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Cellulose Nanofibrils in Bio-Based Multilayer Films and Pouches

Presented by:

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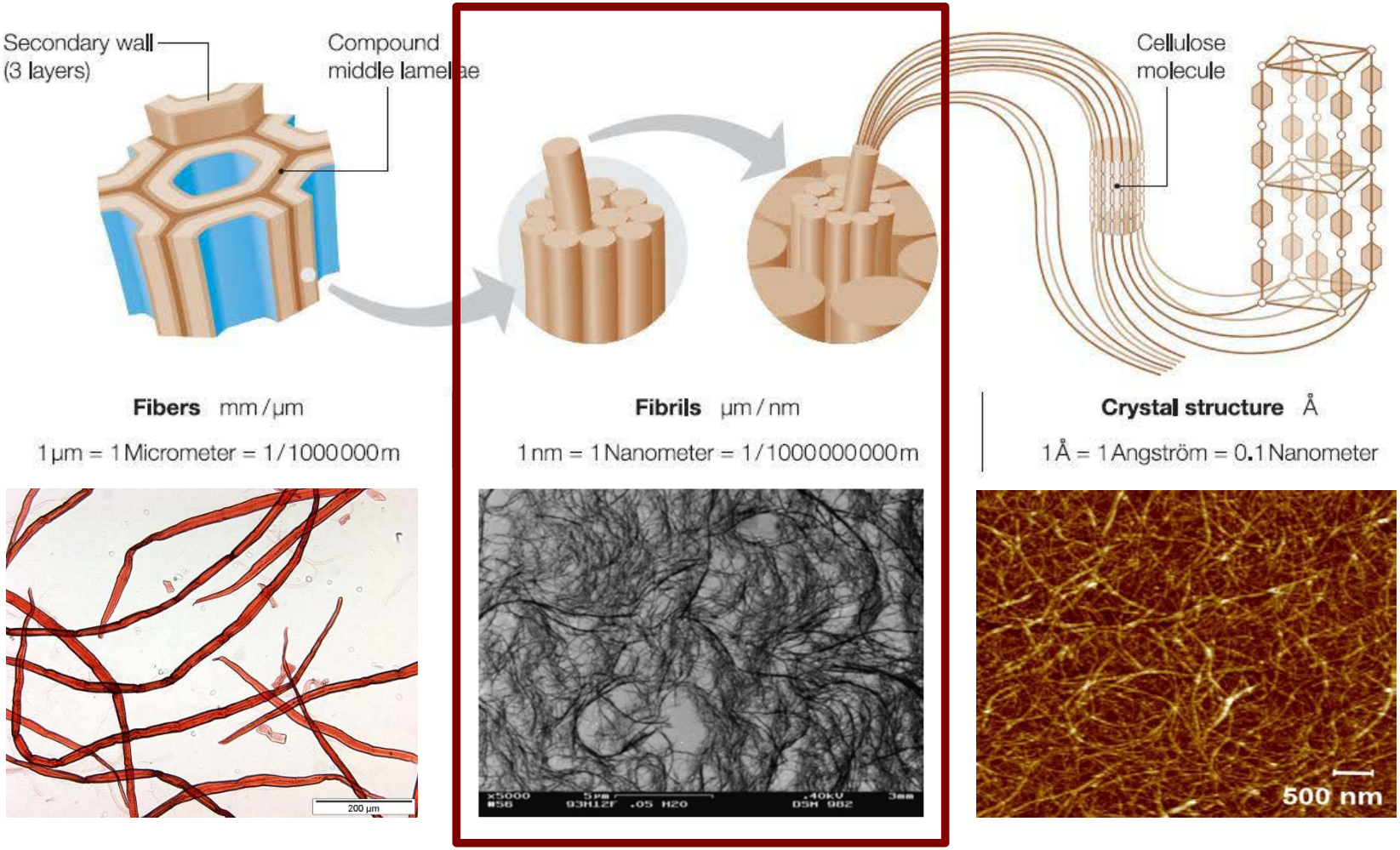
Motivation for Bio-Based Packaging Solutions

- Consumer demand for materials made from bio-based and sustainable resources that are more recyclable, carbon neutral, and have low environmental and health impacts,
- About 80% of Europeans want to buy products with a minimal enrironmental impact, and most are also willing to pay more for environmentally friendly products,
- 92% of business executives in packaging industry see a trend towards green materials at least a fact with real value (McKinsey, 2012),
- Annual growth predictions for bio-based packaging solutions around 20% to 2020.

