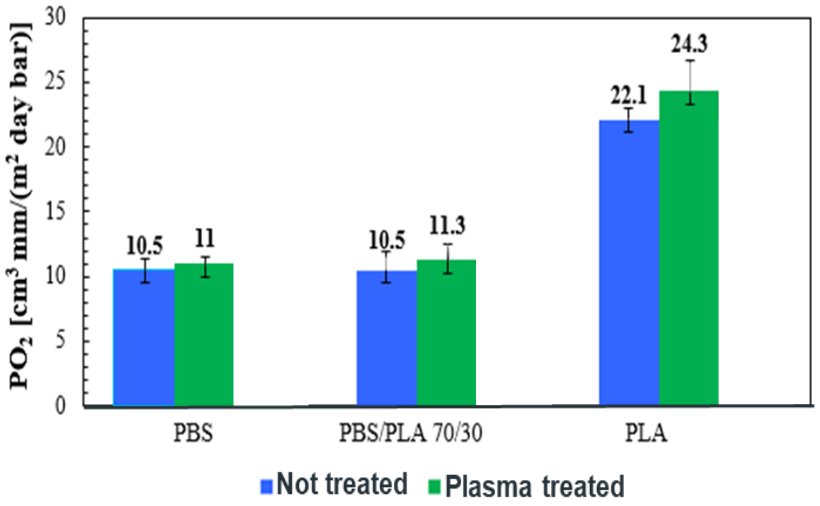
Hydrophobic recovery is caused by the **reorganization of polar groups.**

Molecular mobility is the main factor responsible for surface reorganization.

PBS and **PLA** exhibit different molecular mobility → different hydrophobic recovery.

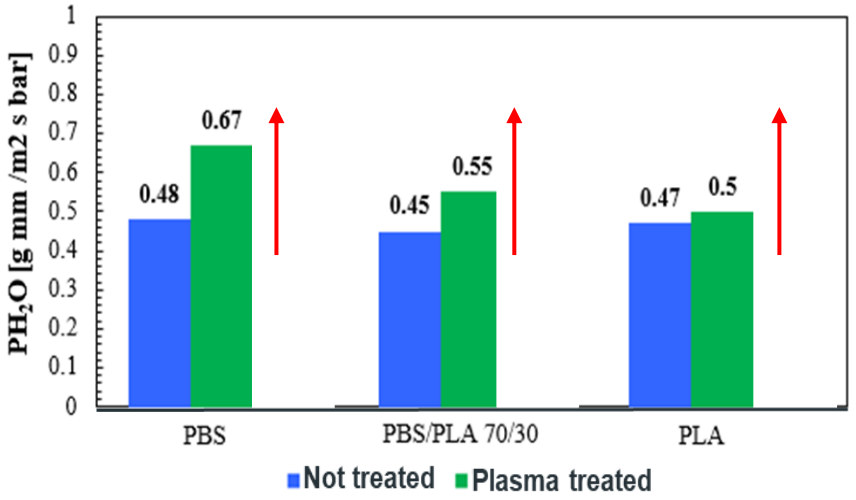
Effect on barrier and mechanical properties

O2 permeability (PO_2)



No significant alterations in PO_2 (<10%)

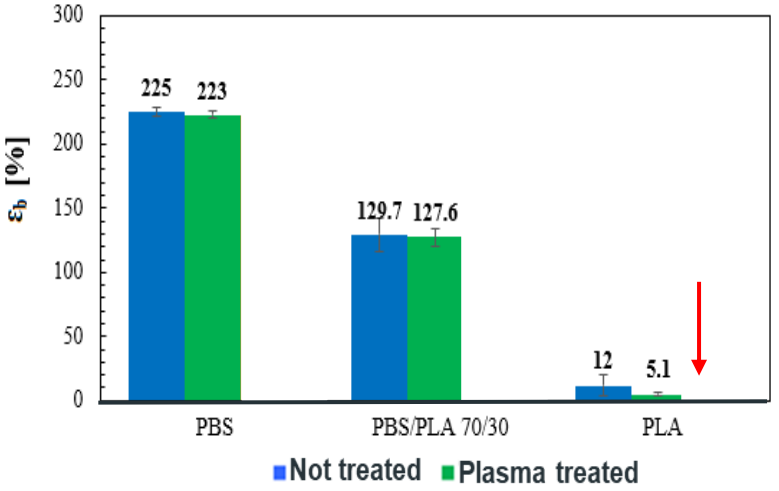
Water Vapor permeability (PH_2O)



Increase in PH2O, between 15% (for the PLA film) and 40% (for the PBS film)

Reasonably attributable to the formation of polar groups on the surface of the materials, which interact with water vapor.

