Multilayer Barrier Paperboard Based on Nanocellulose and Biodegradable Thermoplastics

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What is barrier packaging made of?

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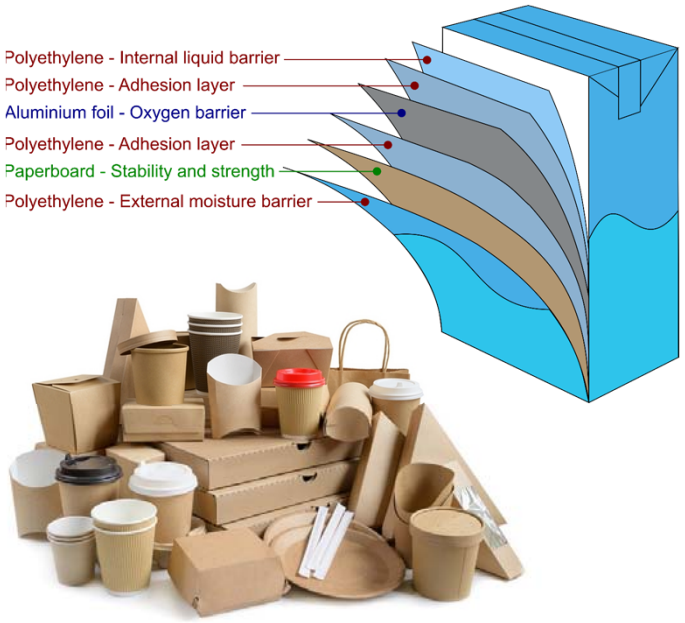
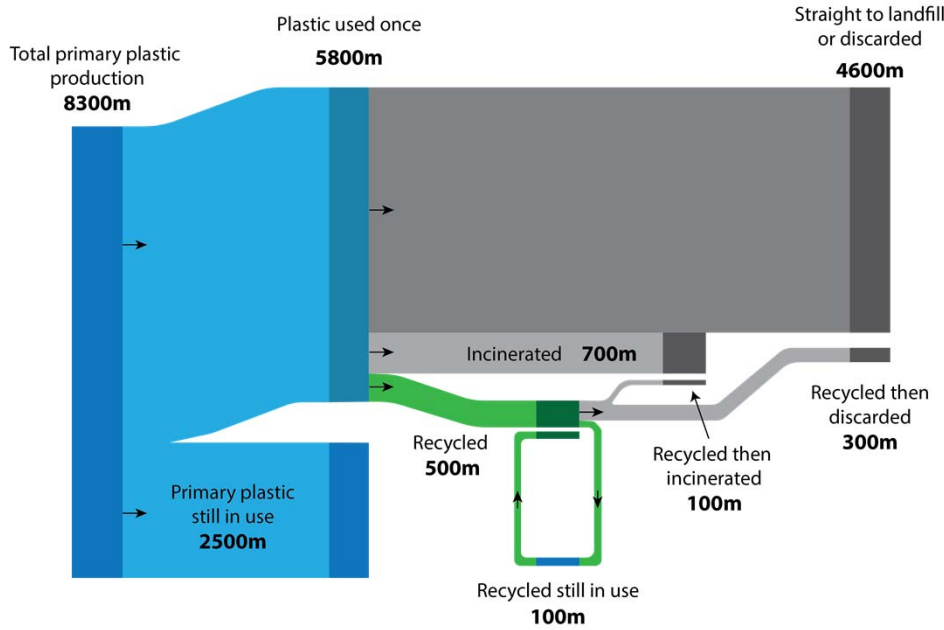
Most often contain multiple functional layers



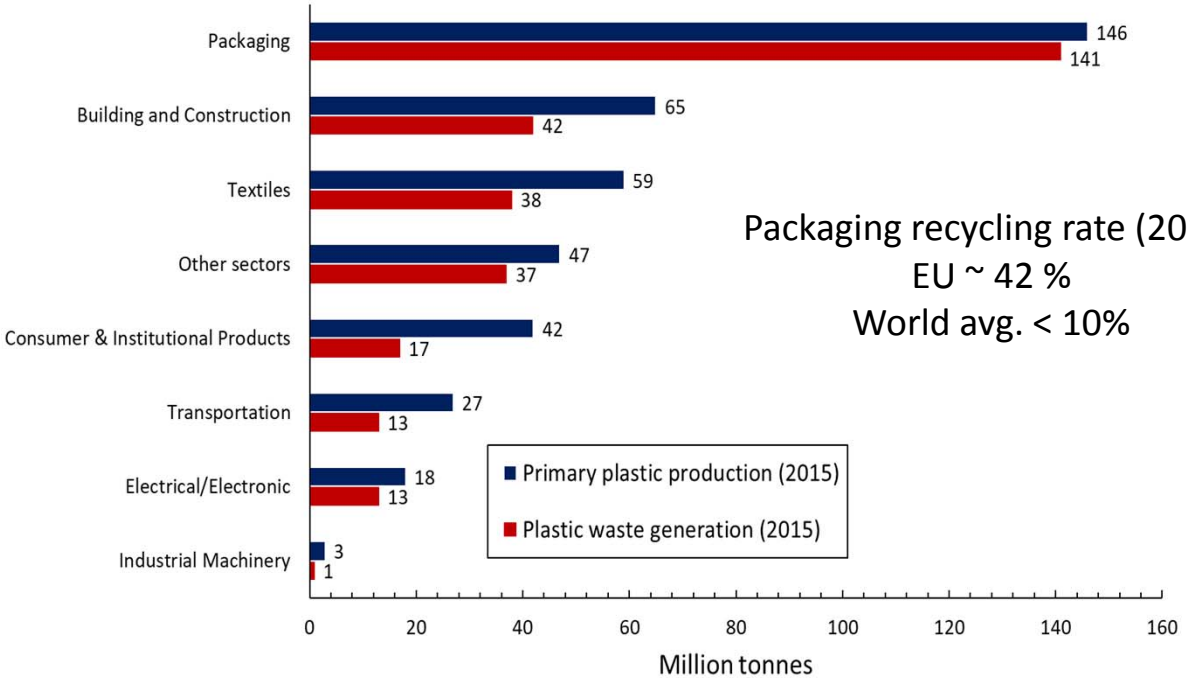
Global plastic production (in million tonnes) and its fate (1950 – 2015)



Approx. 40% of total plastics produced are used for packaging!