Value Proposition of Bio-Based Solutions

- Totally bio-based (C14-content >90%),
  - Saves environment, decreases dependency on exported resources
- High performance,
  - Properties similar to best synthetic plastics
- Light weight,
  - Saves materials & energy
- User friendly, modern & green design,
  - Smart opening mechanisms
  - Visual appearance and visibility
  - End of life options (recycling)
- Cost effective (bearable cost structure).

Fibrillated Cellulose (CNF/CMF)



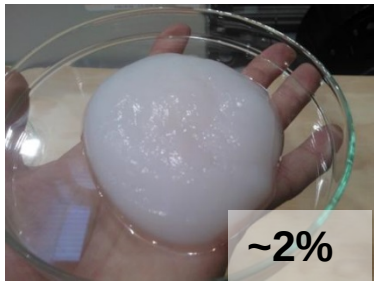
Examples of CNFs for Multilayer Films

GROUND CNF

Typically from softwood pulp,

Number of passes through mechanical treatment,

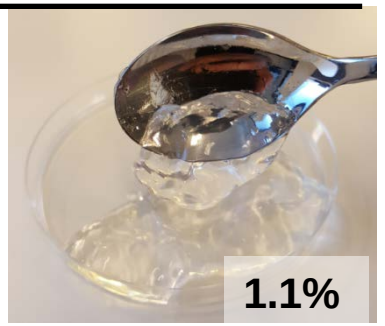
Final Yield ~ 95%.



TEMPO-CNF

Cellulose fibers oxidized with specific chemical mediator,

Followed by **low consistency** treatment to disintegrate fibers.

