
# Biopolymer coatings for cellulose materials


## Dr. Johanna Lahti

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- Introduction of VTT
- Extrusion coating process
- Adhesion in extrusion coating
  - Parameters affecting adhesion
- Polymers for extrusion coating
  - Overview of conventional and biopolymers
  - Case: cellulose + biopolymer

OUR PURPOSE

**We bring together people,**
**business, science and technology,**

# TO SOLVE THE WORLD'S BIGGEST CHALLENGES,

**creating sustainable growth,**
**jobs and wellbeing.**

# VTT – *beyond the obvious*

VTT is a visionary research, development and innovation partner and one of the leading research organisations in Europe.

Our role is to promote the utilisation and commercialisation of research and technology in business and society. Through science and technology, we turn global challenges into sustainable solutions for business and society in a responsible way.

**254 M€**
**turnover and other operating income**

**2,093**
**employees**

**45%**
**of the net turnover from abroad**

**32%**
**a doctorate or a licentiate's degree**

**Establishment year**
**1942**

**Steered by Ministry of Economic Affairs and Employment**

# VTT's research projects

**1 COMMERCIAL PROJECTS**

**Impact:**

- Building competitiveness for VTT's customers through world-class research and innovation services

**2 JOINTLY FUNDED PROJECTS**

**Impact:**

- More efficient technology transfer
- Foundation for new innovations and political decision-making

**3 SELF-FINANCED PROJECTS**

**Impact:**

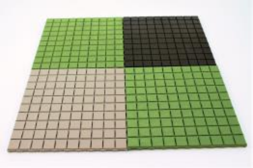
- Developing VTT's own competitiveness and acquiring knowledge and expertise to meet future customer needs

# Examples of some of our customers and co-partners

ABB
AGCO Your Agriculture Company
aivon
Asahi
Bayer HealthCare Bayer Schering Pharma
Fazer
GE Healthcare
gsk GlaxoSmithKline
Honeywell
IOGEN CORPORATION
ISOVER
Kemira
KONE
KONECRANES Lifting Businesses
L&T LASSILA & TIKANOJA
MASCOMA
metso
moventas
NESTE
NOKIA
normet FOR TOUGH JOBS
OKMETIC
ORION
OUTOKUMPU
Outotec
PAROC
Patria
PSA The World's Port of Call
RAMBØLL
Roche
ruukki
rethink. storaenso
SANDVIK
Unilever
UPM
VAISALA
Valio
VTI TECHNOLOGIES
WÄRTSILÄ

# Examples of wood-based research @VTT

**Biocomposites** to different solutions



**Lignin e.**g. glues, concrete and composites


**Wood-based textiles and non-wovens**

**WOOD**


Bark, sawdust, pitch, etc.

Fuels, chemicals

**Cellulose-based coatings and films** to e.g. packaging

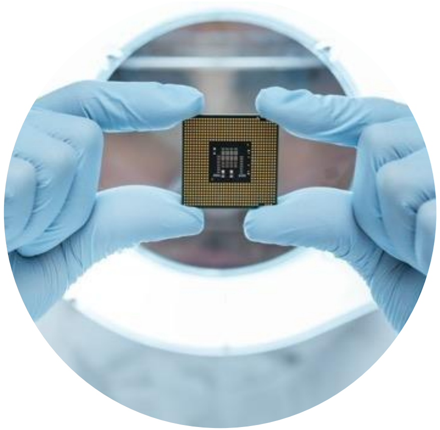
**Fibre-based solutions** to various applications incl. packaging

VTT

VTT is a visionary research, development and innovation partner and one of the leading research organisations in Europe

# We create solutions in three business areas

**Carbon neutral solutions**



**Digital technologies**

**Sustainable products and materials**

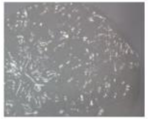
Biopolymers, films, foams, coatings and composites

# ”Tailored Piloting” - We solve your challenges together with you

- ✓ We work on application driven research and development of economically and environmentally sustainable materials and processes.
- ✓ Piloting from lab to pilot/semi-industrial scale and from the raw material production to the end-of-life of the product
- ✓ We tailor the existing processes of e.g. plastic and packaging industry to utilize for example natural fibres, renewable thermoplastic materials, side streams and recycled materials as raw materials aiming to create novel solutions and high impact products for carbon neutral and circular future.

