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Packaging sustainability and innovation: Bio-Based Materials for functional packaging

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UNIVERSITÀ DEGLI STUDI
DI MILANO



DEPARTMENT OF
FOOD, ENVIRONMENTAL AND
NUTRITIONAL SCIENCES

University of Milan

The Department of Food, Environmental and Nutritional Sciences - DeFENS

(formerly DiSTAM, Dept. of Food Science & Microbiology)



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- Home
- Our group →
- Research →
- Facts and figures
- Facilities/Equipments
- Tutorials
- Useful links
- News
- Events
- Contacts

Packlab history

A laboratory exclusively devoted to packaging research (the Packlab) has been established in the Department of Food Science and Microbiology (DISTAM) since 1985. At that time, the first course of Food Packaging and Distribution was offered in our Country, within the curriculum of Food Science and Technology in the Faculty of Agriculture of University of Milan.



From then on an intense activity of both applied research and specialist teaching begun in the Packlab. Due to the very fast and worldwide growing importance of the food packaging sector, also Packlab grew quickly. In these almost 25 years several collaborations have been established with companies in the food as well as in the packaging sector and many relationships have been instituted with other Universities and Research Centers in Italy and abroad. A list of the main significant partnerships is reported in the section "Facts & Figures" of this web site.

A fundamental driving force for Packlab growth during these years, however, has been provided by the great number of students, post graduated, PhD students and post docs



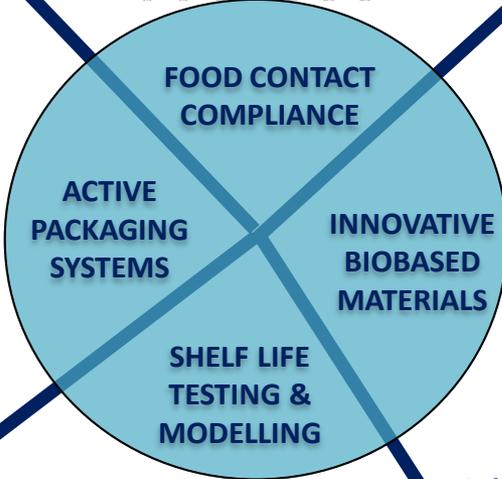
<http://users.unimi.it/packlab/default.htm>

An Operative Unit exclusively devoted to food packaging (the Packlab) has been established in our University since 1985.

Packlab is the only unit in the University of Milan engaged in research, teaching and testing in the Food Packaging field

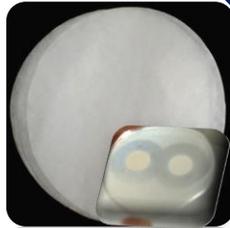


FOOD PACKAGING RESEARCH at PACKLAB

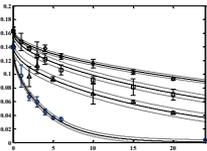
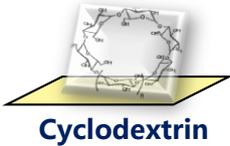


Antimicrobial proteins (LZ and LF) controlled release from paper sheets

The figure shows the activity of paper sheets against food spoilage microorganisms.



Incorporation and diffusion of natural volatile antimicrobials from bio-coating



Low-moisture and dried foods
Modelling of moisture diffusion across the packaging material

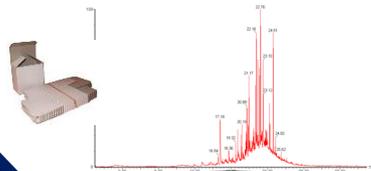
Meat & Processed Meat
Optimization of active packaging solutions

Beverages
Effects of light exposure and protection efficacy of packaging



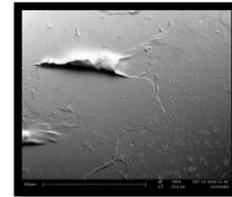
NIAS (non intentionally added substances)

Transference of contaminants from cellulosic packaging and innovative approach for food contact material safety.



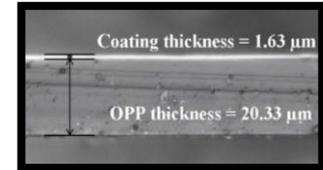
Sealable bio-coatings

SEM image shows a polypropylene coated films after rupture of sealed strips



Barrier bio-coatings

A very thin bio-coating can improve the oxygen barrier property of a plastic film.



Nano-Cellulose applications

Cellulose properties including hydrophilicity, biocompatibility, stereoregularity, biodegradability, chemical stability, multi-chirality, reactive hydroxyl groups and the ability to form superstructures.



Packaging sustainability and innovation: Bio-Based Materials for functional packaging

The TOC of this talk:

- Packaging Sustainability
- Bio-based materials (BBMs) and Bio-plastics in food packaging
- The coating technology for flexible packaging materials
- The Research on BBMs at Packlab:
 1. *Hybrid coatings for high oxygen barrier*
 2. *Multifunctional Nanocellulose coating on plastic films*
 3. *Functional barrier against migration by means of Bio-based coatings*
 4. *Development of a Bio-based active packaging device*
- Conclusions



Sustainable Packaging

“European consumers are more and more prepared to buy goods and services which have reduced environmental impact”

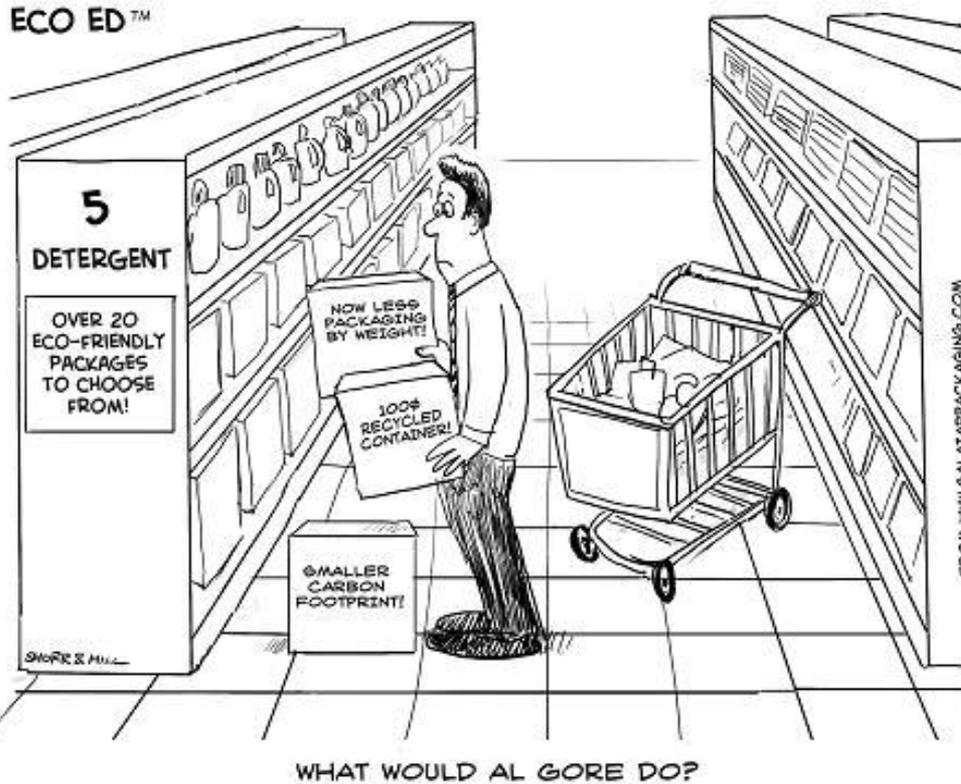
European Commission

Packaging Sustainability is a real special topic.

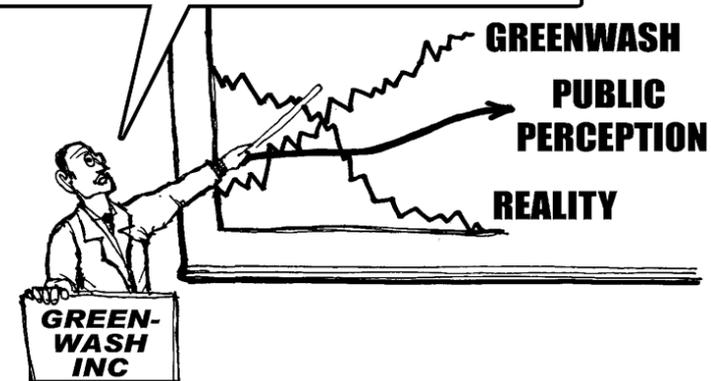
Very often is considered as a marketing tool, i.e. a way of promoting and differentiating a new package or a new packaging material. Packaging Sustainability, however, is a much more serious and complex theme, close to Science and Technology.



Sustainable Packaging



YOU CAN IMPROVE PUBLIC PERCEPTION BY
OFFSETTING THE REALITY OF YOUR PROJECT
WITH MORE INVESTMENT IN GREENWASH INC



Greenwashing is a form of spin in which green PR or green marketing is deceptively used to promote the perception that an organization's products, aims or policies are environmentally friendly. *Wikipedia*



Sustainable Packaging

What “sustainable packaging” really is and how sustainability can be evaluated is still widely discussed at various levels, and a global agreement has not yet reached.



What is COMPASS?

COMPASS (Comparative Packaging Assessment) is online design software that allows packaging designers and engineers to assess the human and environmental impacts of their package designs using a life cycle approach. COMPASS helps packaging designers make more informed material selections and design decisions by providing quick visual guidance on a common set of environmental indicators.

COMPASS provides consistently modeled data sets for USA, Canada and Europe tailored for materials and processes used for packaging to allow reliable apples to apples comparisons of multiple scenarios. In addition, regionalized solid waste modeling provides a waste profile of each scenario to help understand the end of life (EoL) implications of packaging designs.



SPC is GREENBLUE Project
<http://www.sustainablepackaging.org/>

GreenBlue is a nonprofit institute that stimulates the creative redesign of industry by focusing the expertise of professional communities to create practical solutions, resources, and opportunities for implementing sustainability

Sustainable Packaging

What “sustainable packaging” really is and how sustainability can be evaluated is still widely discussed at various levels, and a global agreement has not yet been reached.

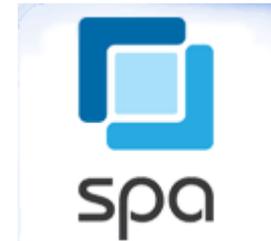


Packaging Impact Quick Evaluation Tool

SPA is the global distributor of PIQET, a web based business tool used for rapid packaging environmental impact assessments. PIQET is used to optimise packaging system design from a sustainability perspective in all stages of the product development process.

PIQET is also used for training to build an understanding of the life cycle impacts of packaging and develop business capability to make more sustainable decisions.

PIQET is accessed through a direct license from SPA. Licenses include training, technical support and access to regular updates. [Click here](#) to download brochure.



Sustainable Packaging Alliance

An Academic initiative in Australia

<http://www.sustainablepack.org/default.aspx>

The Sustainable Packaging Alliance is a joint initiative of Victoria University of Technology, through its Packaging and Polymer Research Unit, RMIT University, through its Centre for Design, and Birubi Innovation Pty Ltd

Sustainable Packaging

A general and widely accepted assumption refers to four main attributes of sustainable packaging: they must be Effective, Efficient, Clean and Cyclic

Effective: the packaging system adds real value to society by effectively containing and protecting products **IT'S USEFUL !**

Efficient: the packaging system is designed to use materials and energy as efficiently as possible throughout the product life cycle. **DON'T WASTE !**



Cyclic: Packaging materials used in the system are cycled continuously, minimizing material degradation **DON'T LITTER !**

Clean: packaging components used in the system do not pose any risks to humans or ecosystems. **DON'T CONTAMINATE !**

Sustainable Packaging

facts and figures

Nothing new, actually !! The previous mentioned attributes are almost standard requirements for modern packaging.

Our environment for sure, is not at risk for Packaging

Crude oil consumption

GASOLINE & JET FUEL : Of all the crude oil refined for use, almost **57%** becomes **FUELS**

DIESEL FUEL AND HOME HEATING: Another **20%** becomes distillate, two-thirds of which is diesel fuel and one-third home heating oil.

BOILER OIL: Boiler oil, or residual fuel oil, which makes up **7%** of crude oil consumption, is used to produce electricity.