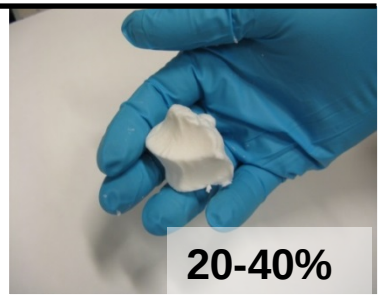


HefCel *(Patent bending)*

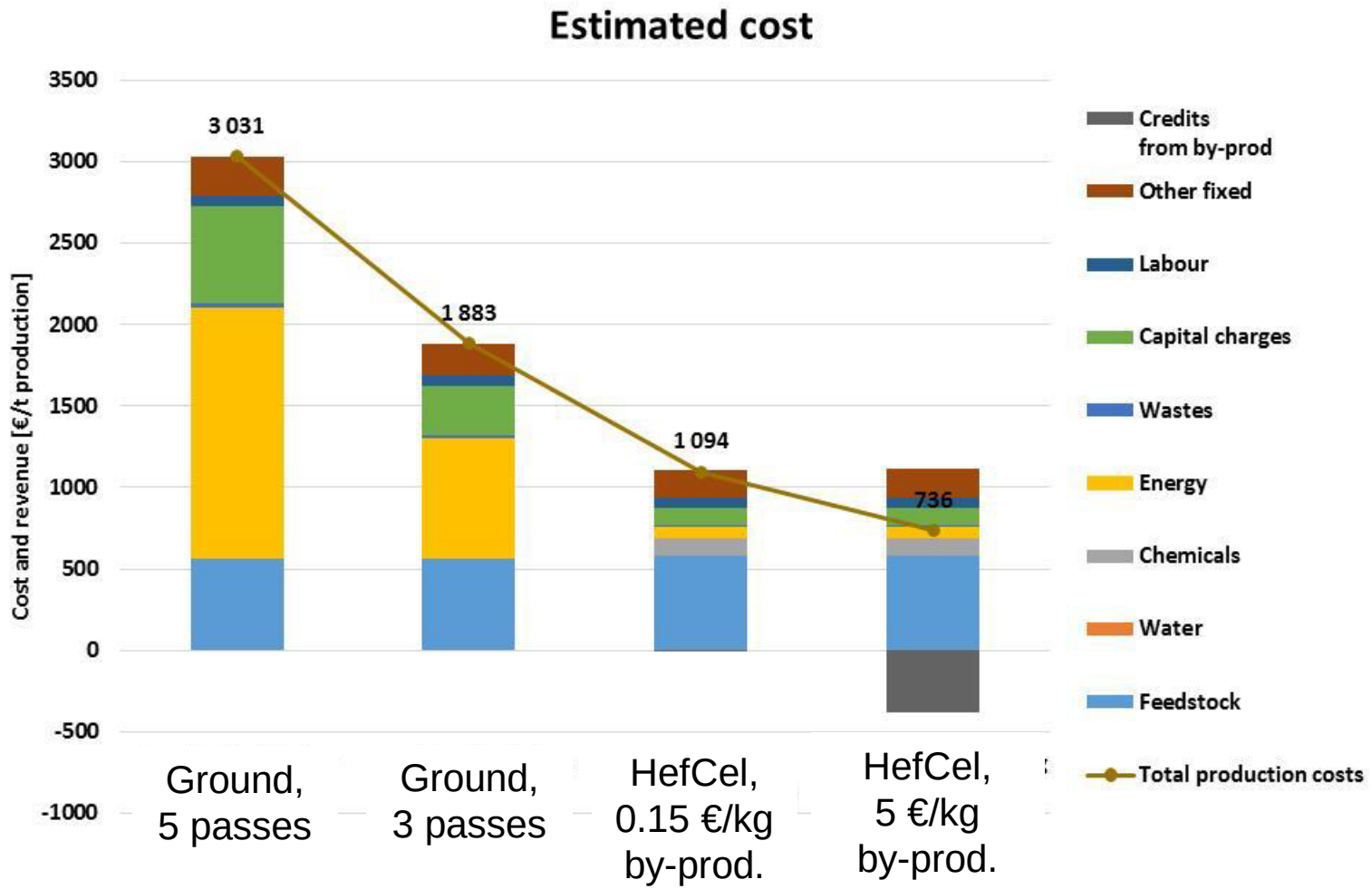
High consistency enzyme assisted cellulose fibrillation,

Mechanical low energy agitation – high fiber-fiber friction,

Valuable by-products



Example of CNF Production Cost Structure



J. Lehmonen et al, Int. Conf. on Nanotechn. for Renewable Materials, 2016

Background:
Roll-to-Roll Method for Producing CNF Film

- Produced with a pilot coating line,
- Properties depend on formulation:
- **Good:**
  - OTR <0.1 $cm^3/m^2/d$ (0% RH; 15 µm)
  - Temperature resistance (200°C)
  - Tensile strength (200 MPa)
- **To be improved:**
  - Water vapor barrier
  - Flexibility (<10% strain)
  - Transparency (<80%)
  - Heat sealing

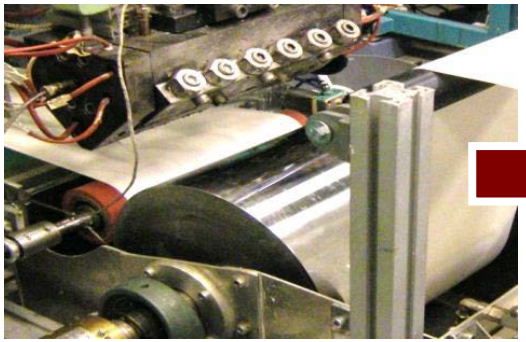
Patent pending

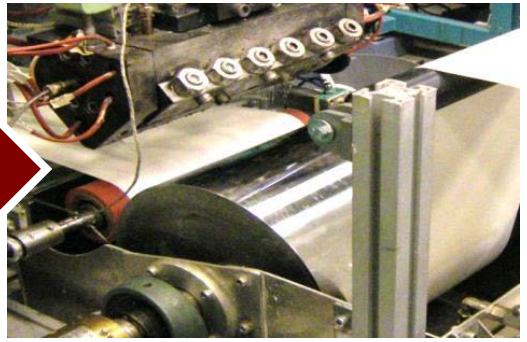
Process for Preparing Bio-Based Multilayer Materials

PlasCo; Cast film and extrusion coating line.

SutCo; Modular pilot dispersion coating line.