Elongation at break (ε_b)

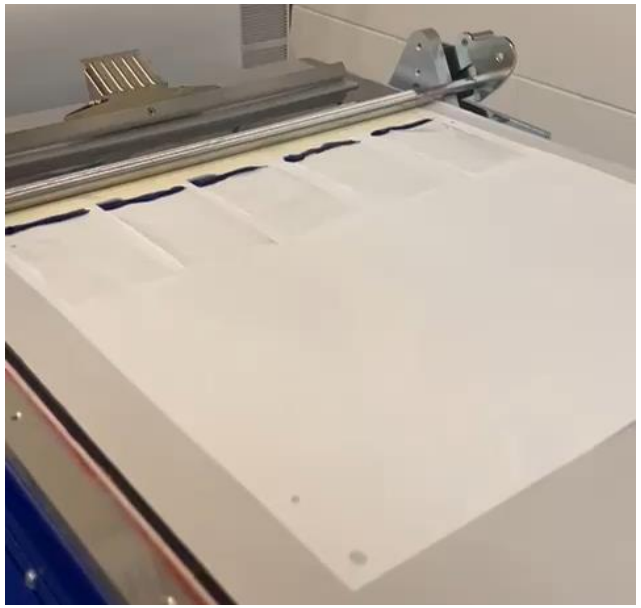


Mechanical properties of PBS and PBS/PLA 70/30 films substantially unhaltered**. PLA film showed embrittlment and stiffness reduction**

PLA has inherent brittleness and **lower thermal resistance** → changes in the surface morphology with formation of microcracks.

Effect on printability

- Treated and non treated PLA, PBS and PBS/PLA 70/30 films were coated with a water-based ink



- Dried samples were subjected to tape test, according to ASTM D3359-23 standard

Not treated

Plasma treated

Effect on printability

FILMS	Not treated	Treated
PBS		
PLA		
PBS/PLA 70/30		

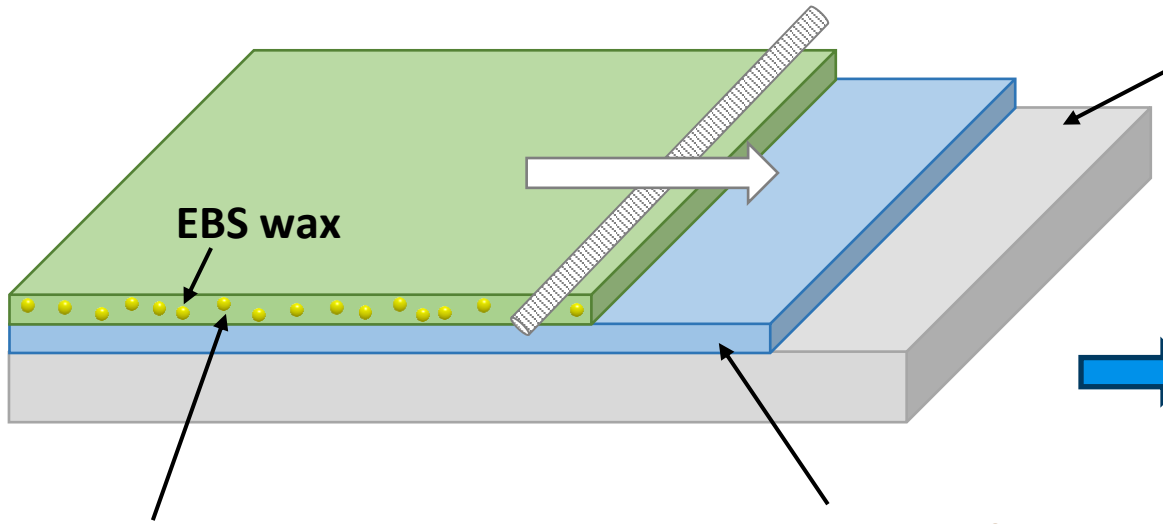
For the three plasma-treated films, no debonding was observed between the coating and the substrate.