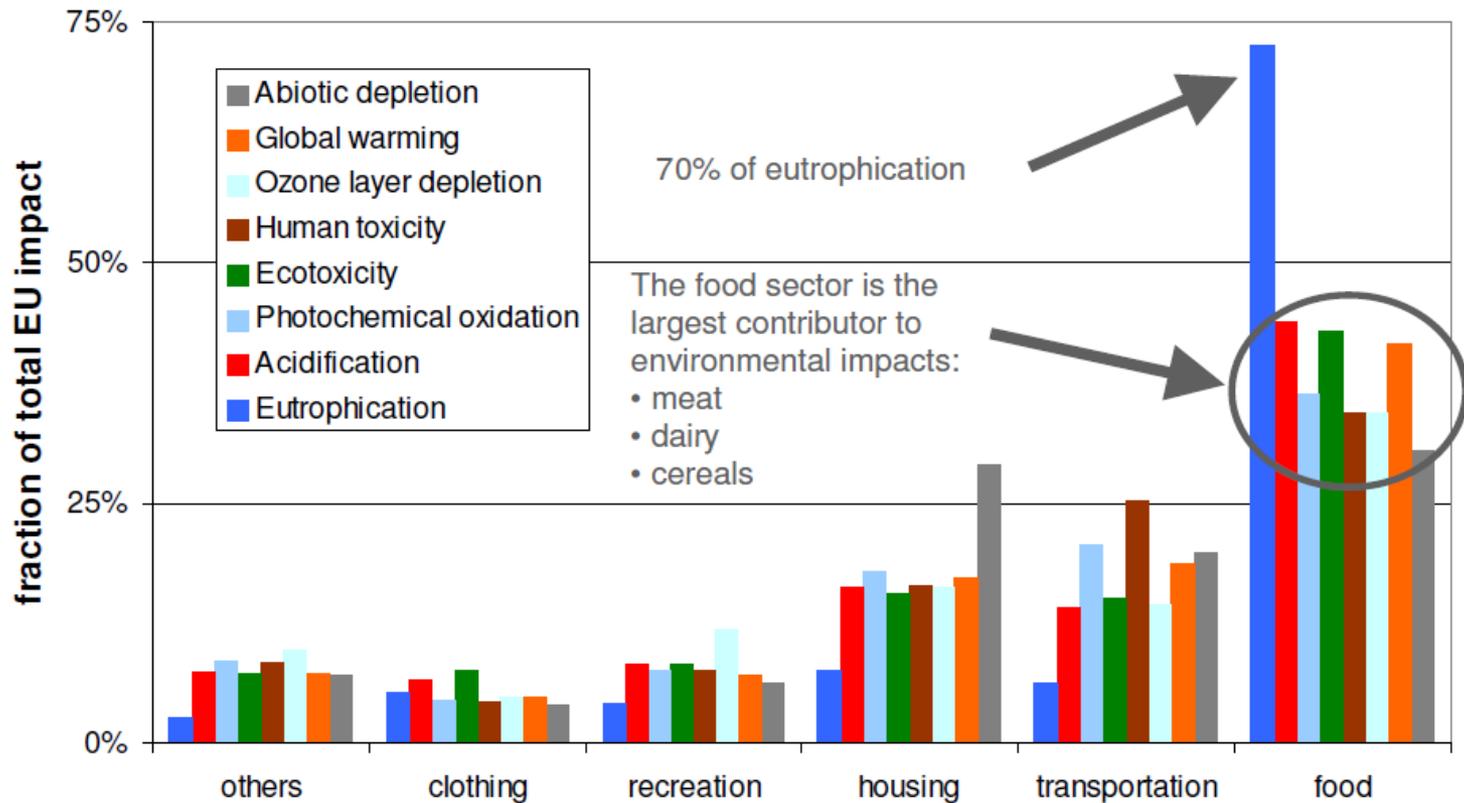
ASPHALT AND OTHER NON-ENERGY FEEDSTOCKS: account for **13%** of crude oil consumption.

PETROCHEMICAL FEEDSTOCKS: products of the refining process, make up the remaining **3%** of all crude oil consumption for plastics and chemicals

Sustainable Packaging

facts and figures

Our environment for sure, is not at risk for Packaging

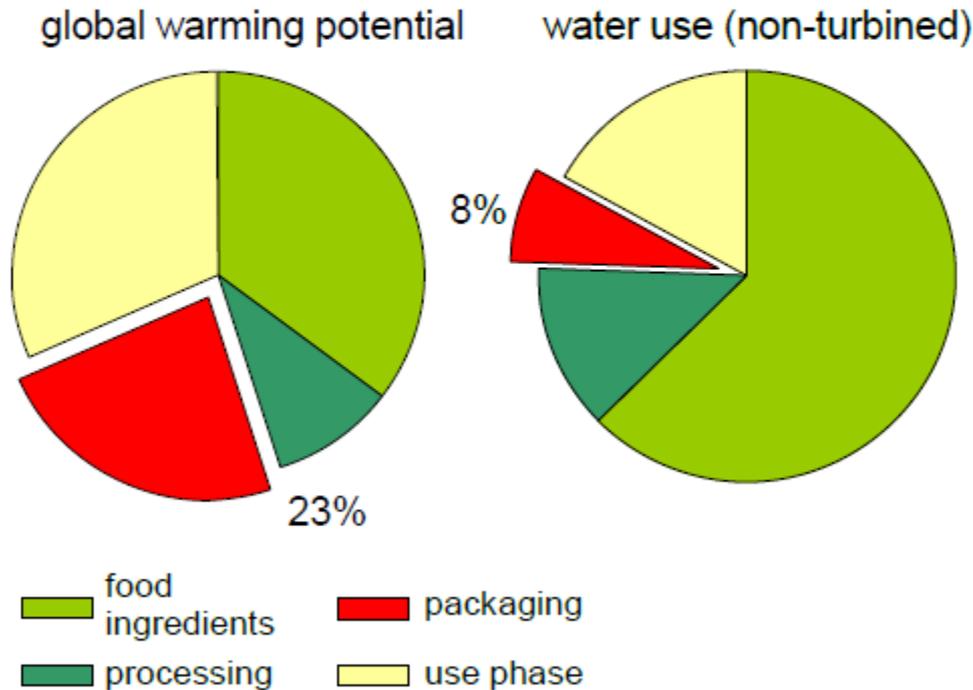


Adapted from: Environmental Impact of Products (EIPRO) - 29.04.05
based on 7 existing studies & own analysis

Sustainable Packaging

facts and figures

Our environment for sure, is not at risk for Packaging

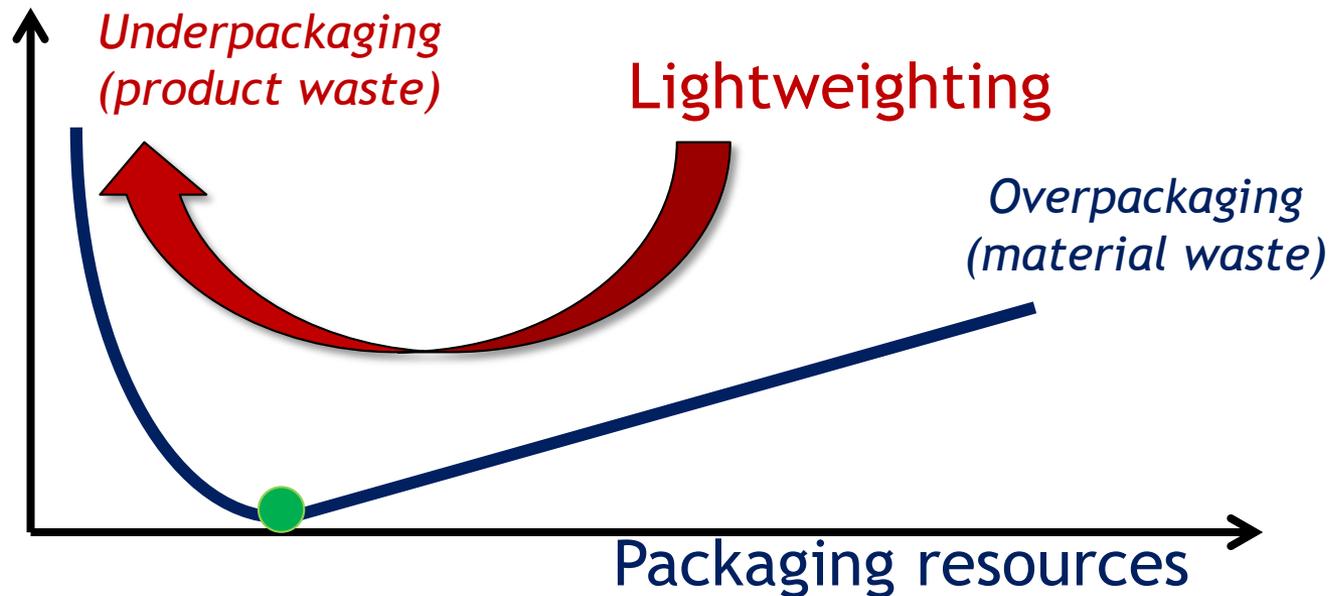


Source: conservative estimate based on internal Nestlé screening LCA studies

Sustainable Packaging

Overpackaging

Resources waste



L. Stramare, COREPLA

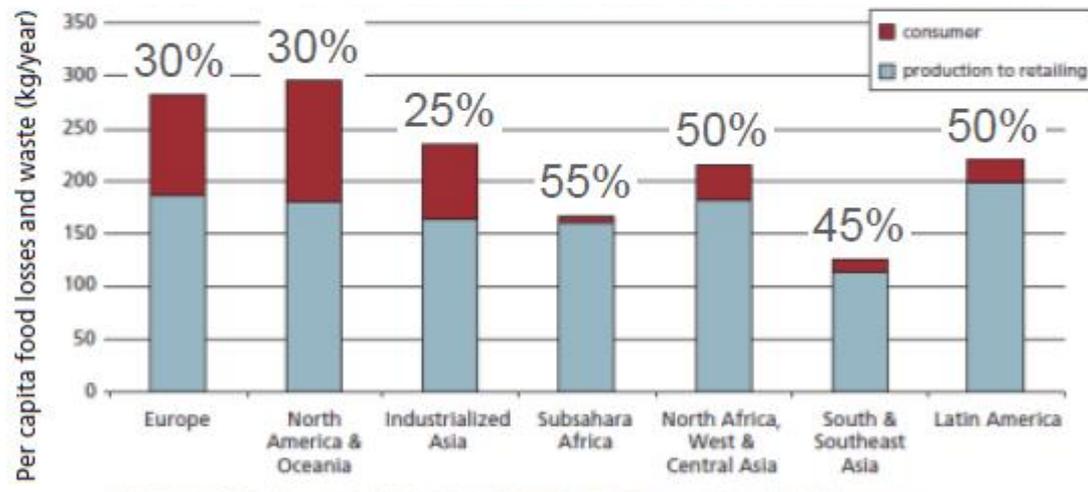
Appropriate packaging saves more waste than it creates. If, due to being badly packed, the contents are spoiled, ten times more waste occurs than that generated by the production of appropriate packaging

Kooijman, J. 1996. Environmental Impact of Packaging Performance in the Food Supply System, Journal of Waste Management and Resource Recovery, Vol. 3, Nr. 2,

Sustainable Packaging

Overpackaging

“Appropriate packaging” ... might mean a correct balance between environmental expectations and high protective performance



Packaging serves to protect the food it contains. Packaging design oriented only towards packaging reduction fails to identify opportunities to a green and sustainable economy

Bio-based materials

A green and sustainable economy needs a revolutionary change in the use of raw materials, it needs to overcome today's dependency on fossil fuels and to bring about a shift towards processes and products based on natural resources.

Within the energy supply sector, the change will be solar and wind power, within the materials sector, very likely, it will be Bio-based materials and their composites.

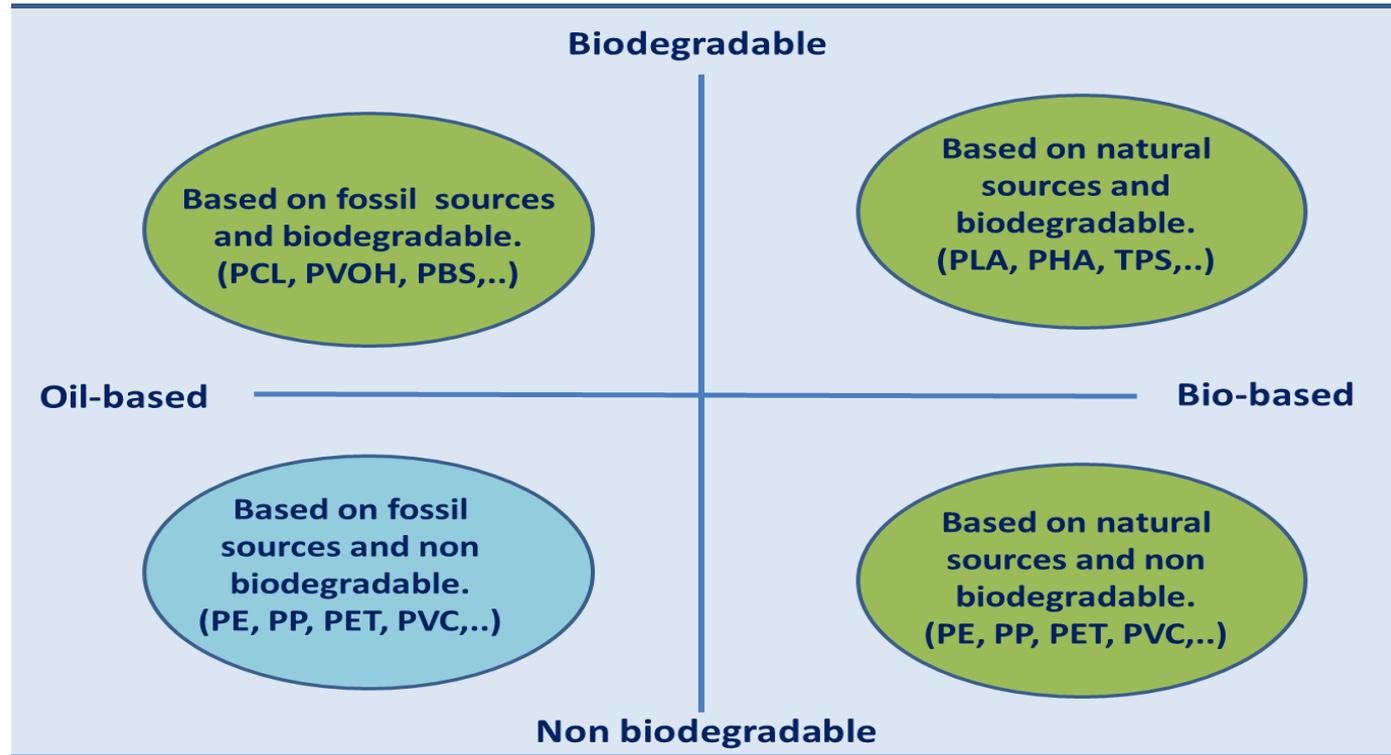
M. Carus, L. Scholz Report on Bio-based Plastics and Composites ISSN 1867-1217,
Edition 7, April 2010



Bio-plastics

Bio-plastics are not a single kind of polymer but rather a family of materials that can vary considerably from one another.