PlasCo; Cast film and extrusion coating line.





~50 µm bio-HDPE + 1-2 µm **TEMPO-CNF**

~50 µm bio-HDPE + <1 µm **TEMPO-CNF** + ~30 µm bio-LDPE

40 g/m^2 unbleached paper + ~25 µm PLA + ~4 µm **HefCel** + ~20 µm bio-LDPE

For more details e.g.: M. Vähä-Nissi et al,. J. Appl. Pol. Sci., 15 May 2017.

Pouches from Bio-Based Multilayer Materials

Bag-in-Box

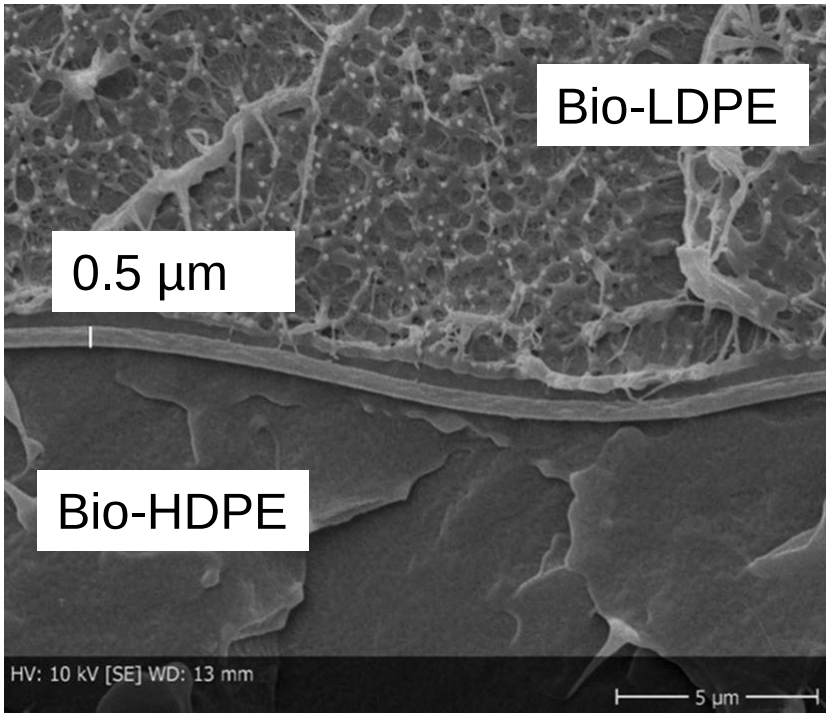
Bio-HDPE
Bio-HDPE / **CNF**
Bio-HDPE / **CNF** / Bio-LDPE