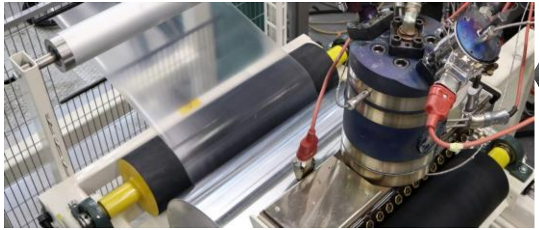
Fibrillated cellulose

ThermoCell technology



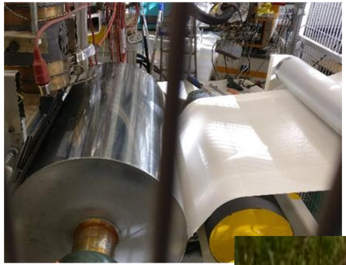
Dissolving/ Regenerating

Films/coatings from cellulose



# Biopolymer and composite solutions -team: Main research areas

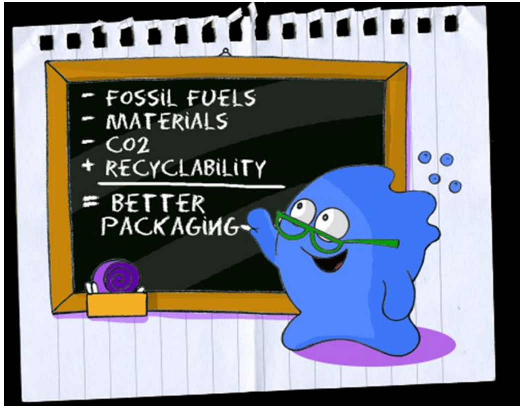
- ❑Thermoplastic film extrusion and coating
- ❑Biocomposites and biopolymers
- ❑Lightweight and foamed solutions



# Packaging (materials) for future

- **Packaging materials are usually multilayer structures**
  - “Less is more” – optimisation of materials (both material selection and amount)
  - Lighter packages save energy and environment

- **Circular and bioeconomy**
  - Materials that are easier to recycle or re-use (“circular by design”)
  - Renewable alternatives for fossil-based materials




- **Legislation (national and EU level)**
  - SUP and PPWR directives, recycling/waste management requirements, etc.

# Processing of polymers

- (co)Extrusion coating
- Film manufacturing
  - Cast film
  - Blown film
- Lamination
- Dispersion coating (WBBC)
- Moulding techniques
- Other converting and coating methods

➢ Single or multilayer materials

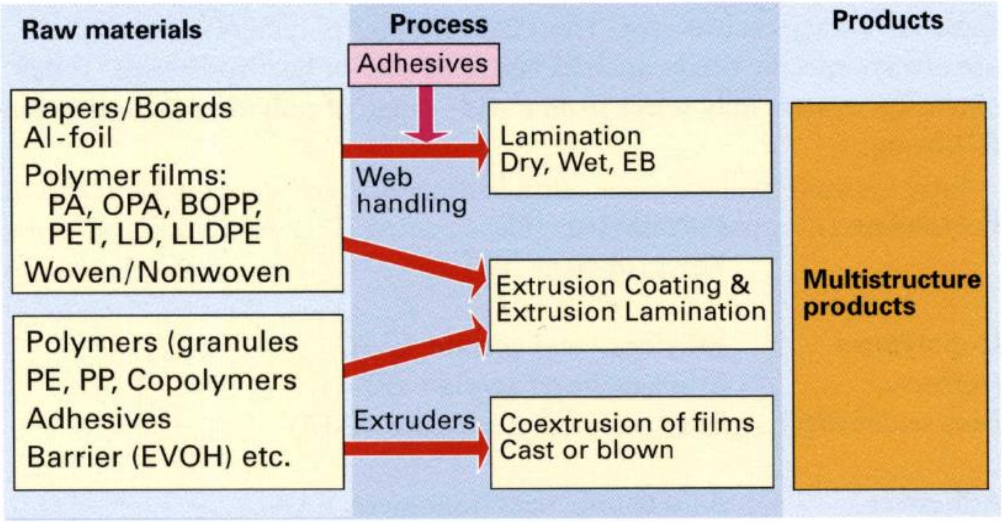
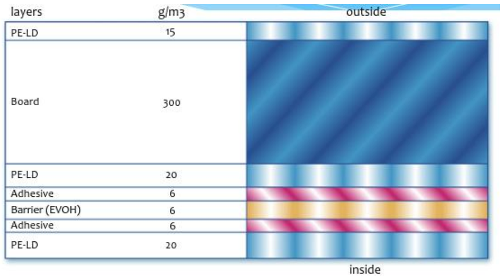
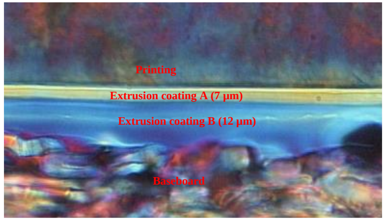