The term bio-plastics encompasses materials which are bio-based, biodegradable, or both.



Thus, there are three groups in the bio-plastics family, each with its own individual characteristics

<http://en.european-bioplastics.org>



Bio-plastics

**Poly(hydroxyalkanoates) (PHAs), Thermoplastic Starch (TPS),
Polylactic acid (PLA),.....**

Bio-based and biodegradable

**Polyethylene and Polyester from renewable resources
(BioPE, HD-LD; Bio PET),.....**

Bio-based and Non-biodegradable

**Polycaprolactone (PCL), Poly(vinyl alcohol) (PVOH),
Poly(butylene succinate) (PBS), Polyglycolic acid (PGA),.....**

Non-renewable and biodegradable



The Research on BBMs at Packlab

The combination of novel bio-based materials with conventional flexible packaging can be also a good way to accelerate the movement towards a sustainable bio-economy, in order to.... “not throw out the baby with the bath water”...

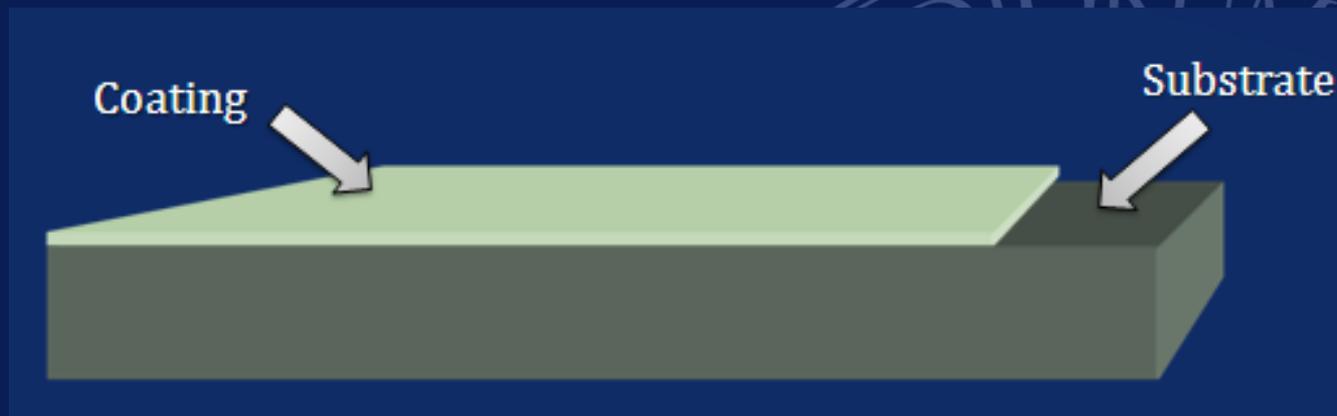
That’s why we are focusing mainly on “coating technology”

L. Piergiovanni, F. Li, S. Farris. 2013. Coatings of Bio-based materials on flexible food packaging: opportunities for problem solving and innovations. In IJEB Special Issue on New Developments in Biotechnology, Guest Editors- RS Singh, Ashok Pandey, CG Dussap & L Piergiovanni, Indian Journal of Experimental Biology, 51(11), 867-1048 (2013) ISSN: 0019-5189 New Delhi



The Research on BBMs at Packlab

Coatings are thin layers of functional material deposited on a substrate, mainly as liquid solutions



From tenths of nm to few μm , generally much thinner than the substrate beneath

S. Farris, L. Piergiovanni . 2012 Advances in coating technologies for food and beverage packaging materials. In: Emerging Food Packaging Technologies (2012), K. Yam and D.S. Lee (Eds.). Woodhead Publishing Ltd, Oxford, UK. pp. 274

The Research on BBMs at Packlab

Coatings applications



Laboratory scale

Pilot scale

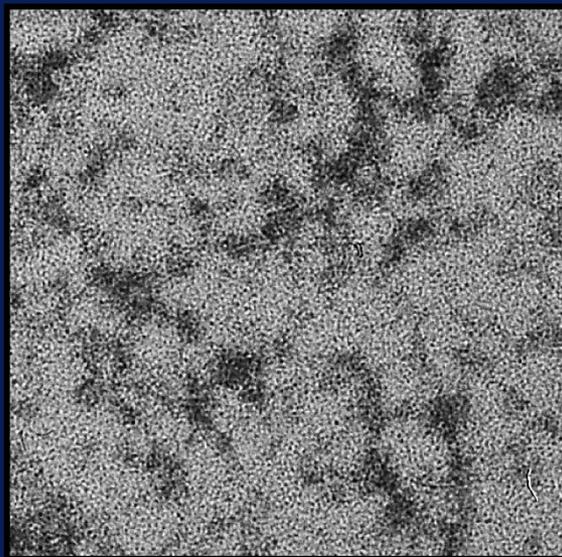


Industrial level



The Research on BBMs at Packlab

Self-assembled Pullulan/Silica hybrid Coatings as Oxygen Barrier at high RH

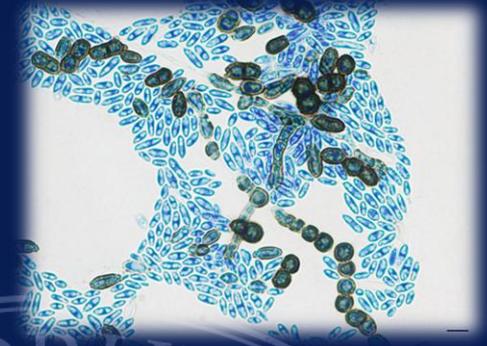


S. Farris, L. Introzzi, J.M. Fuentes-Alventosa, N. Santo, R. Rocca, L. Piergiovanni 2012
Journal of Agricultural and Food Chemistry, 60 (3): 782–790

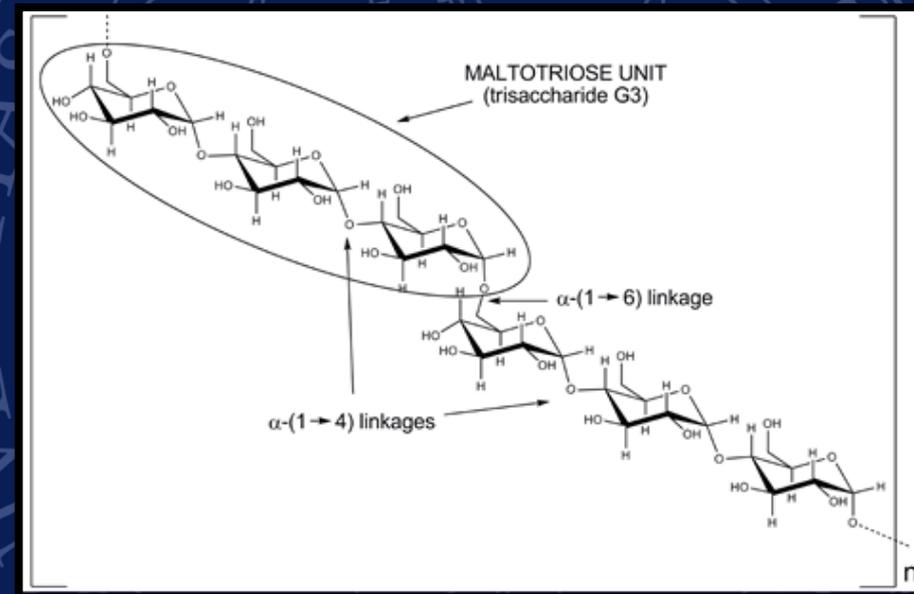
Materials

Pullulan

Exopolysaccharide produced aerobically by a yeast-like fungus *A. pullulans*.



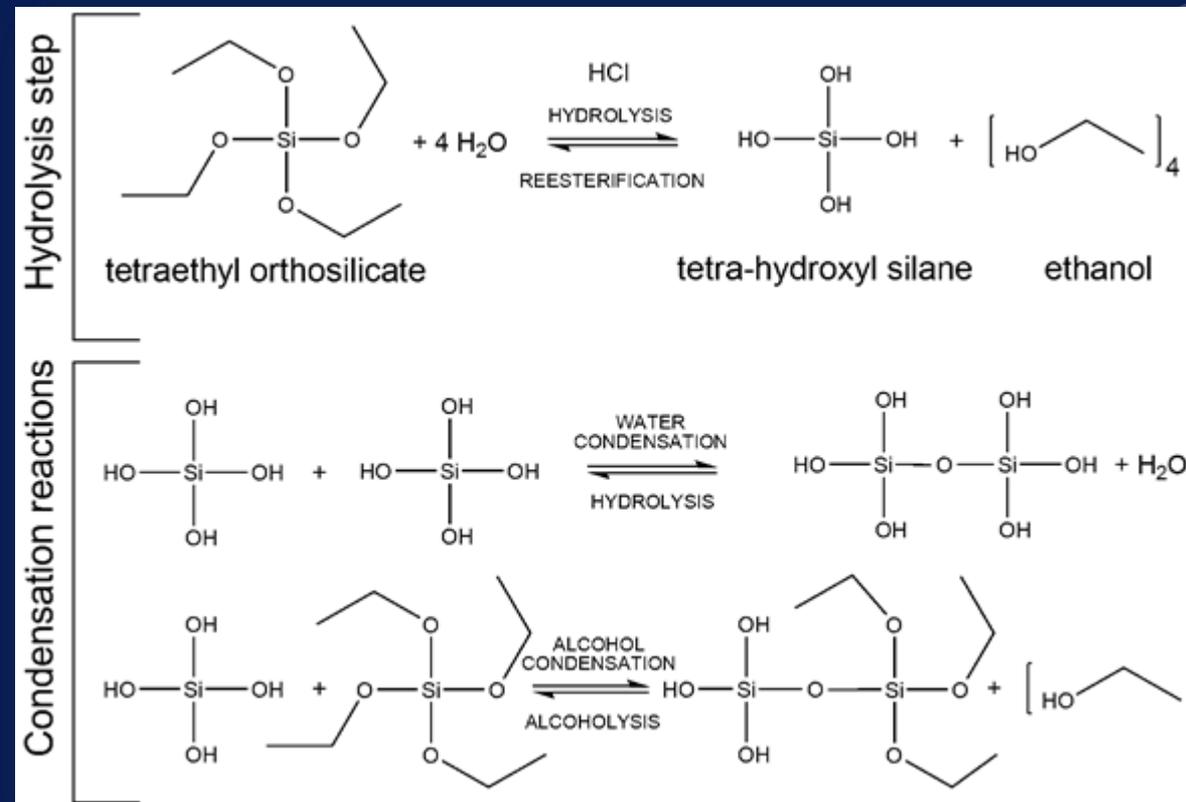
- 👉 High chain flexibility
- 👉 Low viscosity at high concentration
- 👉 Film-forming properties
- 👉 Highly transparent
- 👉 Rich in hydroxyl groups
- 👉 Similar to PVOH
- 👉 High moisture sensitivity
- 👉 High price (~ 20 €/kg)



Materials

Tetraethyl orthosilicate (TEOS)