MAP Pouch

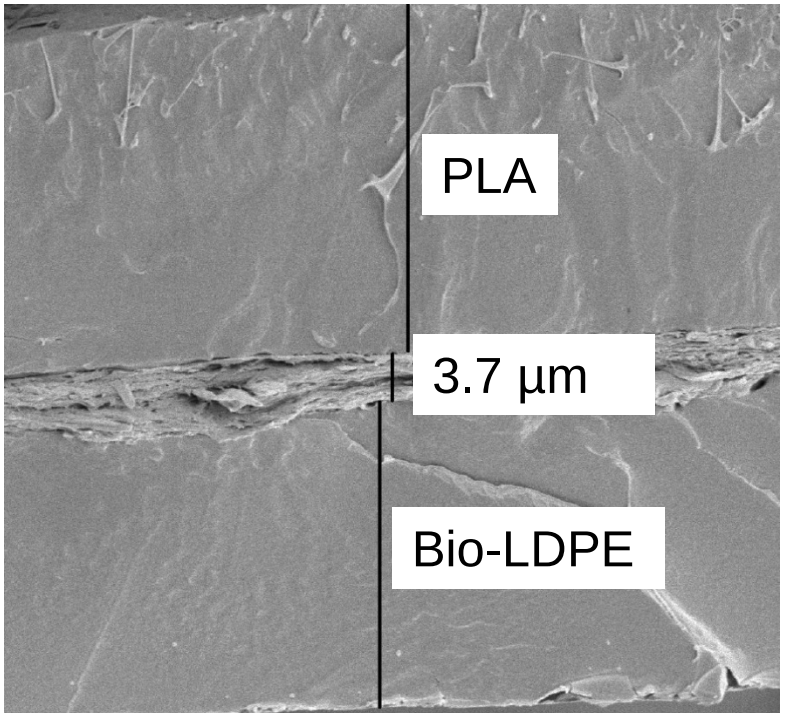
Stand-up Pouch

Bio-LDPE / **CNF** / PLA / Paper

Structure in MAP and SUP Pouches



Bio-HDPE / TEMPO-CNF / Bio-LDPE



Bio-LDPE / HefCel / PLA / Paper

Bio-LDPE / HefCel / PLA / Paper

[a] **WVTR**: 17 g/m^2,d (38 °C, 90% RH)

[b] Sealing strength: 320 N/m

[c] **OTR**: 0.5 cm^3/m^2,d (23 °C, 0% RH)

[a] WVTR; Permatran-W 3/33 MG Plus (Mocon);

[b] Sealability at 140 °C; Labormaster HTC 3000 from Willi Kopp;

[c] OTR; Ox-Tran 2/21 (Mocon) / models 8001/8011 (Systech Instruments Ltd.)

J. Vartiainen et al., Multilayer Packaging Films 2016

Safety Concerns over Mineral Oil Migration

Cornflakes cancer scare: Cereal makers drop recycled cardboard boxes containing deadly oils

By SEAN POULTER FOR THE DAILY MAIL
UPDATED: 02:00 GMT, 9 March 2011

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- **Tests found mineral oils could even leak through plastic inner packaging**

Breakfast cereals, pasta, rice and other foods packed in cardboard boxes could be tainted with toxic chemicals, researchers warn.

The substances appear to be leaching from the recycled paper used to make most cardboard boxes.

Studies in Germany and Switzerland found the levels to be up to 100 times the agreed safe limit in products sold in supermarkets.

The chemicals – mineral oil hydrocarbons – are said to cause inflammation of internal organs.

http://www.dailymail.co.uk/

Bio-HDPE / CNF as Mineral Oil Barrier:
Reduction in Mineral Oil Migration vs Uncoated film

n-decane (C10, linear aliphatic)	**98%**
isobutylbenzene (C10, aromatic)	**98%**
1-cyclohexylbutane (C10, cyclic aliphatic)	**98%**
1-cyclohexylheptane (C13, cyclic aliphatic)	**97%**
1-cyclohexyldecane (C16, cyclic aliphatic)	**83%**