Geyer R. et al., Science Advances, 3(7), (2017)

Current fate of packaging...



Packaging recycling rate (2017)
EU ~ 42 %
World avg. < 10%

Municipal solid waste is predicted to reach to about 2.2 billion tons by 2025

Urgent need to replace fossil-fuel based plastics with bio-based and biodegradable alternatives!

Kawai K. & Tasaki T., J Mater Cycles Waste Manag, 1-13, (2016)
Geyer R. et al., Science Advances, 3(7), (2017)

Objectives

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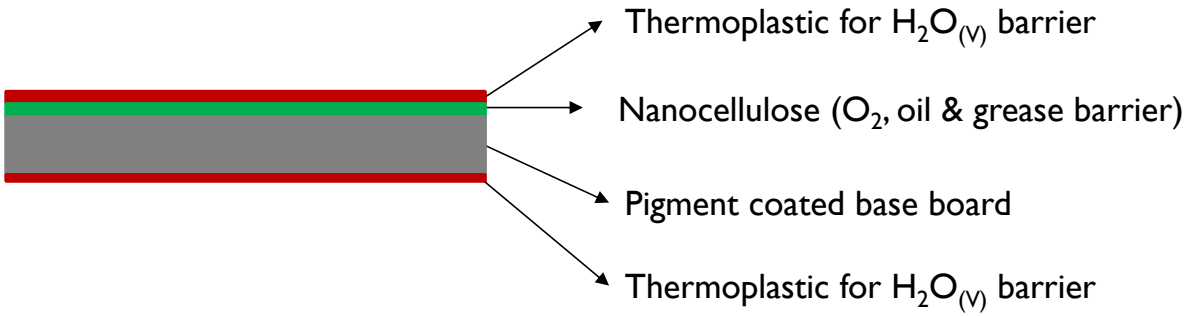
- Demonstrate a biodegradable multilayer packaging paperboard with barrier properties comparable to existing state of the art



- Produce such multilayer paperboard utilizing continuous roll-to-roll (R2R) processes viz. slot-die and extrusion coating

- Influence of nanocellulose type/extrusion polymer/pigment additives/plasticizers on barrier properties

Nanocellulose – A promising biomaterial

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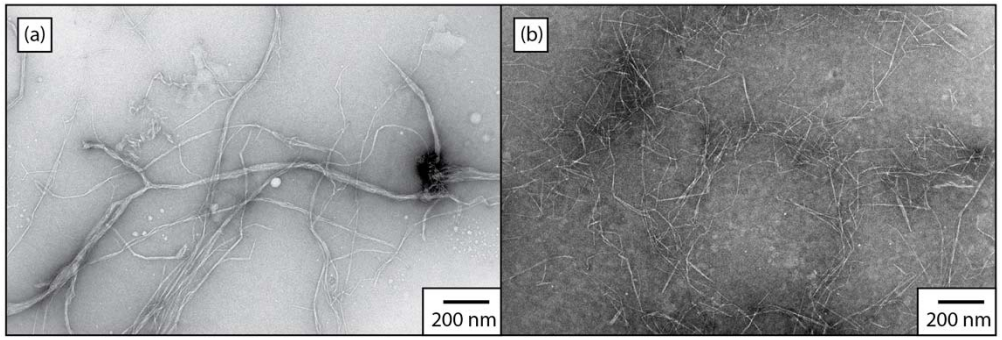
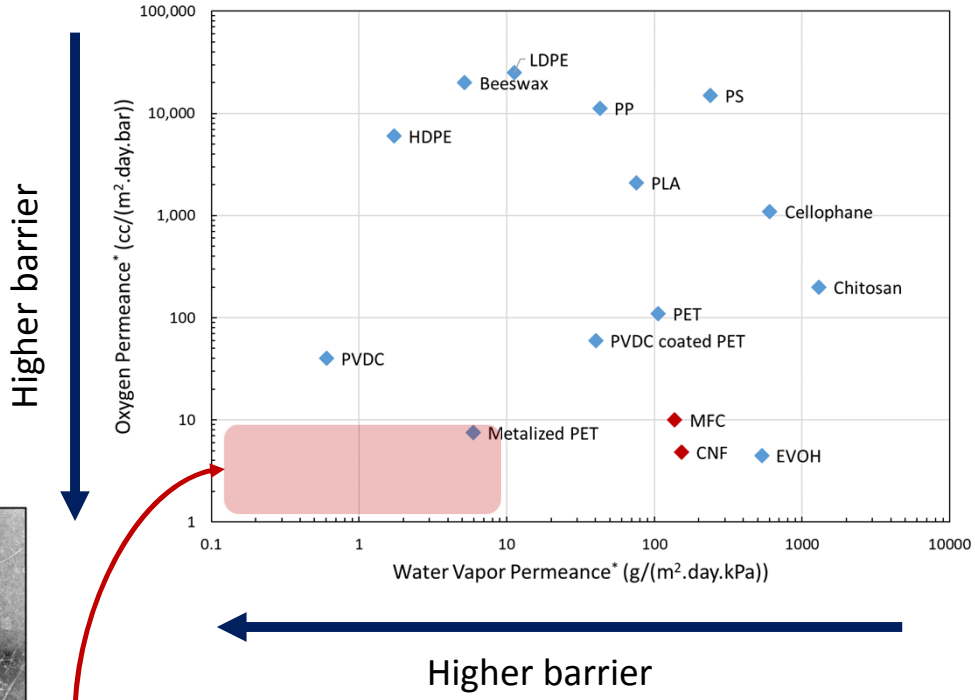
(a) Microfibrillated Cellulose (MFC) from University of Maine, USA
- Diameter: 20 – 60 nm
- Length: few microns
- Referred to as 'M' from hereon

