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

Luciano Piergiovanni, Stefano Farris, Fei Li, Erika Mascheroni, Valeria Guazzotti, Sara Limbo

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University of Milan

The Department of Food, Environmental and Nutritional Sciences - DeFENS

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

http://users.unimi.it/packlab/default.htm
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**

**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.

**FOOD CONTACT COMPLIANCE**

**ACTIVE PACKAGING SYSTEMS**

**INNOVATIVE BIOBASED MATERIALS**

**SHELF LIFE TESTING & MODELLING**

**Beverages**

Effects of light exposure and protection efficacy of packaging

**Meat & Processed Meat**

Optimization of active packaging solutions

**Low-moisture and dried foods**

Modelling of moisture diffusion across the packaging material

**Studies of release of carvacrol from biocoating at different RH**

**Essential oil of carvacrol**

**Cyclodextrin**

**Coating thickness = 1.63 μm**

**OPP thickness = 20.33 μm**
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
“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.
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
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.
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.

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

<table>
<thead>
<tr>
<th>Effective: the packaging system adds real value to society by effectively containing and protecting products</th>
<th>Efficient: the packaging system is designed to use materials and energy as efficiently as possible throughout the product life cycle.</th>
</tr>
</thead>
<tbody>
<tr>
<td>IT’S USEFUL!</td>
<td>DON’T WASTE!</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cyclic: Packaging materials used in the system are cycled continuously, minimizing material degradation</th>
<th>Clean: packaging components used in the system do not pose any risks to humans or ecosystems.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DON’T LITTER!</td>
<td>DON’T CONTAMINATE!</td>
</tr>
</tbody>
</table>
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.
Our environment for sure, is not at risk for Packaging.

The food sector is the largest contributor to environmental impacts:
- meat
- dairy
- cereals

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

Urs Schenker, FST - NRC Lausanno
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
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.

“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.

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 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”

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.

The Research on BBMs at Packlab

Coatings applications

Laboratory scale

Pilot scale

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

Journal of Agricultural and Food Chemistry, 60 (3): 782–790
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)
Tetraethyl orthosilicate (TEOS)

Widely used in the sol-gel processes as a precursor of both orthosilic acid $[\text{Si(OH)}_4]$ and silicon dioxide ($\text{SiO}_2$).
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.

$\text{Pullulan} + \text{SiO}_x \rightarrow \text{Hybrid network}$
"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.

Procedures

Coating formulations tested

<table>
<thead>
<tr>
<th>Exp. n°</th>
<th>Coded name</th>
<th>Pullulan (wt-%)</th>
<th>Si(OH)$_4$ (wt-%)</th>
<th>(O/I*) ratio</th>
<th>Coating thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_0$</td>
<td>10</td>
<td>0</td>
<td>/</td>
<td>1.27 ± 0.12</td>
</tr>
<tr>
<td>2</td>
<td>H$_3$</td>
<td>7.5</td>
<td>2.5</td>
<td>3</td>
<td>1.37 ± 0.18</td>
</tr>
<tr>
<td>3</td>
<td>H$_2$</td>
<td>6.66</td>
<td>3.33</td>
<td>2</td>
<td>1.31 ± 0.07</td>
</tr>
<tr>
<td>4</td>
<td>H$_1$</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>1.26 ± 0.14</td>
</tr>
<tr>
<td>5</td>
<td>H$_{0.75}$</td>
<td>4.3</td>
<td>5.7</td>
<td>0.75</td>
<td>1.19 ± 0.08</td>
</tr>
<tr>
<td>6</td>
<td>H$_{0.5}$</td>
<td>3.33</td>
<td>6.66</td>
<td>0.5</td>
<td>1.15 ± 0.09</td>
</tr>
</tbody>
</table>

* "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 (□), reacted TEOS (○) 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

SiO$_2$ network after hydrolysis and condensation of the metal alkoxide precursor

Pullulan chains with high extent of entanglement

Pullulan/SiO$_2$ (1:1) hybrid network
Results by OTR measures
Multi-functional Coating of Cellulose Nanocrystals for Flexible Packaging Applications

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, 12μm), oriented polypropylene (OPP, 20μm), oriented polyamide (OPA, 12μm), 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.
Both practical or empirical tests and scientific investigations were carried out in order to understand the real feasibility of such bio-based coatings.
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

<table>
<thead>
<tr>
<th></th>
<th>T%</th>
<th>Haze</th>
<th>OTR</th>
<th>WVTR</th>
<th>Antifog</th>
<th>COF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>↑↑↑↑↑</td>
<td>↓</td>
</tr>
<tr>
<td>OPP</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>↑↑↑↑↑</td>
<td>↑</td>
</tr>
<tr>
<td>OPA</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td></td>
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<td>Cell</td>
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<td>↓</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Description</th>
<th>Thickness (mm)</th>
<th>Name</th>
<th>MOSH (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully coated white lined chipboard with kraft back suitable for dry food, 320g/m²</td>
<td>0,405</td>
<td>paperboard recycled</td>
<td>484,4</td>
</tr>
<tr>
<td>Fully coated white lined chipboard with manilla back suitable for dry food, 320g/m²</td>
<td>0,425</td>
<td>paperboard recycled</td>
<td>486,5</td>
</tr>
<tr>
<td>Paperboard with kraft back suitable for dry food, 135g/m²</td>
<td>0,300</td>
<td>paperboard 100% virgin</td>
<td>-</td>
</tr>
<tr>
<td>One side machined glazed white paper suitable for dry food, 50g/m²</td>
<td>0,060</td>
<td>paper</td>
<td>84,9</td>
</tr>
<tr>
<td>One side machined glazed kraft paper suitable for dry food, 50g/m²</td>
<td>0,060</td>
<td>paper raw</td>
<td>91,6</td>
</tr>
</tbody>
</table>
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.
Each test material (neat or coated paperboard) were sandwiched between a glass Migration Cell (MIGRACELL - Fabes)

After conditioning in thermostatic hoven, 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.
The **Weibull kinetic model** was fit to the experimental data.

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

The model has two parameters:

- $\tau$, the system time constant, associated to the process rate and related to the **diffusion coefficient** and the material **thickness**
- $\beta$, the shape parameter, related to the initial rate of the process

<table>
<thead>
<tr>
<th></th>
<th>$C_\infty$</th>
<th>$\tau$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C20</td>
<td>2.49</td>
<td>9.05</td>
<td>2.00</td>
</tr>
<tr>
<td>C22</td>
<td>2.39</td>
<td>10.56</td>
<td>2.31</td>
</tr>
<tr>
<td>C24</td>
<td>2.19</td>
<td>13.79</td>
<td>2.35</td>
</tr>
<tr>
<td>C26</td>
<td>1.75</td>
<td>20.64</td>
<td>1.88</td>
</tr>
<tr>
<td>C28</td>
<td>0.87</td>
<td>26.79</td>
<td>1.89</td>
</tr>
</tbody>
</table>
Results

Coated paperboard (pilot scale made):

- fractures zones
- pinholes homogenously distributed

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

Coated paperboard (pilot scale made) with defects

![Graph showing migration into Tenax at 40 °C for 3 days.](image)

- **Starch with high amylose content**
- **Normal Starch**
- **Starch with high amylopectin content**
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 polysaccaryde 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

Release under specific conditions
- Time
- Temp.
- Relative humidity

Biopolymer
- Pullulan (food grade)
- β-cyclodextrin

Aroma compound

Electrospinning
- Syringe filled with polymeric emulsion
- Electrosyn nanofibrous mat
- Collector of the fibers
- High voltage power supply
- Non-woven membrane

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

Thanks for your attention!