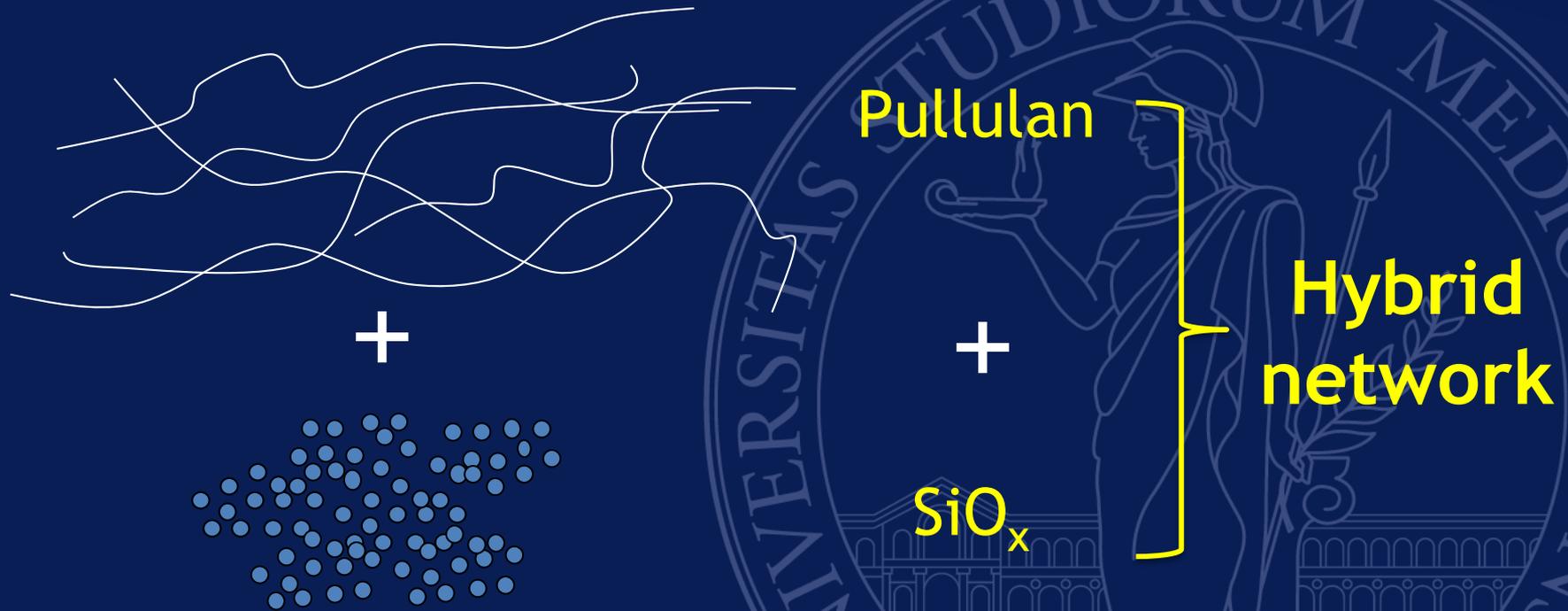
Widely used in the **sol-gel** processes as a precursor of both orthosilicic acid [$\text{Si}(\text{OH})_4$] and silicon dioxide (SiO_2).



Glass-like features

Rationale

Combining the features of the individual phases (i.e. organic and inorganic) can be useful to obtain **a hybrid network** for the production of coatings with high oxygen barrier properties even **at high relative humidity values**



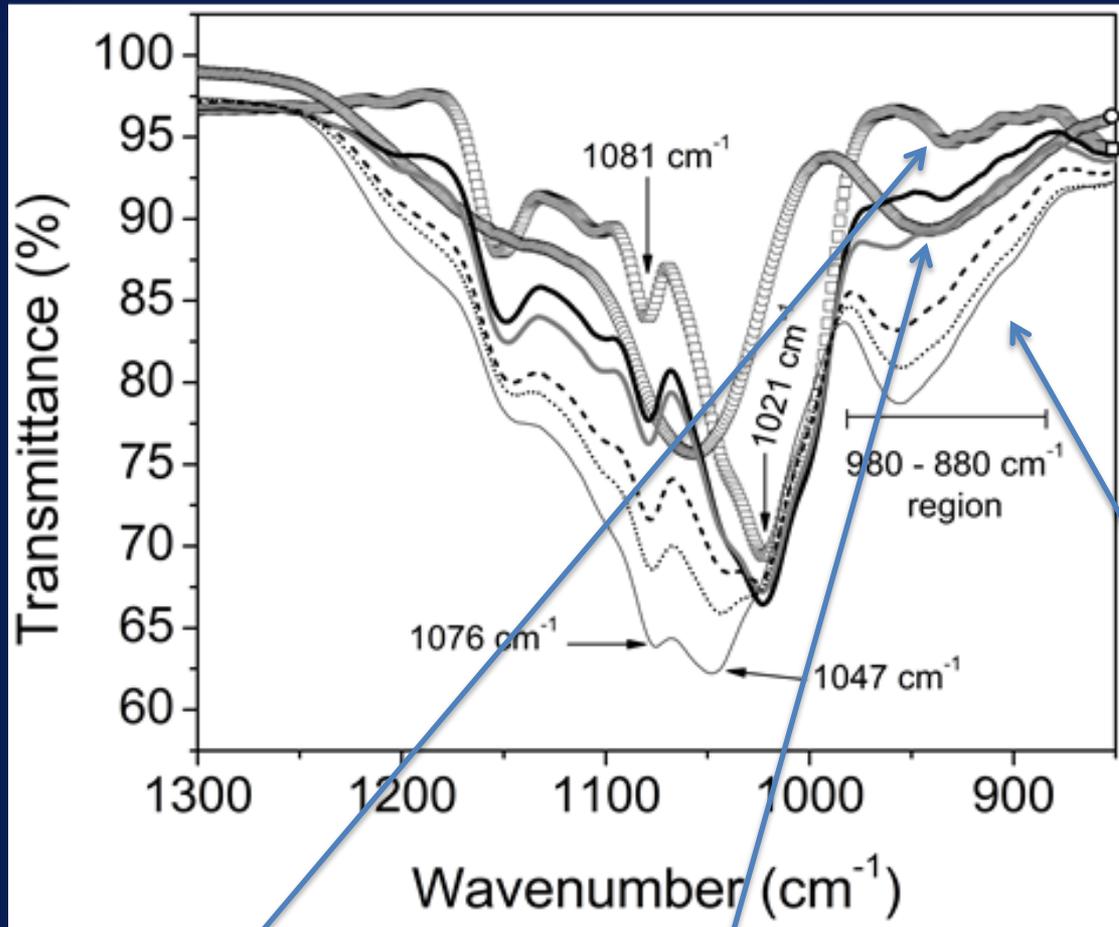
Procedures

Coating formulations tested

Exp. n°	Coded name	Pullulan (wt-%)	Si(OH) ₄ (wt-%)	(O/I*) ratio	Coating thickness (μm)
1	H ₀	10	0	/	1.27 ± 0.12
2	H ₃	7.5	2.5	3	1.37 ± 0.18
3	H ₂	6.66	3.33	2	1.31 ± 0.07
4	H ₁	5	5	1	1.26 ± 0.14
5	H _{0.75}	4.3	5.7	0.75	1.19 ± 0.08
6	H _{0.5}	3.33	6.66	0.5	1.15 ± 0.09

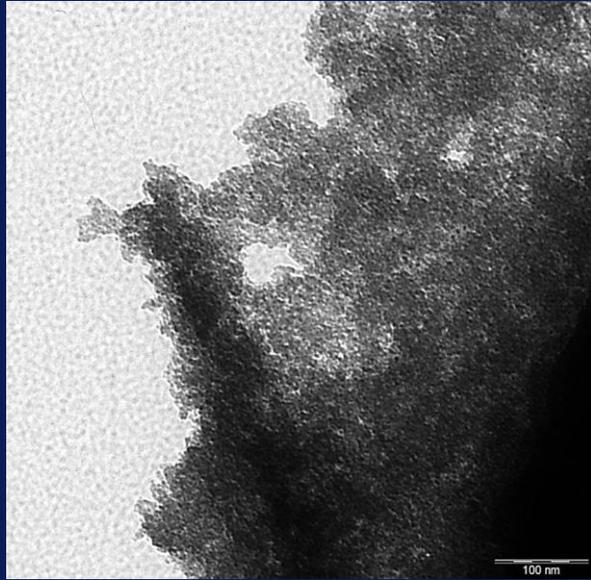
* “O/I” is Organic/Inorganic Ratio; “I” refers to the silanol form, Si(OH)₄, calculated by the initial TEOS content and assuming the completion of the hydrolysis reaction;

Results by ATR-FTIR

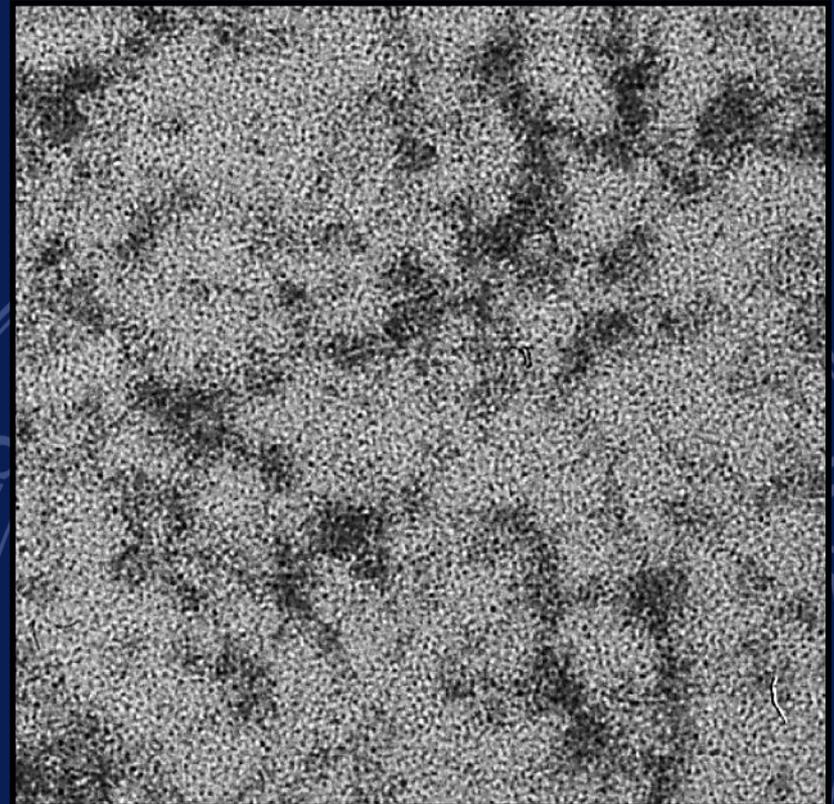


Spectra of pullulan (\square), reacted TEOS (\circ) and hybrid coatings $H_{0.5}$ (—), $H_{0.75}$ (·····), H_1 (- - - -), H_2 (—), H_3 (—) within 1300 cm⁻¹ - 850 cm⁻¹ (d) spectral range