(b) Carboxymethylated Cellulose Nanofibrils (CNF) from RISE, Sweden
- Diameter: 5 – 15 nm;
- Length: < 1 µm;
- Referred to as 'N' from hereon





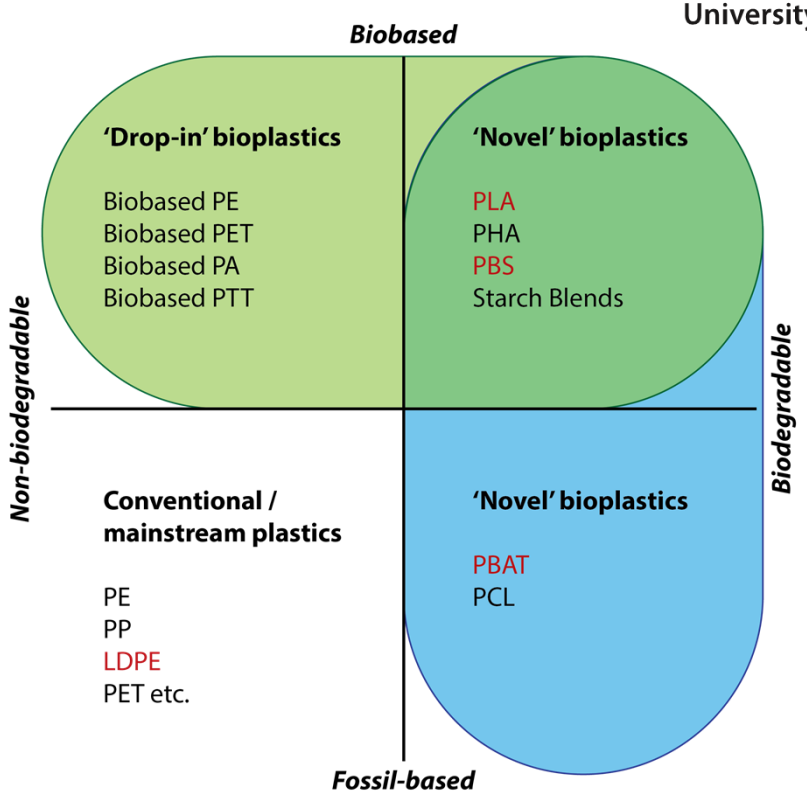
Can we get there with a multilayer structure?

*All values for 10 µm films at 23 °C / 50 % RH

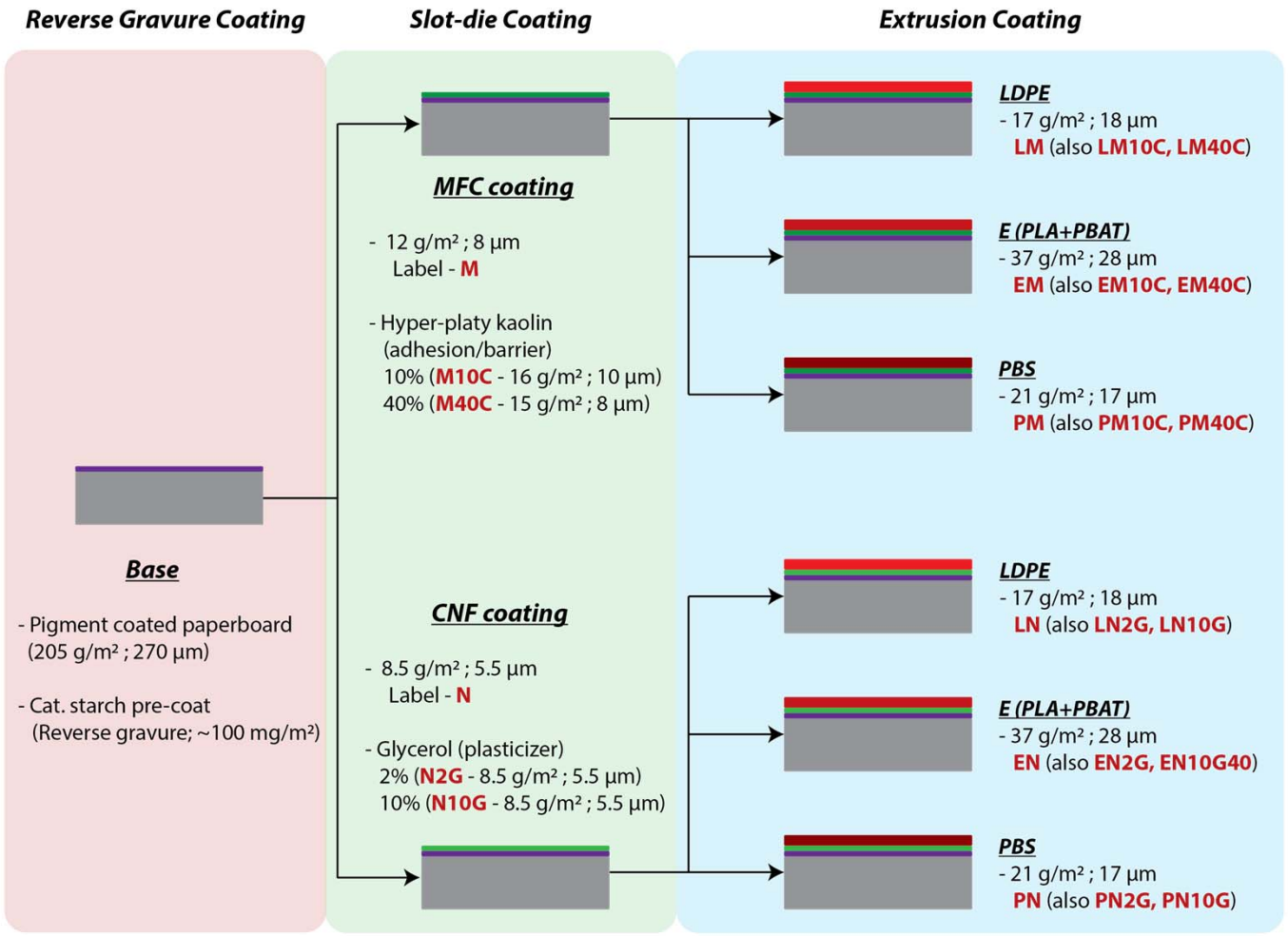
Lindström T. & Österberg G., Nord Pulp Paper Res J, 34-4, (2020) | An D.S. et al., J Food Process Eng., 41, (2018)