For the untreated samples, the ink was removed with the adhesive.

Adhesion properties of the films were improved

UNISA CASE STUDY 2: Development of high-barrier films by double-coating technique

Tri-layer films with a *high barrier*, *heat-sealable properties* and *improved moisture resistance* were realized by means double coating tecnique



Structural layer/ printable

SUBSTRATE:
Plasma treated PBAT/PLA film

- ✓ Good ductility and tear resistance also at refrigeration temperatures
- ✓ Printability
- ✓ Plasma treated to improve adhesion with water-based PVOH coating

Heat sealable + hydrophobic layer

COATING LAYER 2: PLA+wax

PLA4060 (Natureworks, USA) + **EBS wax** (DEUREX AG, Germany) loaded at 5%, 10% and 20% w/w_{PLA}

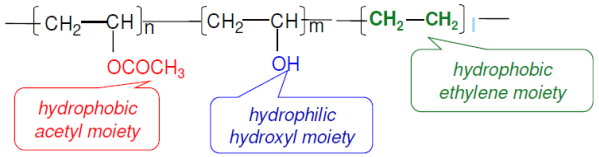
- ✓ Heat-Sealable
- ✓ Easy to be removed
- ✓ Additional water resistance provided by the wax
- ✓ Wax from the valorization of sugar cane processing waste

Barrier layer

COATING LAYER 1: m-PVOH

Fully hydrolyzed, water soluble, chlorine-free polyvinyl alcohol (Kuraray Europe GmbH)

- ✓ High barrier to gases and aromas
- ✓ Low sensitivity to moisture (thanks to a chain modification)
- ✓ Water soluble, easy to be removed



Gas Barrier properties and MAP application

Test conditions:
23°C, 50% RH

O2 permeability (PO_2)

Sample films	Oxygen permeability coefficient, P_{O_2} $\left[\frac{cm^3\ mm}{m^2\ d\ bar}\right]$
Biofilm	48.4 ± 4.8
Biofilm/m-PVOH	0.22 ± 0.04
Biofilm/m-PVOH/PLA	0.33 ± 0.06
Biofilm/m-PVOH/PLA+5%wax	0.31 ± 0.07
Biofilm/m-PVOH/PLA+10%wax	0.32 ± 0.06
Biofilm/m-PVOH/PLA+20%wax	0.30 ± 0.1

PO_2 decrease of up to 2 o.o.m. with respect to the Biofilm substrate

CO2 permeability (PO_2)

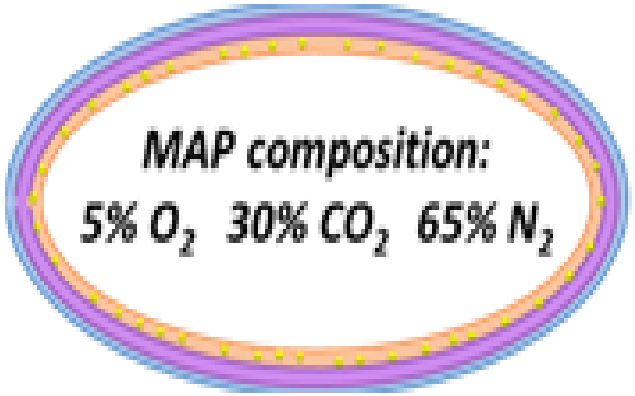
Sample films	CO_2 permeability coefficient, P_{CO_2} $\left[\frac{cm^3\ mm}{m^2\ d\ bar}\right]$
Biofilm	305 ± 79
Biofilm/m-PVOH	0.37 ± 0.11
Biofilm/m-PVOH/PLA	0.46 ± 0.14
Biofilm/m-PVOH/PLA+5%wax	0.44 ± 0.30
Biofilm/m-PVOH/PLA+10%wax	0.45 ± 0.18
Biofilm/m-PVOH/PLA+20%wax	0.46 ± 0.10

PCO_2 decrease of up to 3 o.o.m. with respect to the Biofilm substrate

EXCELLENT GAS BARRIER TO O2 AND CO2 → This strategy is promising in extending the application range of biodegradable films in the food packaging field.