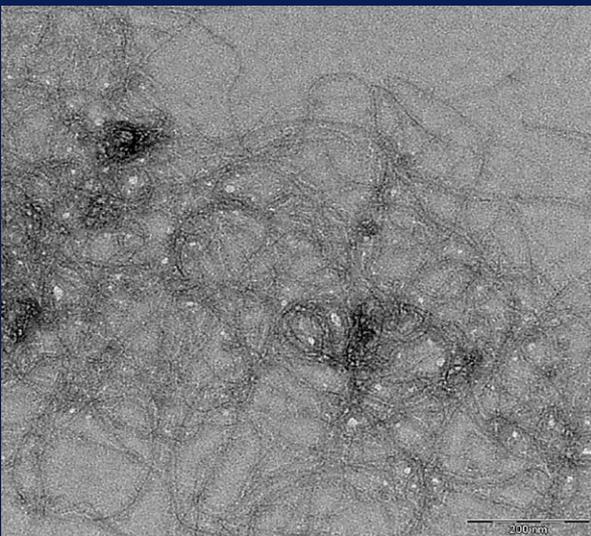
Results by TEM



SiO₂ network
after hydrolysis
and condensation
of the metal
alkoxide
precursor

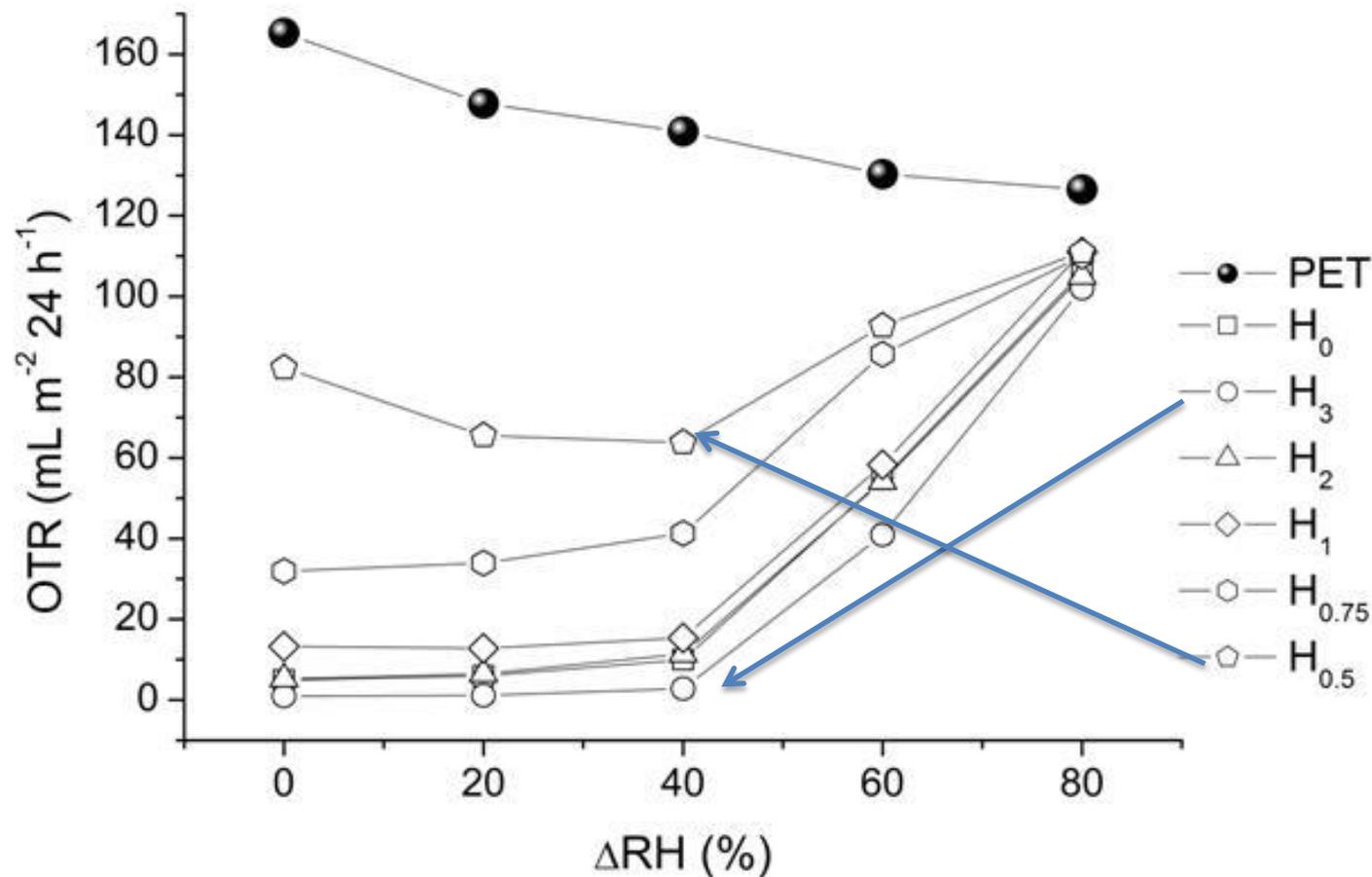


**Pullulan/SiO₂ (1:1)
hybrid network**



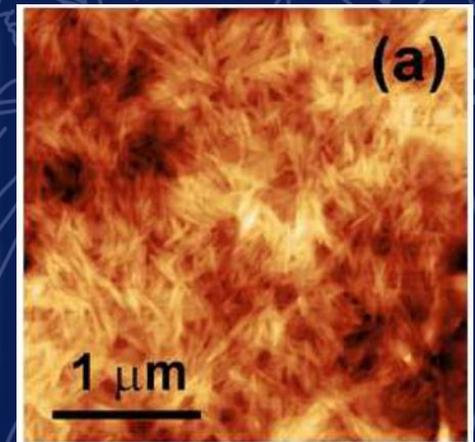
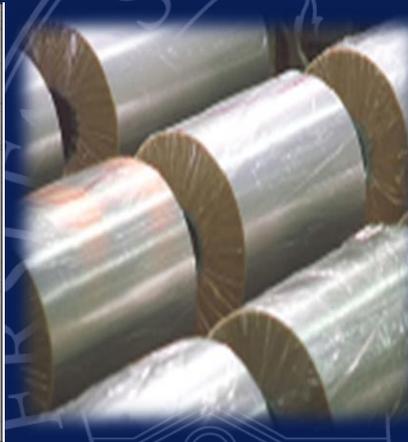
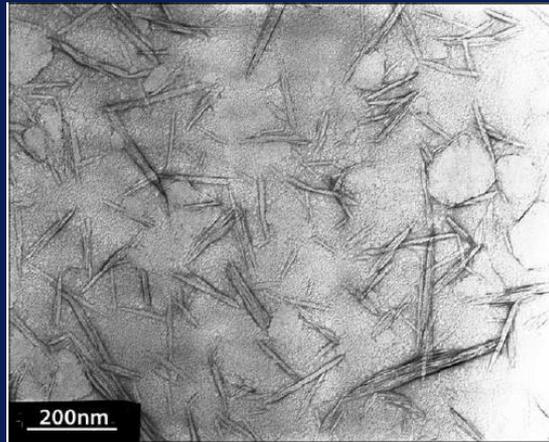
Pullulan chains
with high
extent of
entanglement

Results by OTR measures



The Research on BBMs at Packlab

Multi-functional Coating of Cellulose Nanocrystals for Flexible Packaging Applications



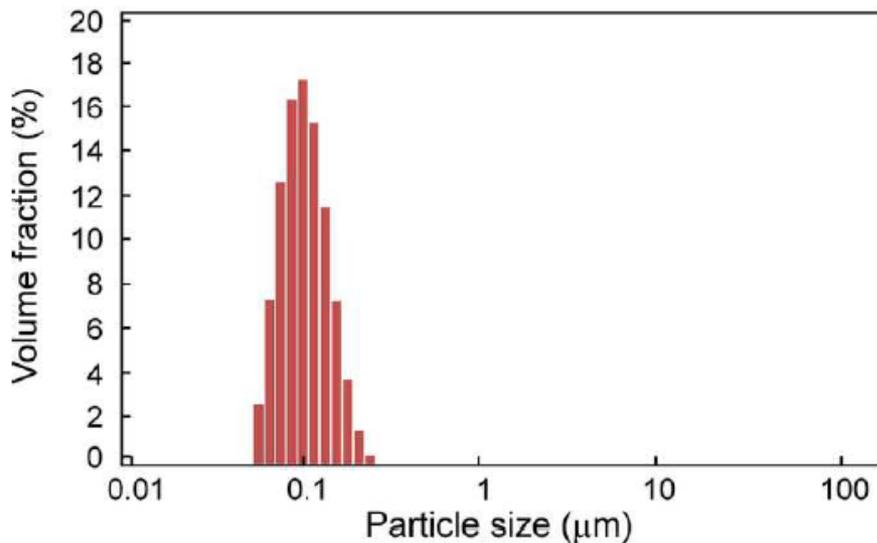
F. Li, P. Biagioni, M. Bollani, A. Maccagnan, L. Piergiovanni. 2013 Multi-functional coating of cellulose nanocrystals for flexible packaging applications *Cellulose* 20 (5): 2491-2504

Materials

Cellulose nanocrystals (CNCs)

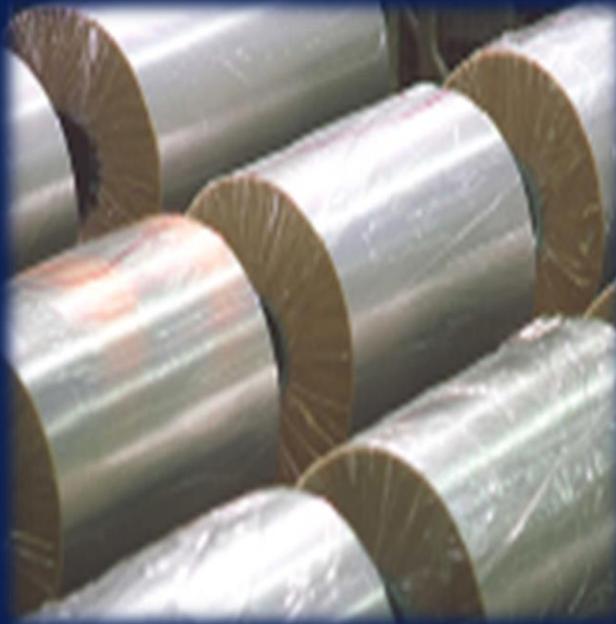


Milled cotton linters were hydrolyzed by 64 wt% sulfuric acid at 45 ° C for 45 minutes to obtain 1 wt% Cellulose nanocrystals dispersion. After further purification the suspension was sonicated, adjusted to pH ~7, freeze-dried and used to prepare a given concentration of cellulose nanocrystals for coating operations



Materials

Poly(ethylene terephthalate (**PET**, 12 μm), oriented polypropylene (**OPP**, 20 μm), oriented polyamide (**OPA**, 12 μm), and cellophane (**CELL**, 12m).

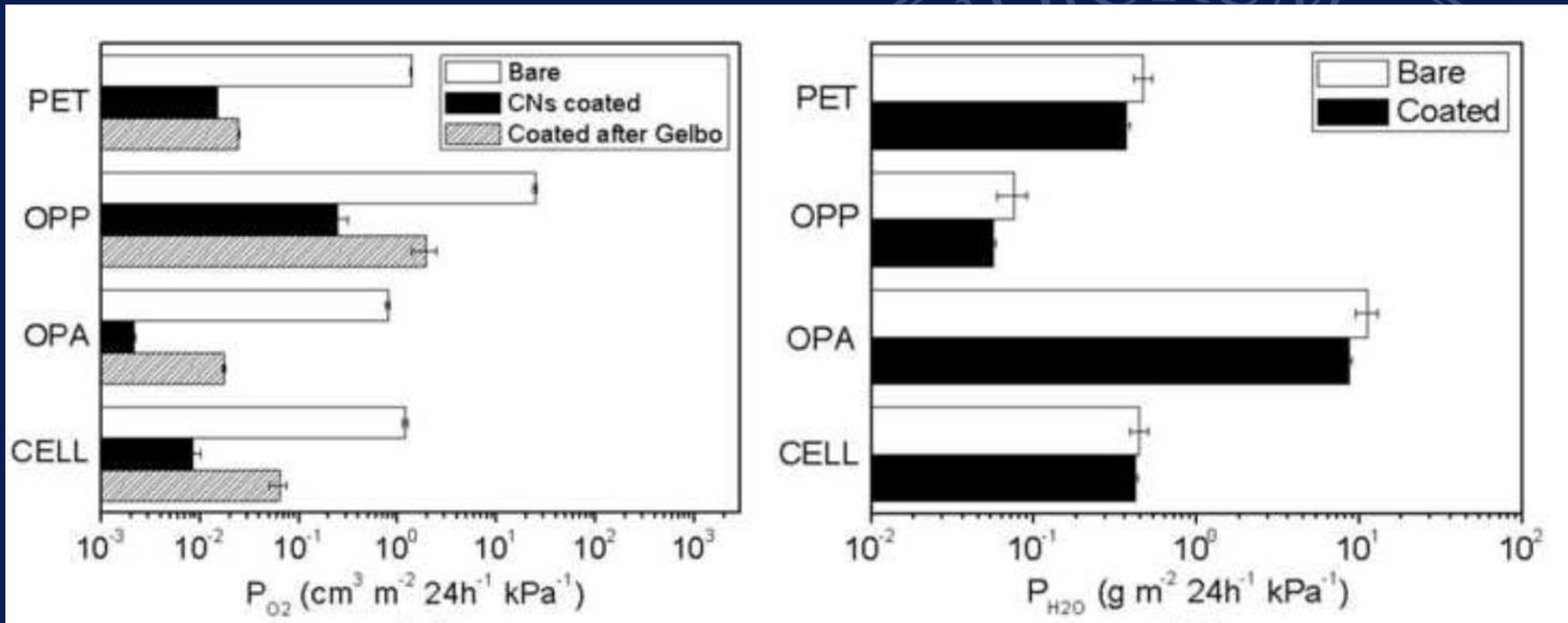


According to ASTM standard the corona-treated sides of the 4 different plastic films were coated by an automatic film applicator at a constant speed



Rationale

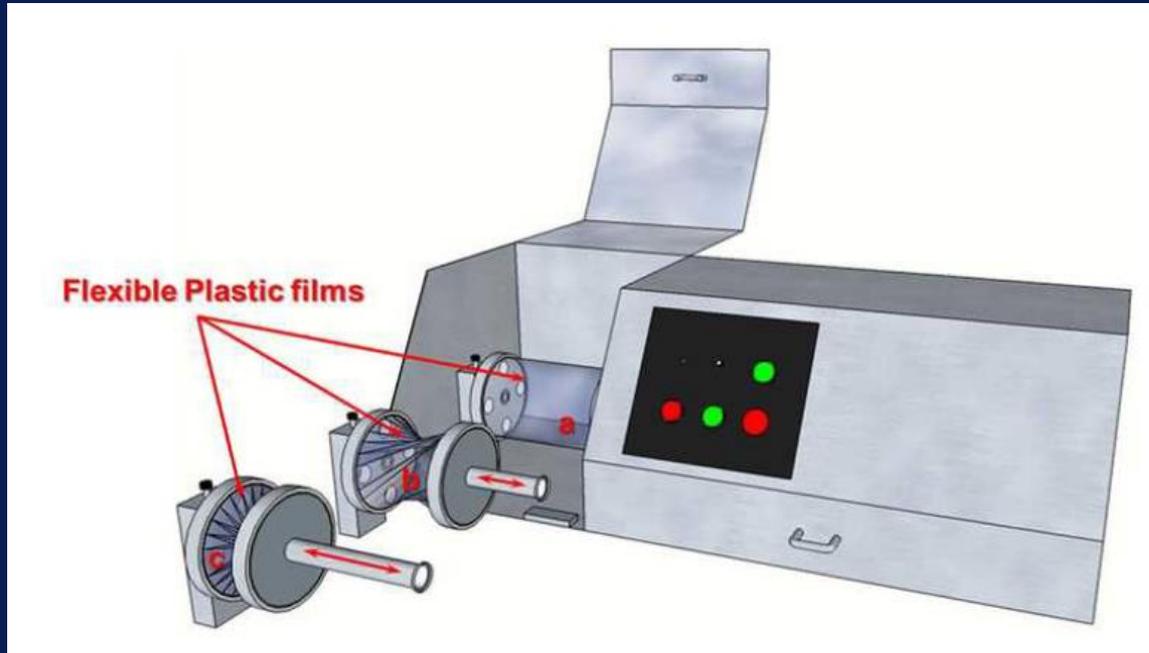
To produce a multi-functional coating, by means of a dispersion of **CNCs** as coating material, in order to enhance the **coefficient of friction, anti-fog, optical, oxygen barrier and water vapor barrier** properties of various substrates films