In addition,
99% reduction in oxygen transmission

Disclaimer: The commercial product used herein not related to the invention

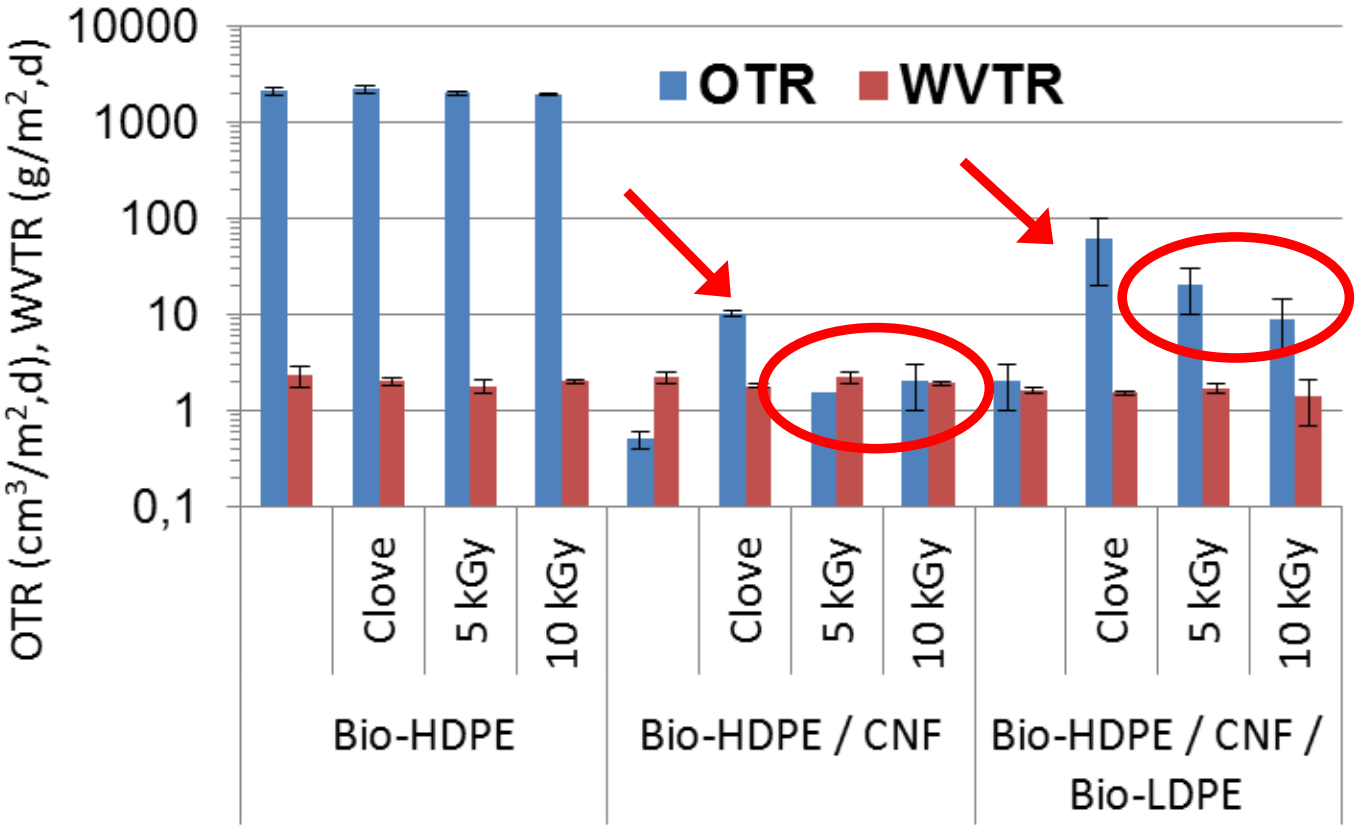
Effect of Foodstuff and Processing on CNF

Direct exposure to freshly ground clove for 3-4 weeks followed by barrier testing.

Method:
A. Mikkelson, et al.,
TAPPI 12th European PLACE Conference

Exposure to gamma irradiation (5 and 10 kilogray) followed by barrier and FTIR analyses.