Biodegradable thermoplastics

- Over 90% of the total mass of plastics produced are thermoplastics
- Processed via injection moulding, blow moulding, thermoforming, and hot-melt extrusion
- Barrier against water vapor
- **LDPE (as ref), Ecovio (PLA + PBAT), and PBS are used in this work.** Referred to as L, E and P respectively from hereon



'Policies for bioplastics in the context of bioeconomy', OECD Science, Technology and Industry Policy Papers, (10), (2013)



Both MFC & CNF have 5 % CMC (Finnfix 4000G, CP Kelco) added on dry nanocellulose as rheology modifier

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Sample setup

- All coatings were done as roll-to-roll processes
- A few LDPE samples were also back-side coated with LDPE to protect MFC from backside moisture penetration

Sample name: LML (LDPE/MFC/LDPE)

Coating processes

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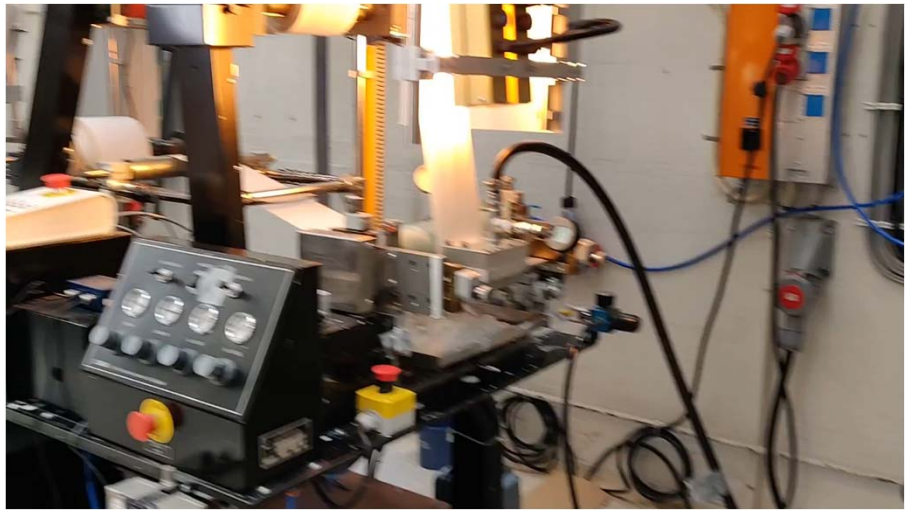
Mini-pilot scale slot-die coater at Åbo Akademi University

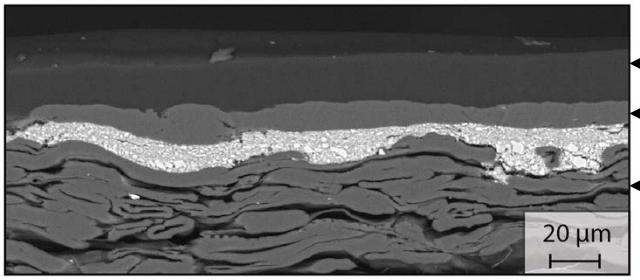


- 300 mm max. web width, 50 m/min max. line speed
- Custom fitting of slot-die (100 mm wide)
- Nanocellulose coating – 100 mm wide & ~ 5 m/min line speed

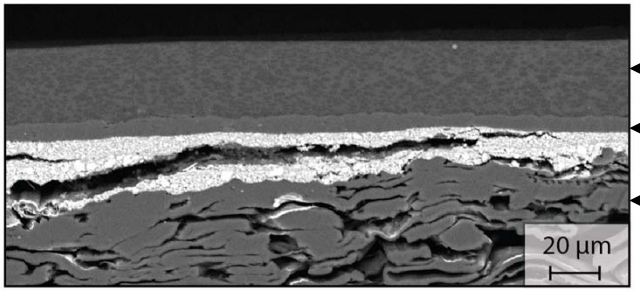
Pilot scale extrusion coater at Tampere University