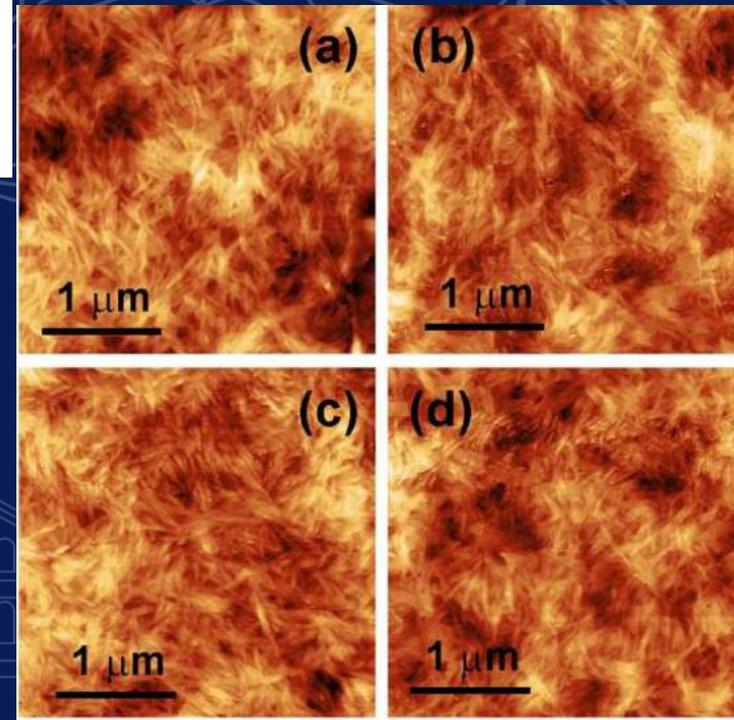
Procedures

GELBO FLEX
testing machine

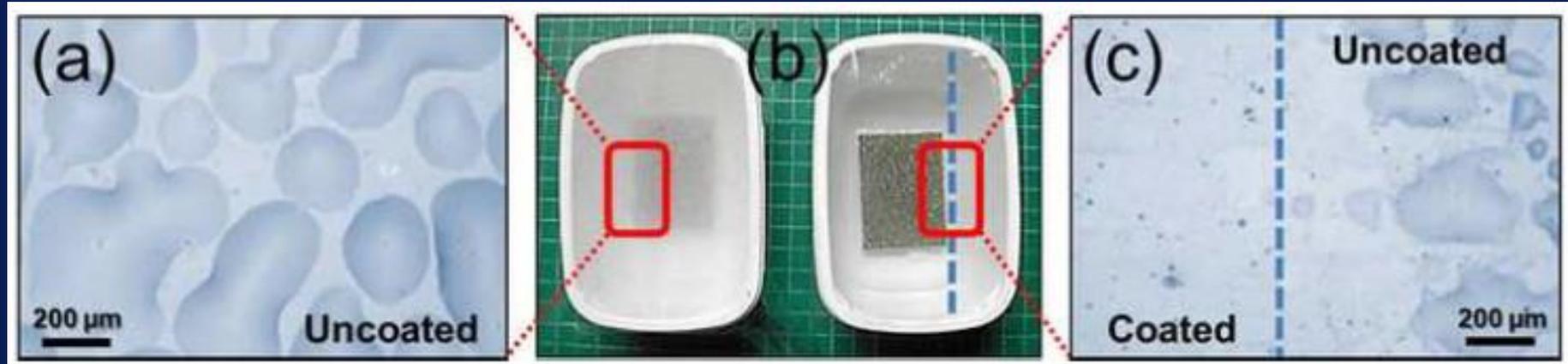
The CNCs network
onto the 4 films



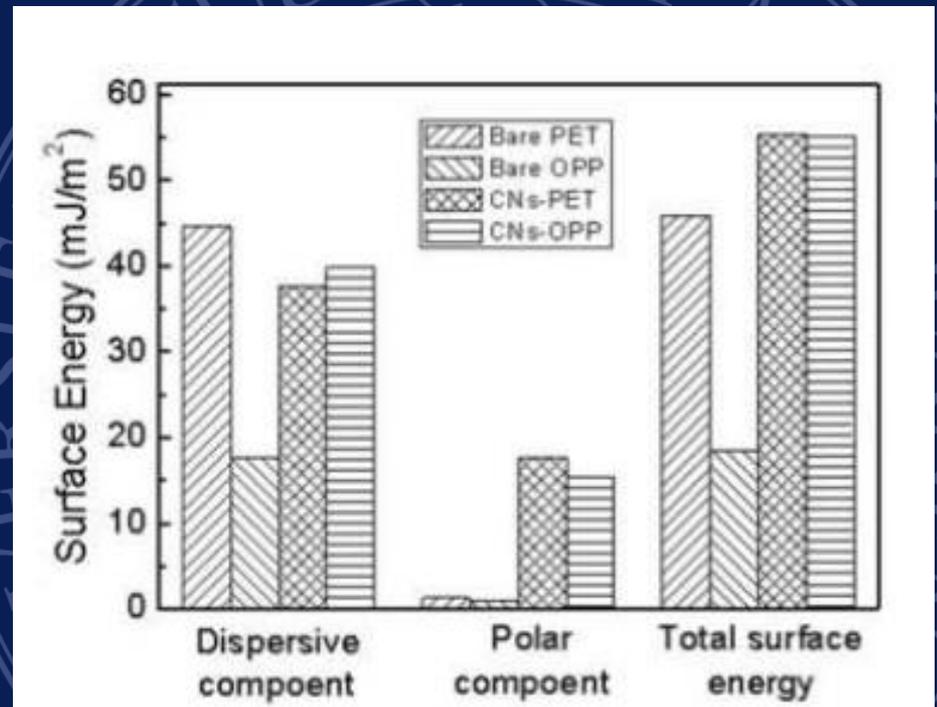
Both practical or empirical tests and scientific investigations were carried out in order to understand the real feasibility of such bio-based coatings



Procedures/Results



Both practical or empirical tests and scientific investigations were carried out in order to understand the real feasibility of such bio-based coatings



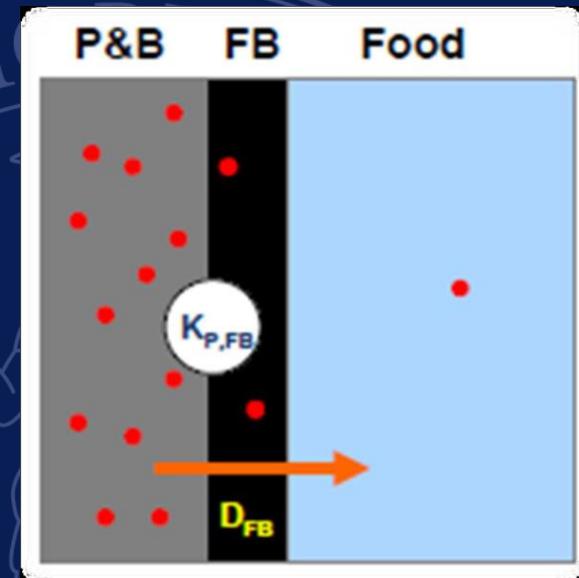
Results

Multi-functional Coating of Cellulose Nanocrystals for Flexible Packaging Applications

	T%	Haze	OTR	WVTR	Antifog	COF
PET			 	 	  	 
OPP				 	  	
OPA			 	 		 
Cell			 	 		 

The Research on BBMs at Packlab

Bio-based coatings as potential barrier to chemical contaminants from recycled paper and board packaging



V. Guazzotti, S. Limbo, L. Piergiovanni, R. Fengler; D. Fiedler, L. Gruber 2014. A study into the potential barrier properties against mineral oils of starch-based coatings on paperboard for food packaging submitted to Food Packaging and Shelf Life

Rationale

Paper and Paperboard, if produced using recycled cellulosic materials, can be contaminated by **MOSH** (Mineral Oil Saturated Hydrocarbons) and **MOAH** (Mineral Oil Aromatic Hydrocarbons); a bio-based coating can provide a **functional barrier** to reduce the possible contamination below a threshold of concern.

Description	Thickness (mm)	Name	MOSH ($\mu\text{g/g}$)
Fully coated white lined chipboard with kraft back suitable for dry food, 320g/m²	0,405	paperboard recycled	484,4
Fully coated white lined chipboard with manilla back suitable for dry food, 320g/m²	0,425	paperboard recycled	486,5
Paperboard with kraft back suitable for dry food, 135g/m²	0,300	paperboard 100% virgin	-
One side machined glazed white paper suitable for dry food, 50g/m²	0,060	paper	84,9
One side machined glazed kraft paper suitable for dry food, 50g/m²	0,060	paper raw	91,6

Materials

Starch coated on a virgin paper as FB

1. Maize Cationic waxy starch
2. Maize Cationic starch
3. Cationic starch mixture with high amylose content

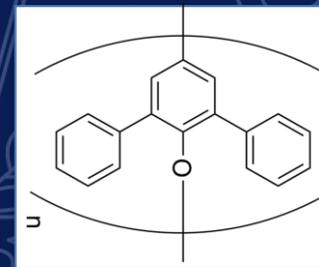


Spiked Paper as donor

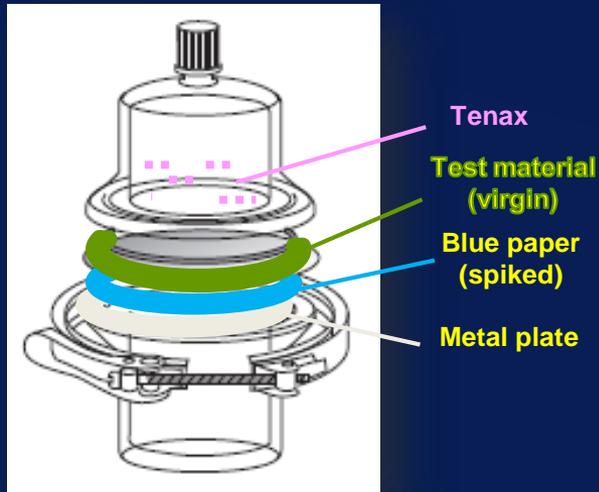
Industrial towel, 60 g/m², spiked with 100μL of a mixture of all even n-alkanes from C₁₀ to C₄₀, 50 mg/L in n-heptane each and allowed to dry

Poly(2,6-diphenyl-p-phenylene oxide) (PPPO) - TENAX as acceptor

For regenerating Tenax, ASE 300 DIONEX was used. As solvent Ethanol and a mixture of Hexane/Ethyl Acetate 56:44.



Procedures

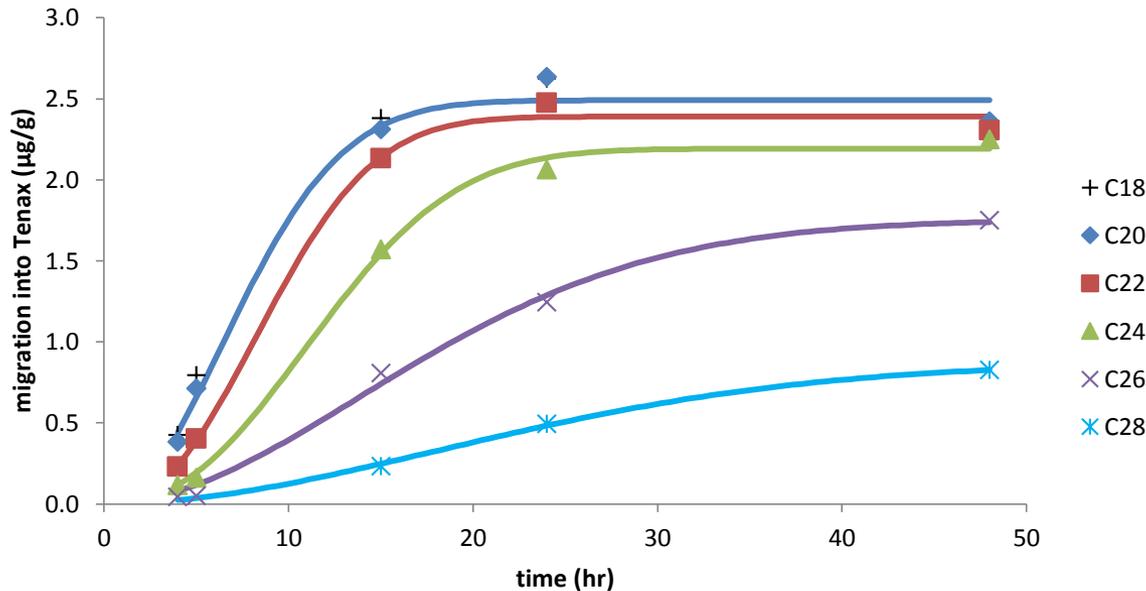


Each test material (neat or coated paperboard) were sandwiched between a glass Migration Cell (MIGRACELL - Fabes)

After conditioning in thermostatic oven, both blue paper and Tenax were extracted following the BfR methodology for quantification of alkane's residue or migration, respectively in the donor and receptor. Extracts were analysed by online normal phase HPLC-GC-FID.