Impact of Clove and Irradiation Treatment on CNF



OTR 23 °C, 0% RH; WVTR 23 °C, 75% RH

M. Vähä-Nissi, et al., TAPPI 2017 European PLACE Conference

MAP Packaging of Ground Hazelnuts

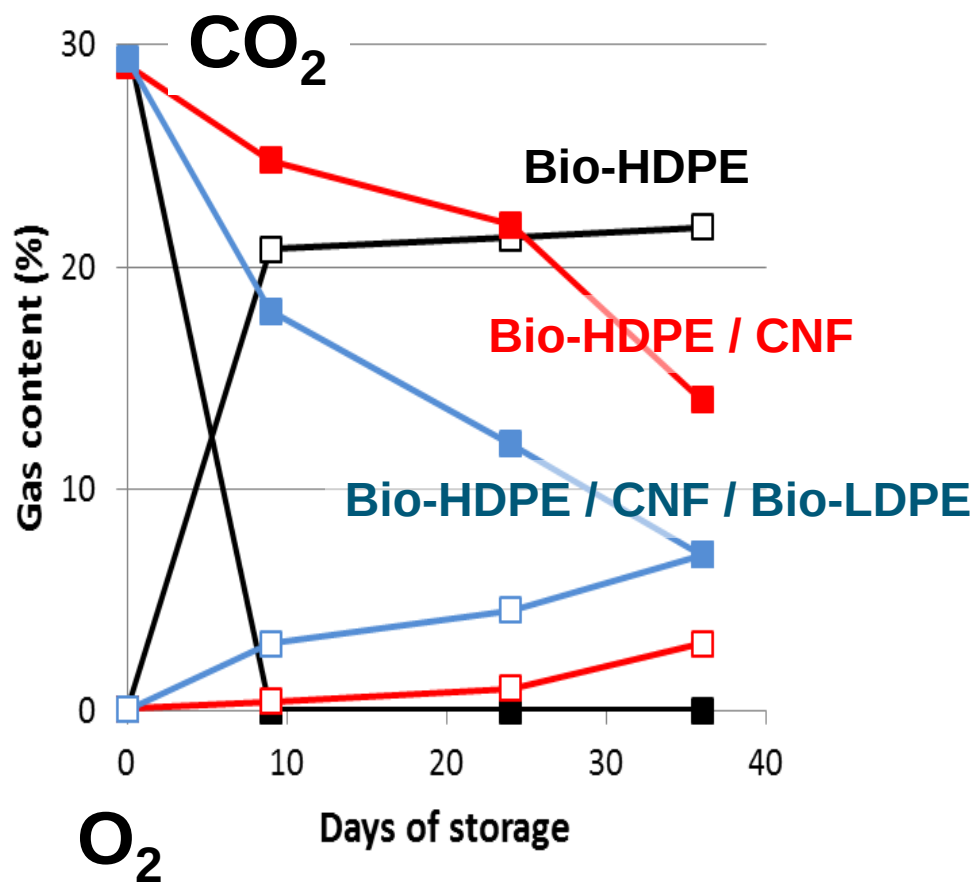
- Hazelnuts contain high amount of unsaturated fatty acids sensitive to oxidation,
- Vacuum, flushing with 70% N_2 and 30% CO_2, and heat sealing
- Storage in dark & under artificial light
- Test parameters:
  - Package shape,
  - Head space gas composition,
  - Product composition.

A3000 Multivac

MAP Pouches Filled with 50 g of Hazelnuts

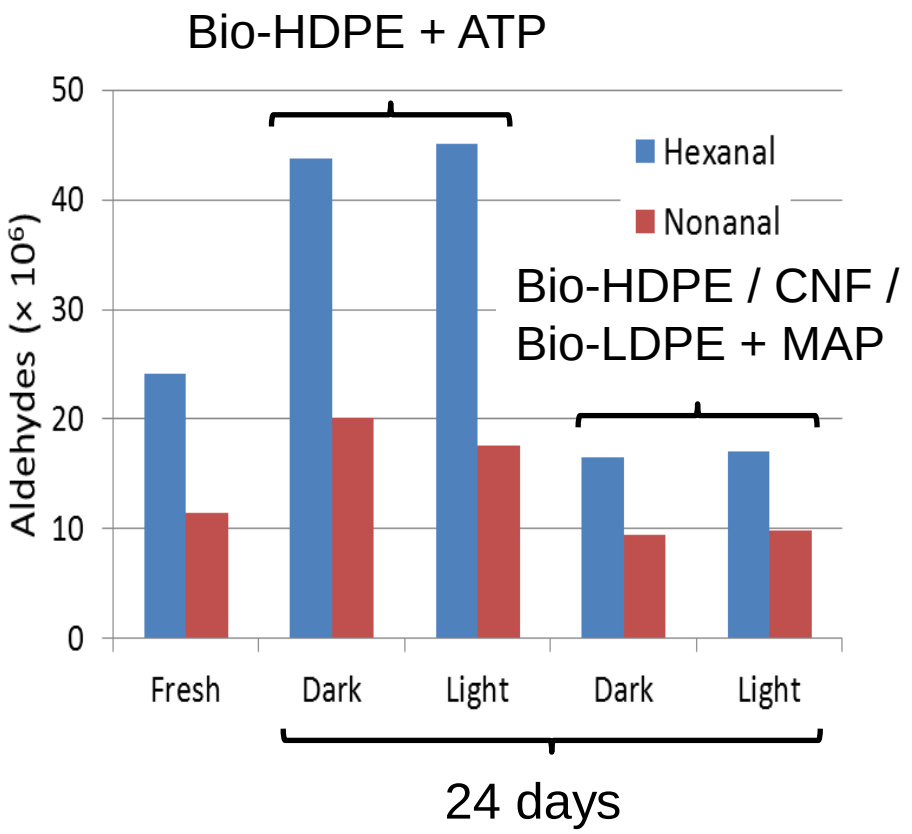
Pouches with CNF Retain Shape after 36 Days

- Results correlate with O_2 barrier,
- Difference between films with CNF and plain HDPE obvious;
  - **HDPE film:** Headspace atmospheric within first 12 days and lost shape during storage,
  - **Pouches with CNF** retained their shape and modified atmosphere,
  - Impaired gas barrier of 3-layer film affects results between CNF containing films.