- 550 mm max. web width, 400 m/min max. line speed
- (co)Extrusion coating & lamination
- Corona pre-treatment and 70 m/min line speed (for current work)

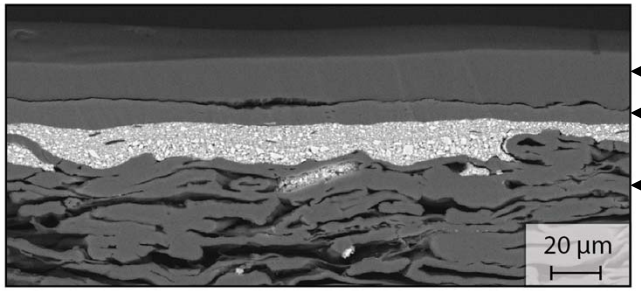
SEM cross-sections



LDPE
MFC
Baseboard



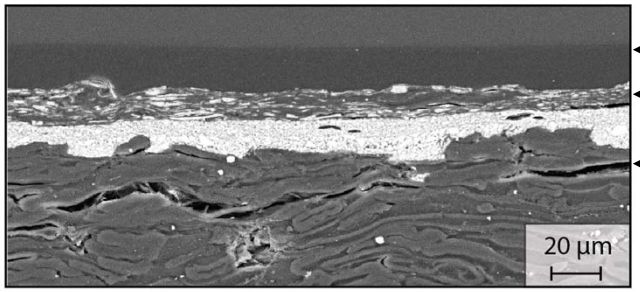
E (PLA+PBAT)
MFC
Baseboard



PBS
MFC
Baseboard

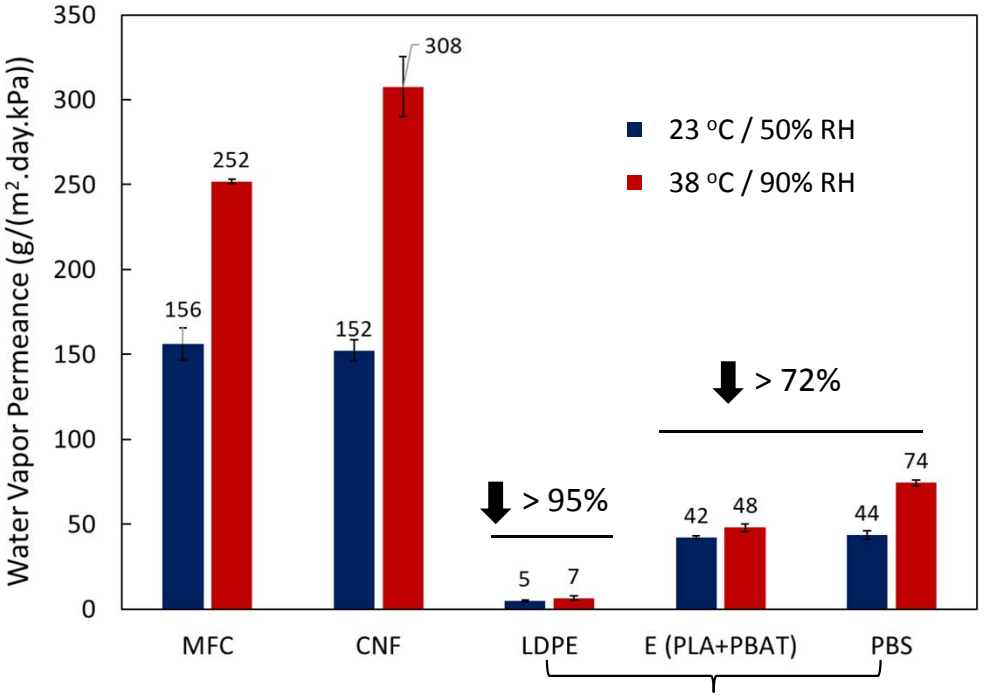
- PBS does not have sufficient adhesion with nanocellulose
- Blending kaolin into MFC improves adhesion with PBS
- Plasma treatment/ultra-thin pigment coating on nanocellulose might also improve adhesion with thermoplastics

PM40C – Improved adhesion at PBS/MFC interface



PBS
MFC + 40% kaolin
Baseboard

Water vapor barrier



Similar values for multilayer samples

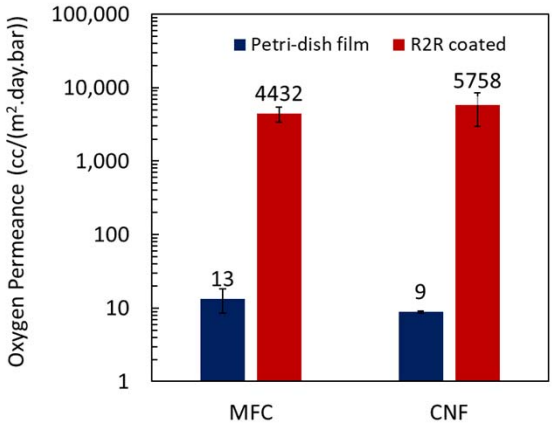
- Water vapor permeance (WVP) measured at two conditions:
  - 23 °C / 50 % RH & 38 °C / 90% RH
- Extrusion coated top layer influences the water vapor barrier for multilayer coated samples
- Over 95% reduction in WVP with LDPE as top layer
- Over 72% reduction in WVP with E (PLA+PBAT)/PBS top layers
- Kaolin and glycerol addition does not influence WVP