Results

60 °C migration kinetics into Tenax



Weibull parameters			
	C_{∞}	τ	β
C20	2,49	9,05	2,00
C22	2,39	10,56	2,31
C24	2,19	13,79	2,35
C26	1,75	20,64	1,88
C28	0,87	26,79	1,89

Their shape of migration curves is well represented by the **Weibull model** (Pocas M 2011. *Food Control* 22 (2011), 303-312)..

The **Weibull kinetic model** was fit to the experimental data.

$$\frac{C(t)}{C_{\infty}} = 1 - \exp \left[- \left(\frac{t}{\tau} \right)^{\beta} \right]$$

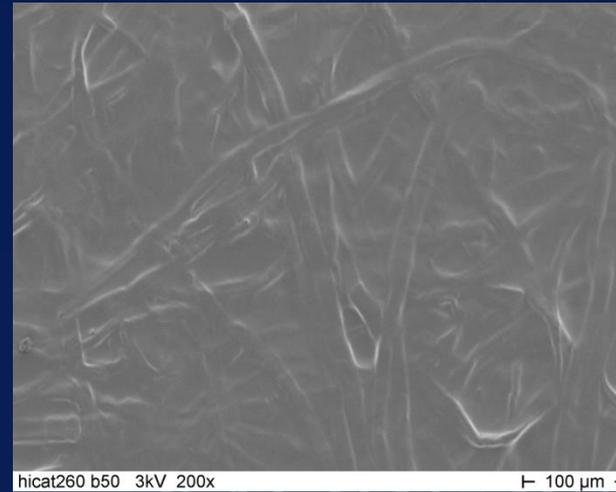
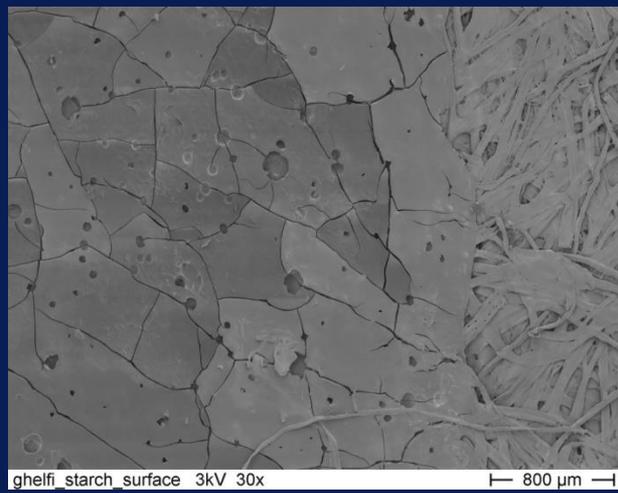
The fitting function was applied to the experimental data using the software Table Curve 2D (Jandel Scientific).

The model has two parameters:

τ the system time constant, associated to the process rate and related to the **diffusion coefficient** and the material **thickness**

β the shape parameter, related to **the initial rate of the process**

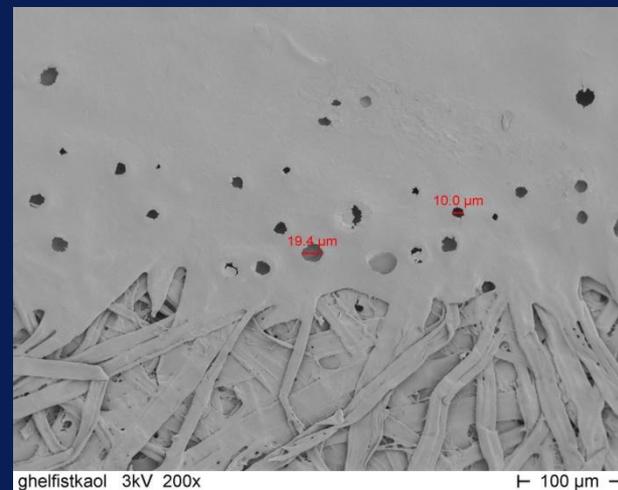
Results



Coated (A= cationic starch) paperboard, lab scale

Coated paperboard (pilot scale made):

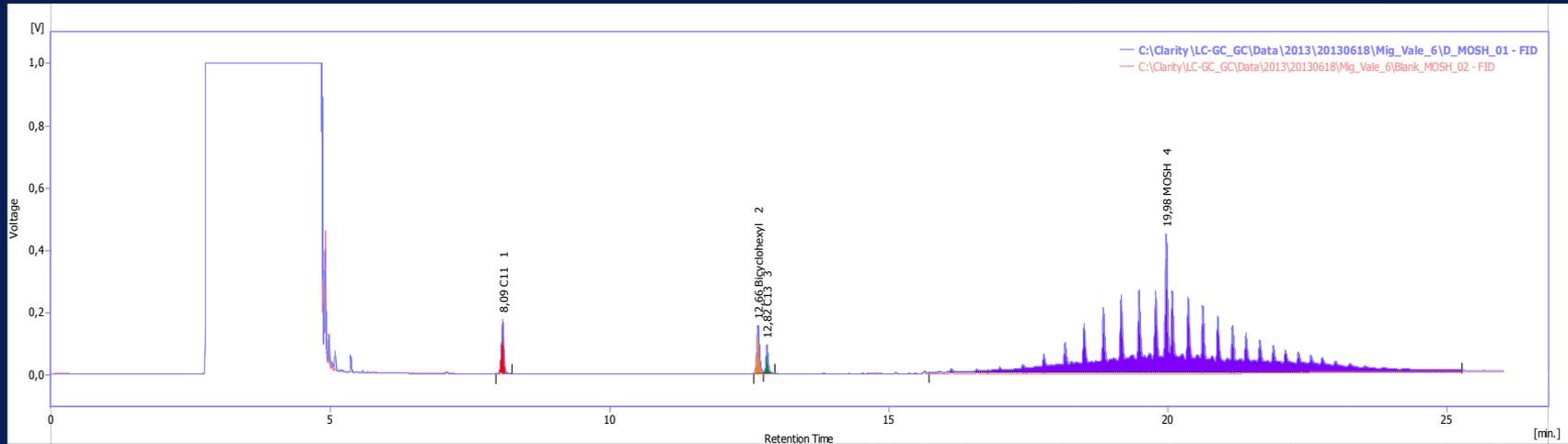
- **fractures zones**
- **pinholes homogenously distributed**



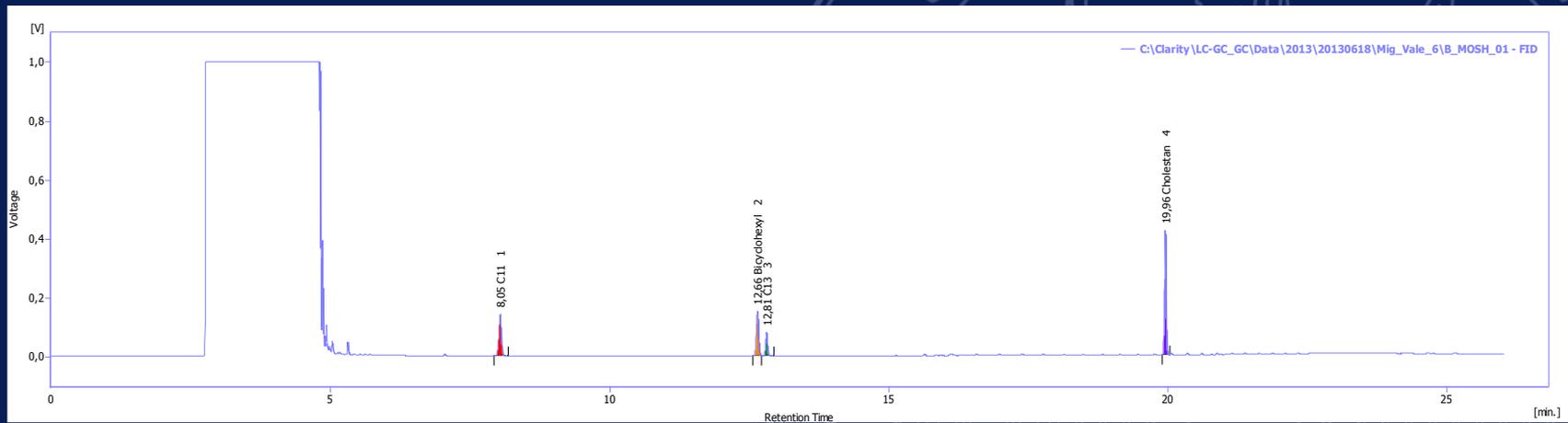
Coated (B = cationic waxy starch) paperboard, lab scale

Only bio-coated paperboard lab scale made could be considered for further investigations of the barrier properties against mineral oil components. The bonds between anionic fibres and cationic starch are very strong with virtually total fixation of the starch to the fibres.

Results



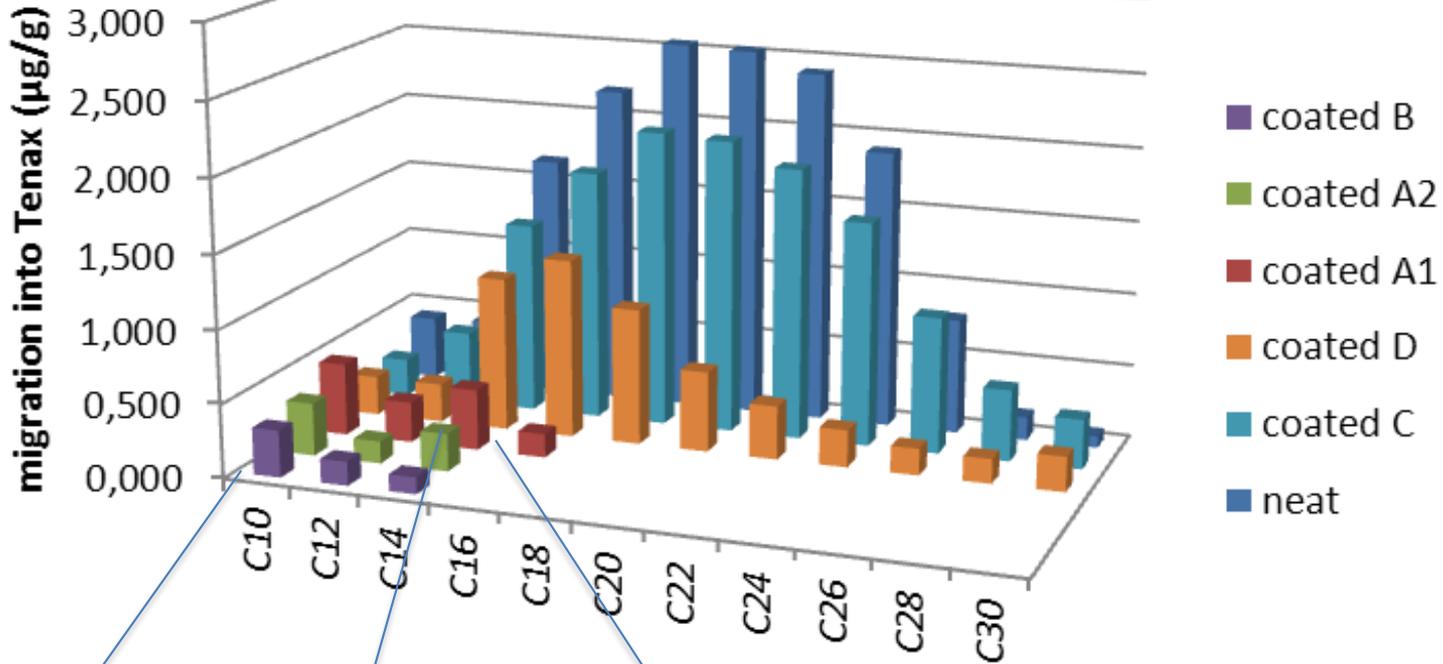
Coated paperboard (pilot scale made)