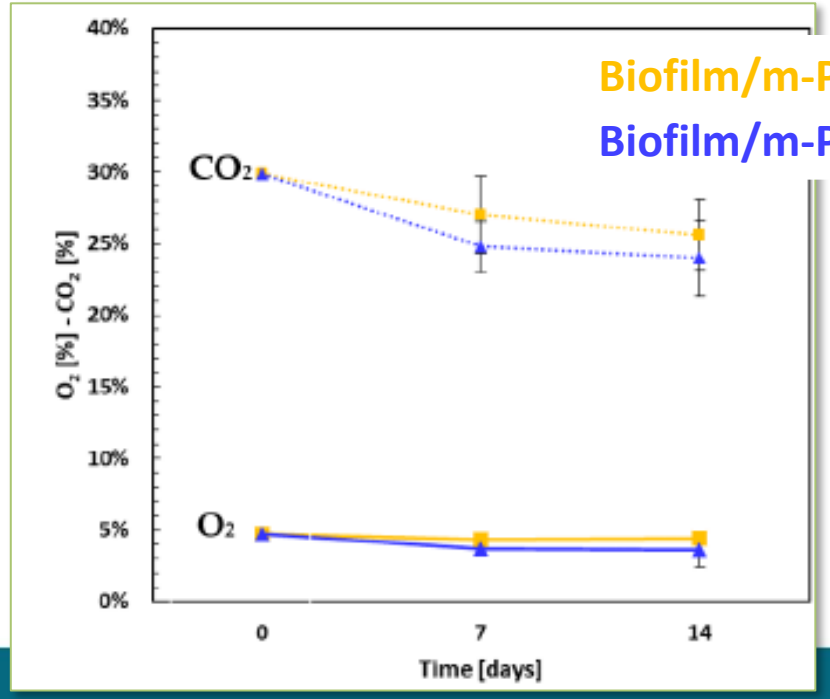
Sensitive foods with high gas barrier requirements

Gas Barrier properties and MAP application



MAP retention tests

- ✓ **Samples:** Bags made *by* ***Biofilm/m-PVOH/PLA*** and ***Biofilm/m-PVOH/PLA+5%wax***
- ✓ **Gas composition:** gas mixture of **5% O_2/30% CO_2/65% N_2**
- ✓ **Storage: 14 days.**
- ✓ **No foods** to avoid alterations due to *respiration*, *solubilization* or *spoilage* effects.