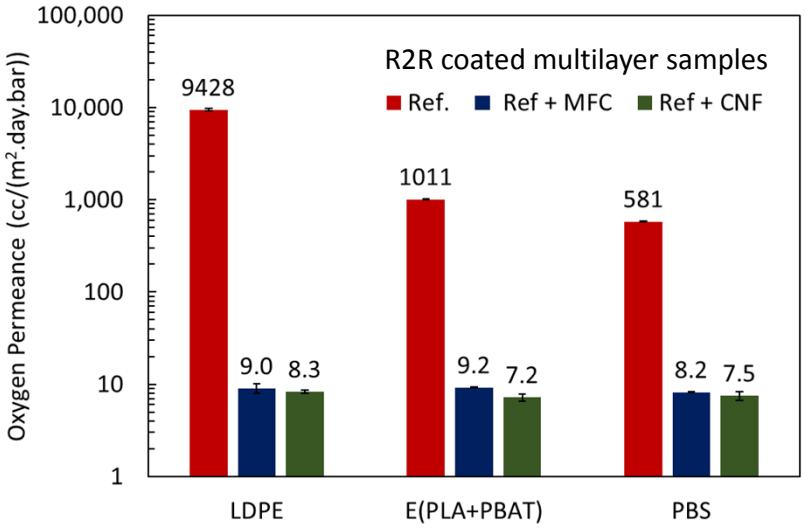
WVP measured according to ASTM E96/96M-10; Desiccant method

Oxygen barrier

(Influence of extrusion coating)

- Oxygen <u>permeance</u> (OP) measured at 23 °C / 50 % RH
- Extreme drying conditions in a R2R process leads to cracks/defects in nanocellulose coated layer → very high OP compared to pure films
- During extrusion coating, molten polymer fills in cracks/ defects in nanocellulose layer → OP values similar to pure nanocellulose films
- R2R produced multilayer paperboard shows similar values to that of pure nanocellulose films!





OP measured according to ASTM D3985-05 (coulometric sensor)/F3136-15 (dynamic accumulation)

Oxygen barrier

(Influence of kaolin/glycerol additives)

Test conditions: 23 °C / 50% RH
All measurements for multilayer coatings

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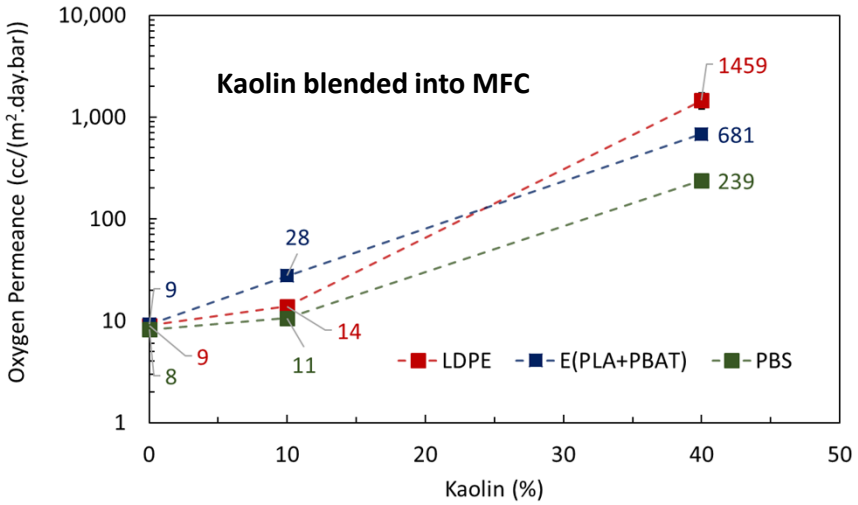

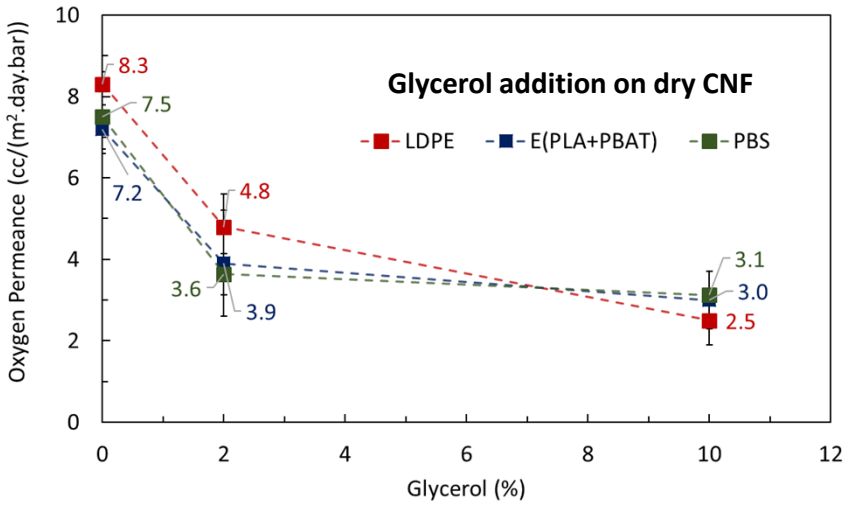

- 10% kaolin blend has similar OP as pure MFC coating
- A small % of pigment can be blended into nanocellulose to aid adhesion without compromising Oxygen barrier

- Glycerol addition → flexible & uniform nanocellulose layer → improved Oxygen barrier → comparable to OP for pure films at 0% RH!