Coated (B = cationic waxy starch) paperboard, lab scale

Results

Tenax 40 °C 3 days



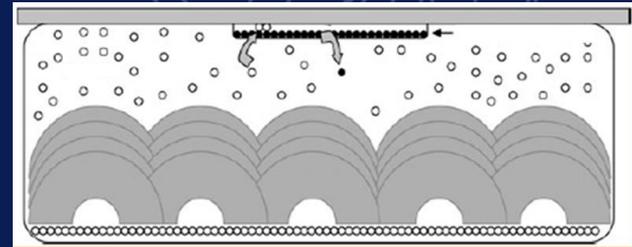
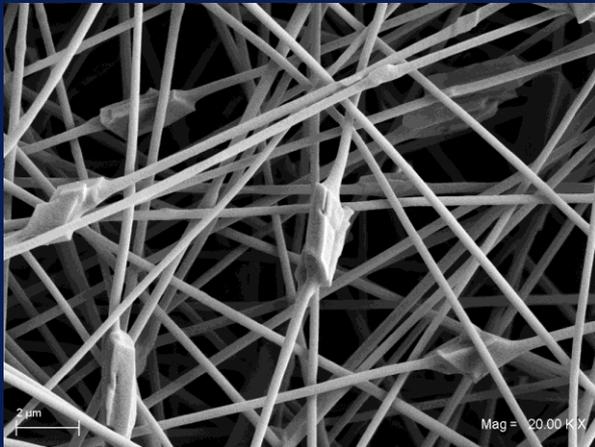
Starch with high amylose content

Normal Starch

Starch with high amylopectin content

The Research on BBMs at Packlab

Encapsulation of natural antimicrobial & antioxidants for a Bio-based Active Packaging device



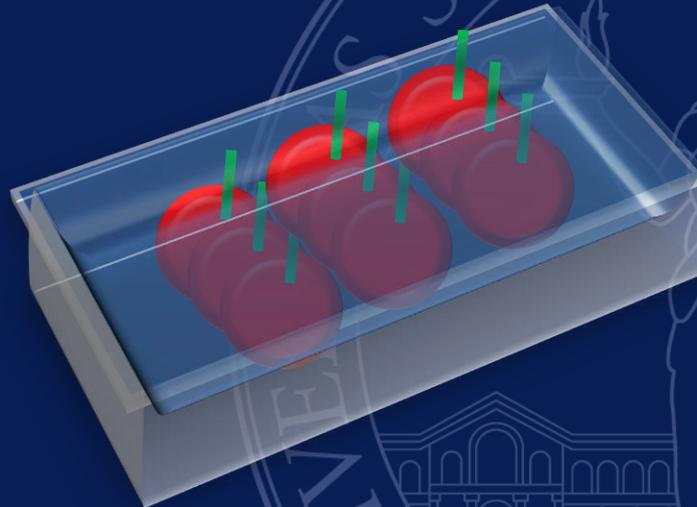
E. Mascheroni, C. Feunmajor, S. Cosio, G. DiSilvestro, L. Piergiovanni, S. Mannino, A. Schiraldi. 2013 Encapsulation of volatiles in nanofibrous polysaccharide membranes for humidity-triggered release. Carbohydrate Polymers. 2013:

Rationale

To set up an **active packaging device**, for fresh foods, triggered by product's moisture and using antioxidant and antimicrobial essential oils (**Perilla, propolis, limonene**) encapsulated in a Bio-based material

Increase of the shelf life of fresh products by active protection against microbial degradation

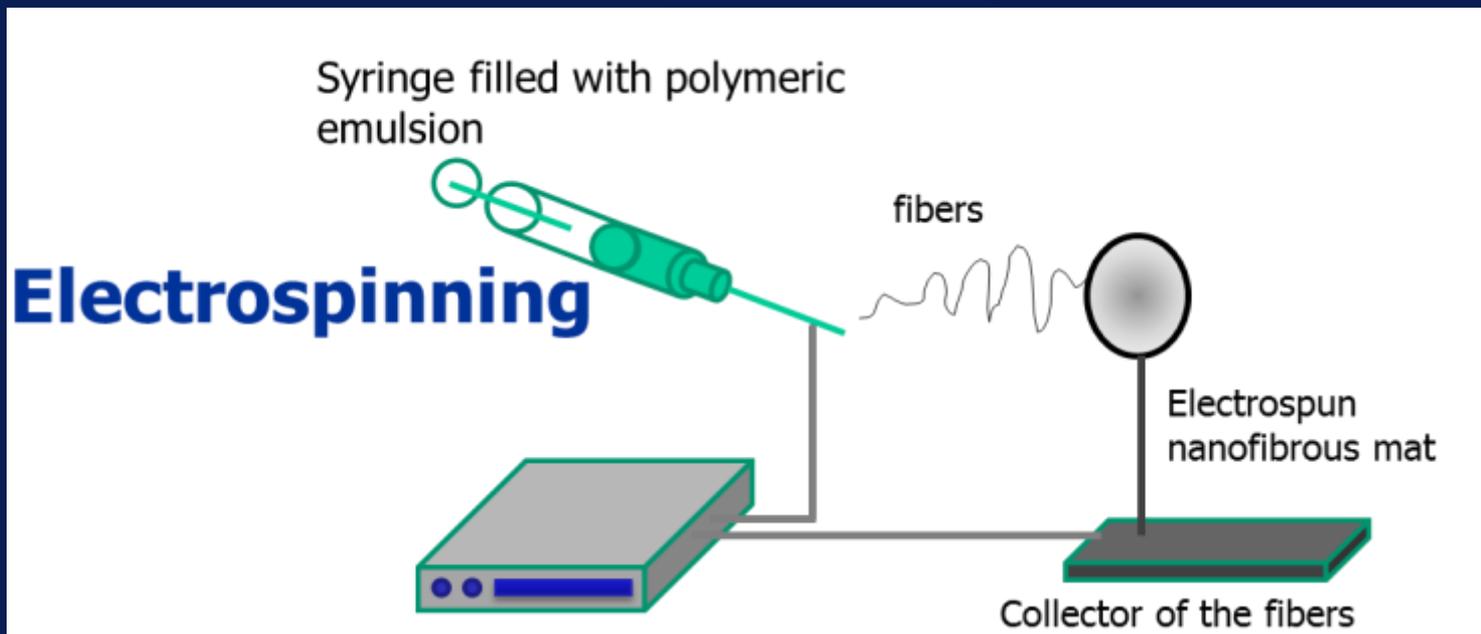
Release of volatile compounds during production and storage



The release is mainly governed by concentration-dependent passive diffusion

Rationale

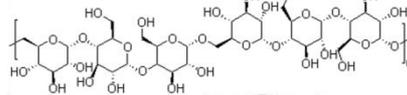
To have, in a single step, the formation of both the inclusion complex (β -cyclodextrine) and the active device (the releasing membrane)
by **Electrospinning of Pullulan nanofibers**



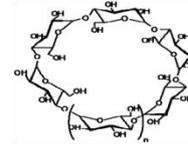
Procedures

Biopolymer

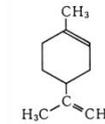
Aroma compound



Pullulan (food grade)



β -cyclodextrin



Electrospinning

Syringe filled with polymeric emulsion



fibers

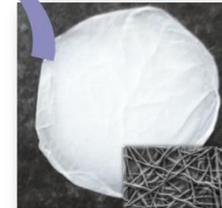


Electrospun nanofibrous mat



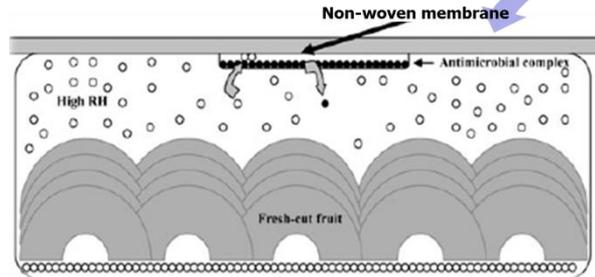
High voltage power supply

Collector of the fibers



Release under specific conditions

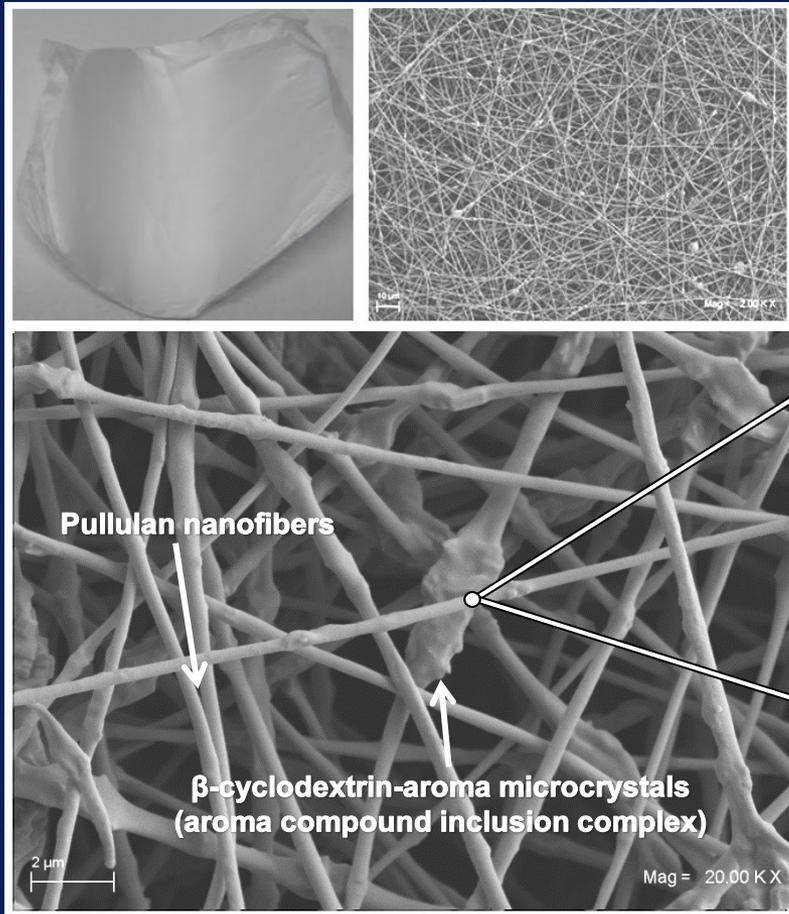
- Time
- Temp.
- Relative humidity



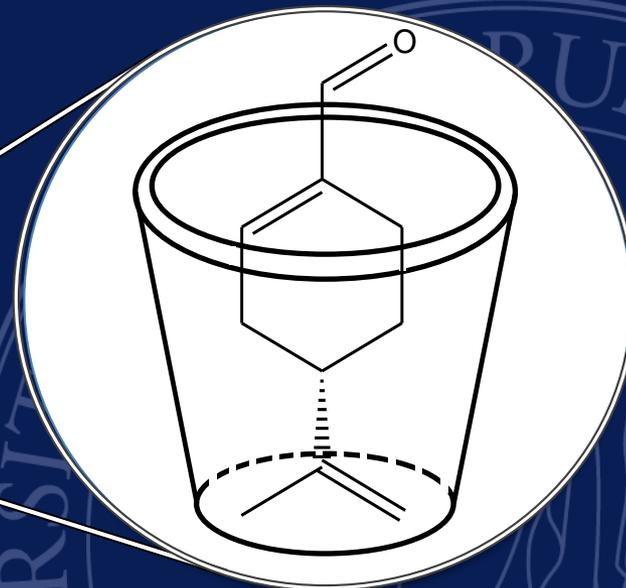
Biopolymeric Active System

- Morphology
- Aroma retentive capacity
- Thermal properties

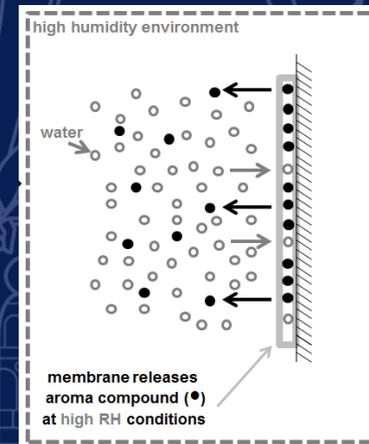
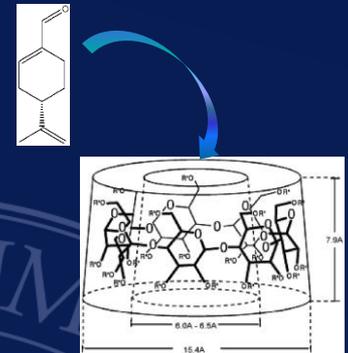
Morphology of the encapsulation membranes



optimal parameters for obtaining pure pullulan nanofibers. 20 wt% pullulan solution, 0.5 mL/h flow rate, 15kV applied voltage and 12 cm tip-to-collector distance.



β-cyclodextrin molecules carrying bioactive aroma (volatile) compound



General Conclusions

Coating technology can be really useful in implementing new and improved properties on flexible packaging materials.

Bio-based materials, derived from renewable sources largely available particularly in underdeveloped countries, can contribute significantly to these achievements

The combination of novel bio-based materials with conventional flexible packaging can be a good way to accelerate the movement towards a sustainable bio-economy,

The PACKLAB



DEPARTMENT OF
FOOD, ENVIRONMENTAL AND
NUTRITIONAL SCIENCES



Thanks for your attention !