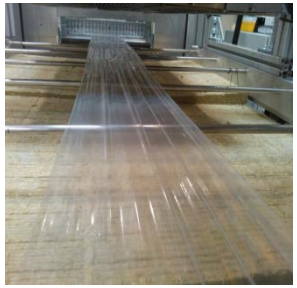
CNF Containing Films Retain Product Quality

- Extraction and GC analyses,
- Hexanal and nonanal used to indicate oxidation of oils,
- Peak areas for hazelnuts from HDPE pouch with ATP double compared to fresh hazelnuts,
- With CNF containing film and MAP peak areas stay similar or decrease slightly,
- Within storage of 24 days, no significant effect of light on oxidation observed.



Recycling Tests

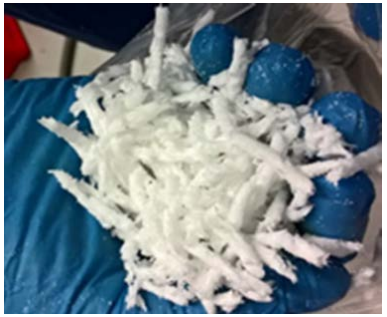
Multilayer film



80 µm LDPE
1-5 µm CNF
(+ plasticizer)

Shredding (liquid N_2)

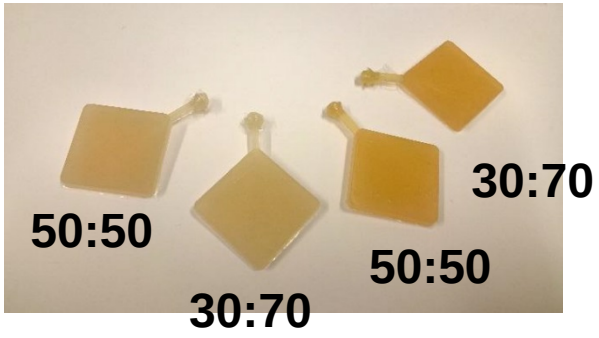
Compacting (pelletizer) & **compounding**



Virgin PE
and PE-MAH

Cast film

Injection moulding



PE + PE-MAH : Multilayer film

No Significant Changes in Key Characteristics

Barrier (**cast film**)

	WVTR*	WVTR**
LDPE Ref.	0.8	2.3
Ground CNF	0.9	2
Ground CNF + plasticizer	0.8	1.9
HefCel	1	2.2
HefCel + plasticizer	1	2.2

PE + PE-MAH : Multilayer film **30:70**

* g(100µm)/m^2/d, 23˚C, 50% RH

** g(100µm)/m^2/d, 38˚C, 90% RH

Mechanical properties (**injection mouldings**)

	At break	
	Stress (MPa)	Strain (%)
LDPE Ref.	13.7	111
Ground CNF	13.7	143
Ground CNF + plasticizer	12.4	155
HefCel	12.9	134
HefCel + plasticizer	13.4	155

PE + PE-MAH : Multilayer film **30:70**

Same thermal history; testing 2 mm/min

Conclusions

- Fully bio-based multilayer packaging films utilizing nanofibrillated cellulose (CNF) coatings were prepared successfully for MAP and bag-in-box packages, and for stand-up pouches,
- These multilayer materials demonstrated promising barrier properties, for example, for demanding dry food products,
- However, aggressive compounds and gamma irradiation impaired the oxygen barrier of the thin CNF coatings, while the water vapor barrier of the multilayer materials was not affected,
- Multilayer film pouches filled with ground hazelnuts were able to retain product quality and modified atmosphere/shape for the storage time used in this study,
- CNF coated films can be recycled back into films without sacrificing the characteristic properties of the base polymer (such as PE).

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For clove and hazelnut samples

Pietro Ragni

https://www.youtube.com/watch?v=c4iIbhibeLg


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