OP measured according to ASTM D3985-05 (coulometric sensor)/F3136-15 (dynamic accumulation)

Oxygen barrier

(Influence of relative humidity/double-sided extrusion coating)

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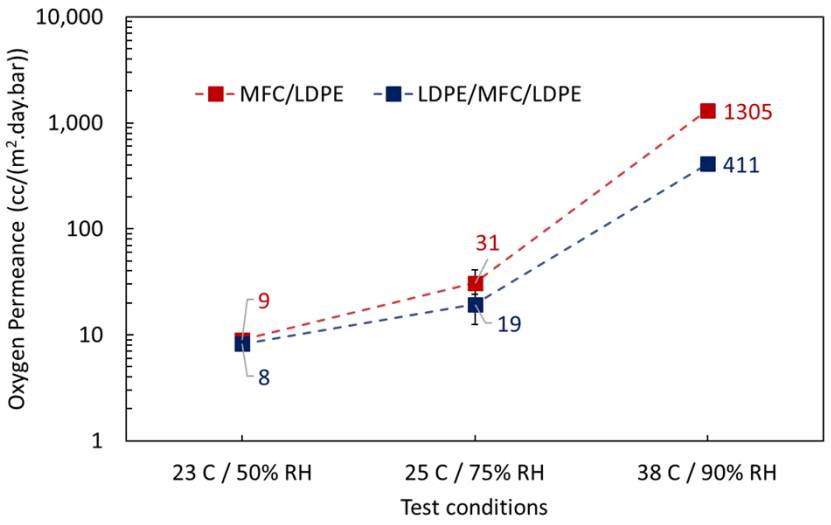
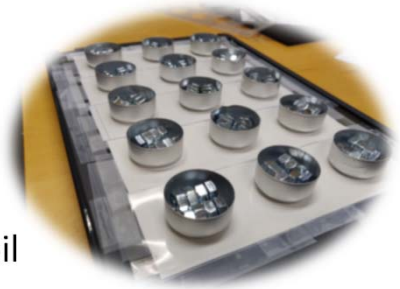


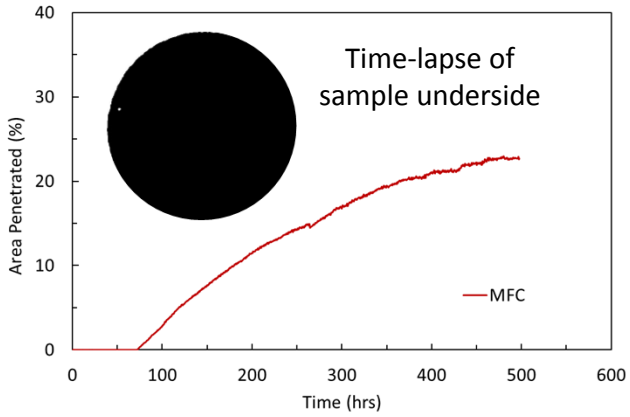
- Oxygen barrier gets worse at higher temperatures and relative humidities
- Backside extrusion coating LDPE protects nanocellulose to an extent → Yet, falls short of required OP value for certain applications
- Water vapor might be seeping in through along the cross-section
- Sealing the cross-section/sandwiching nanocellulose in-between water vapor impermeable layer might help

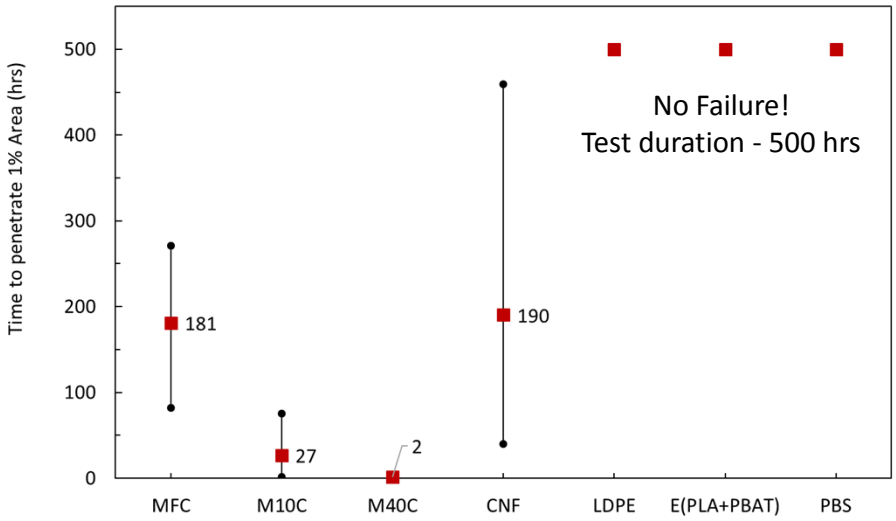
OP measured according to ASTM D3985-05 (coulometric sensor)/F3136-15 (dynamic accumulation)