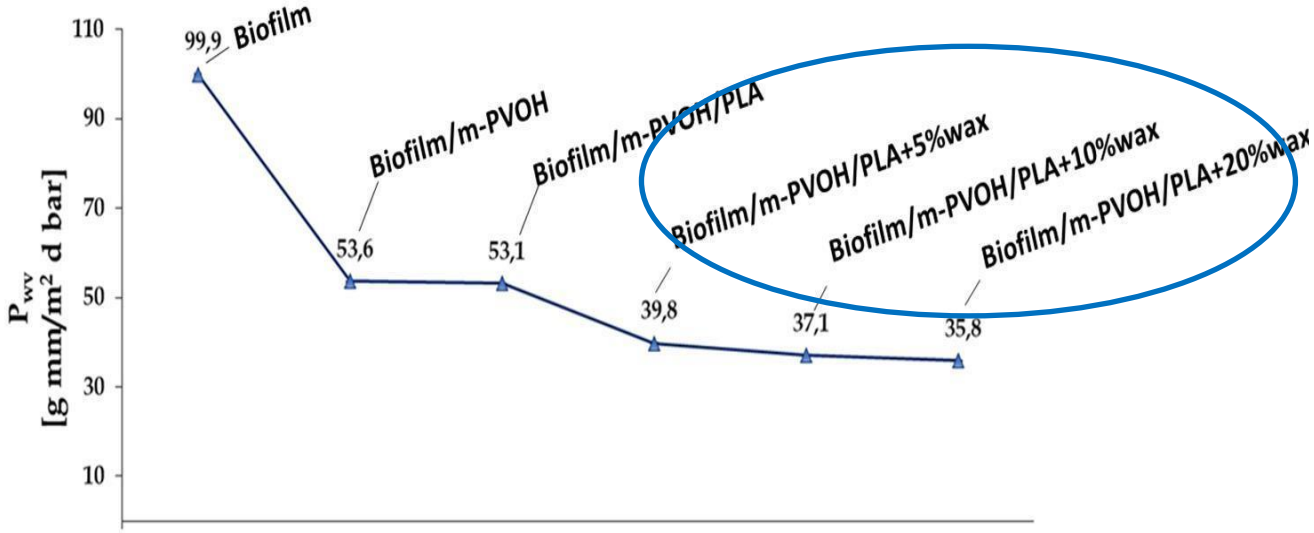


- **O_2 concentration remains constant** in both film samples throughout the investigated period.
- **CO_2 concentration slightly decreases** during the time from an initial level of 30%, on day 0, to a final value of ca. 25% by day 14, for both samples.

The films can be used as sustainable alternatives for the preservation of foods stored under modified atmosphere packaging.

Water Vapor Barrier and sealability

Water Vapor permeability (PH_2O)

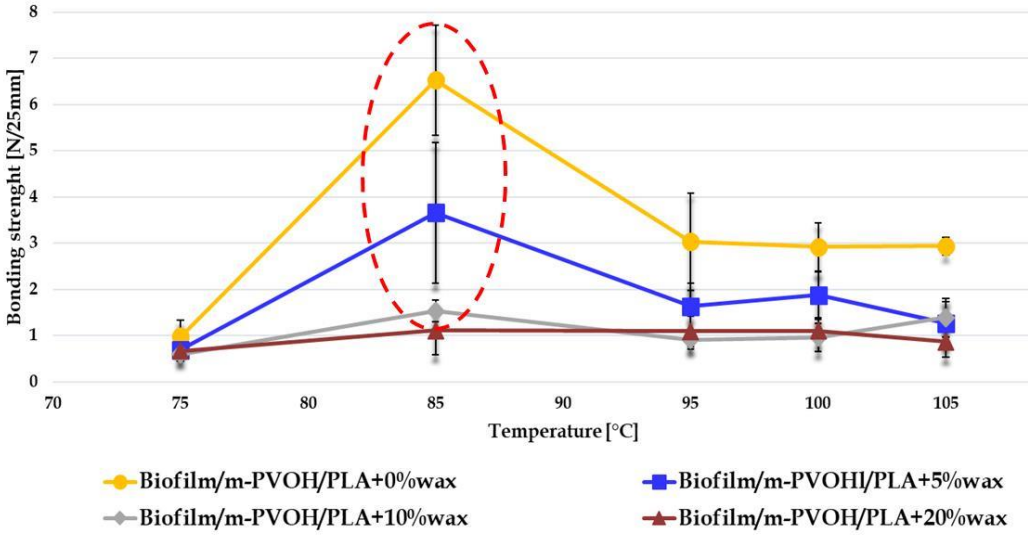


Test conditions: 23°C; 85% R.H.

m-PVOH layer decreased up to 45% the P_{WV} of neat Biofilm.

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

Heat sealability



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

- PLA provided sealability function
- bonding strenght and optimal seal temperature (85°C) suitable for food packaging industry

Conclusions and Key remarks

❑ COLD-PLASMA TREATMENT OF BIODEGRADABLE FILMS

- **Effective strategy** to improve the adhesion properties of biodegradable films for printing and coating.
- **Evaluate a combined effect of different gases** to promote crosslinking and thus **greater treatment stability.**
- Use cold plasma to perform **Plasma Assisted Chemical Vapor Deposition** → produce high-barrier coatings.
- Assess the **effect of plasma on the biodegradability** of the systems.

Conclusions and Key remarks

❑HIGH-BARRIER DOUBLE COATED FILMS

- The **design** allowed to combine the **ductility of the substrate** with the **excellent barrier properties of m-PVOH** and with the **sealability and hydrophobicity provided by the PLA layer** with natural wax.
- **Ideal for packaging applications like Modified Atmosphere Packaging (MAP)** of gas-sensitive foods with extended shelf life, providing robust gas exchange control.

Thank you for the kind attention!

Annalisa Apicella

Dipartimento di Ingegneria Industriale

Università di Salerno

ANAPICELLA@UNISA.IT