Grease barrier



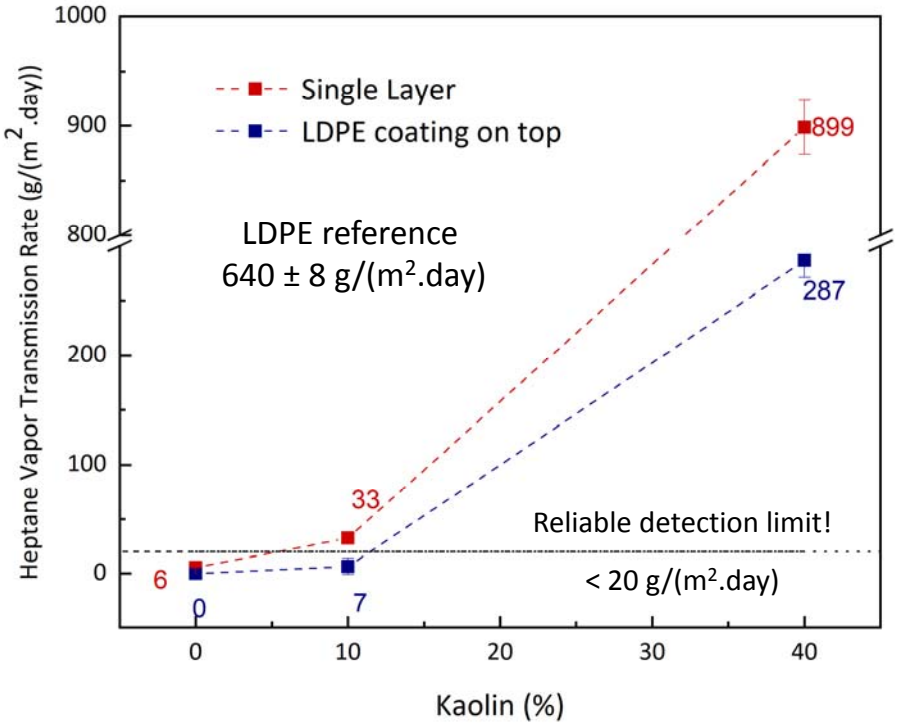
- The samples were placed on top of a scanner with coated side facing up; olive oil & 50 g weights placed on the coated side
- Underside of the samples scanned at regular intervals. Test temperature: 40 °C
- Time for oil to penetrate 1% of the area is reported
- Sensitive to coating defects
- Kaolin negatively effects grease barrier; No influence of glycerol
- No failure for extrusion coated samples even after 500 hrs.





Grease barrier measured according to ASTM F119-82

Mineral oil barrier



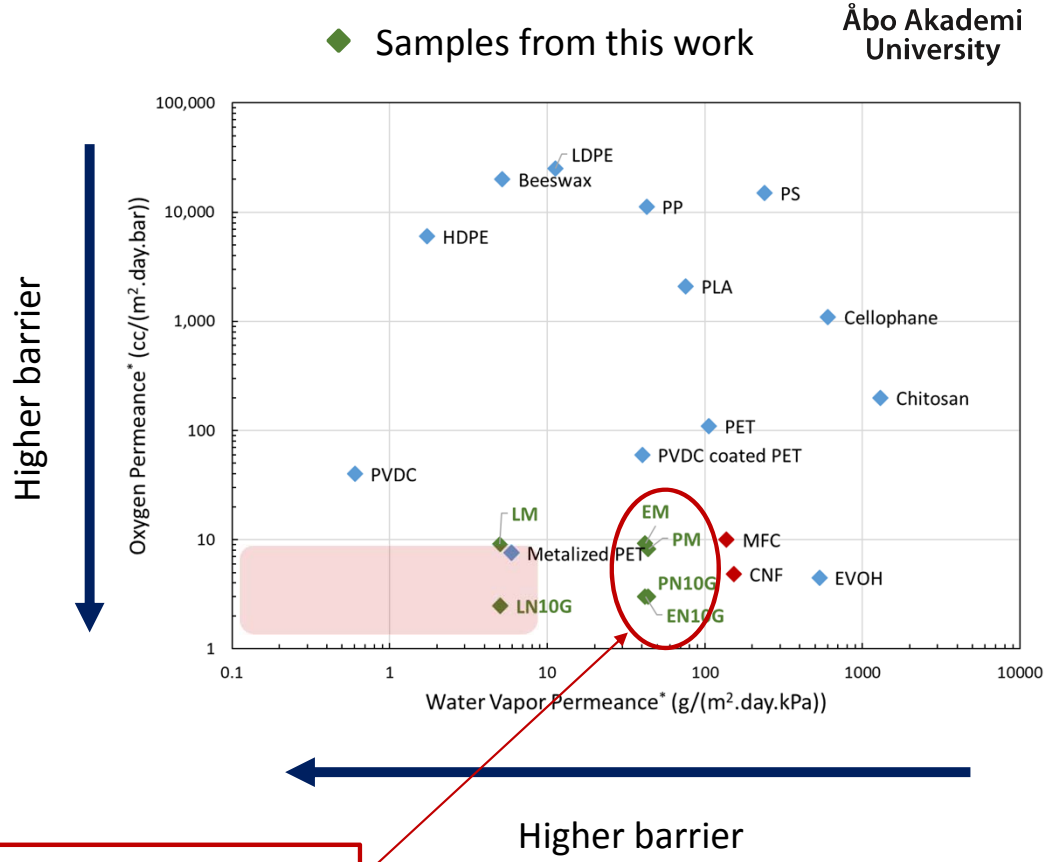
Kaolin blended into MFC

- Heptane vapor transmission rate (HVTR)
  Test conditions: 23 °C / 50% RH
- MFC, CNF, E (PLA+PBAT) and PBS have 'zero' HVTR i.e no n-heptane vapors escaped during 48 hour test interval
- Glycerol has no influence on HVTR
- LDPE top coating improves HVTR for MFC-Kaolin blends
- KIT values for all coatings is higher than 12!

HVTR measured according to Miettinen P., et al., 27th PTS Coating Symposium, 16-18, (2015)
KIT value measured according to TAPPI T559 cm-12

Summary

- Two continuous coating methods used in tandem to produce multilayer barrier paperboard:
  - ✓ Slot-die coating of Nanocellulose (MFC/CNF)
  - ✓ Extrusion coating of thermoplastics (LDPE, E (PLA+PBAT), PBS)
- Extrusion coating helps offset coating defects in nanocellulose layer → improved overall barrier performance
- A small % of pigment blended into nanocellulose helps with adhesion with thermoplastics
- Plasticizers viz. glycerol promote uniform nanocellulose coating → better barrier
- Sandwiching nanocellulose in-between water vapor impermeable layers could help with O_2 barrier at higher humidities



100% biodegradable multilayer barrier paperboard!

*All values at 23 °C / 50% RH

Thank you!

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