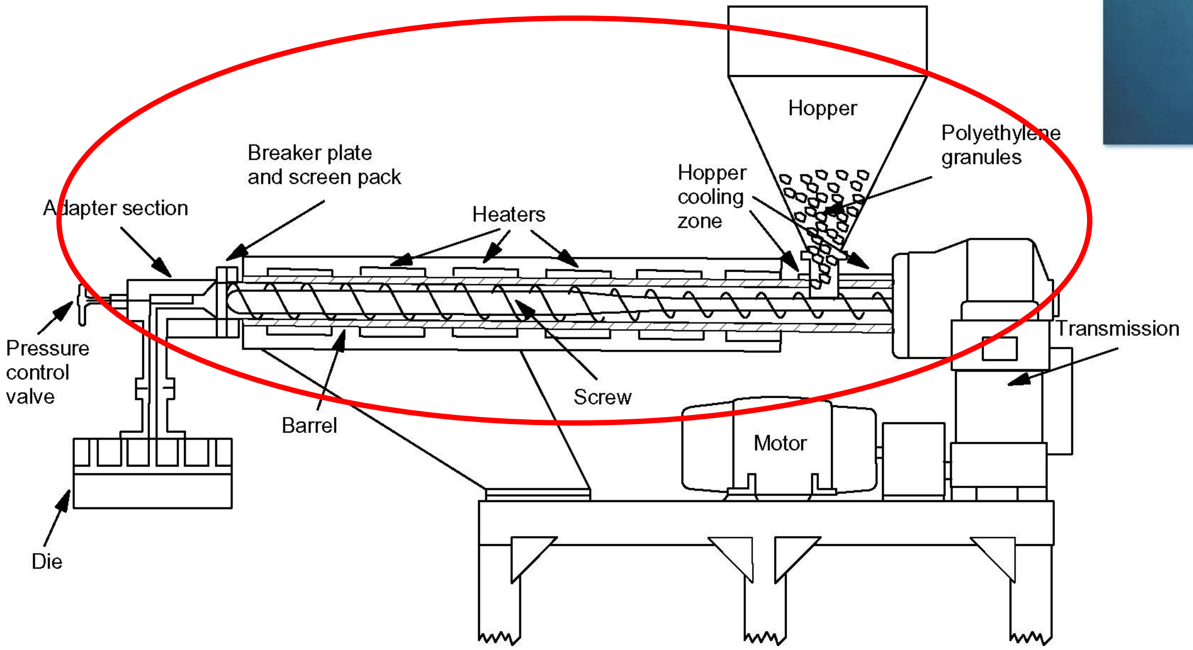

Figure 3. Multistructure product flow



# Extrusion coating

# Extrusion

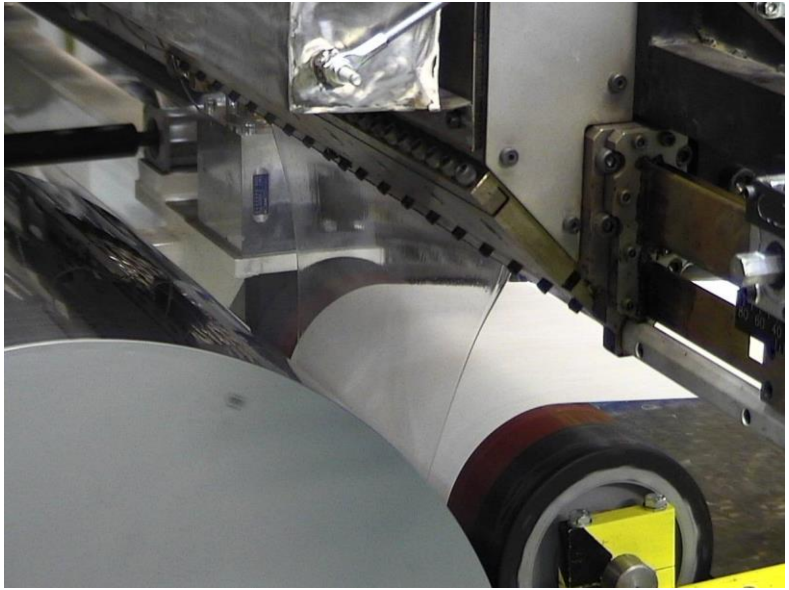


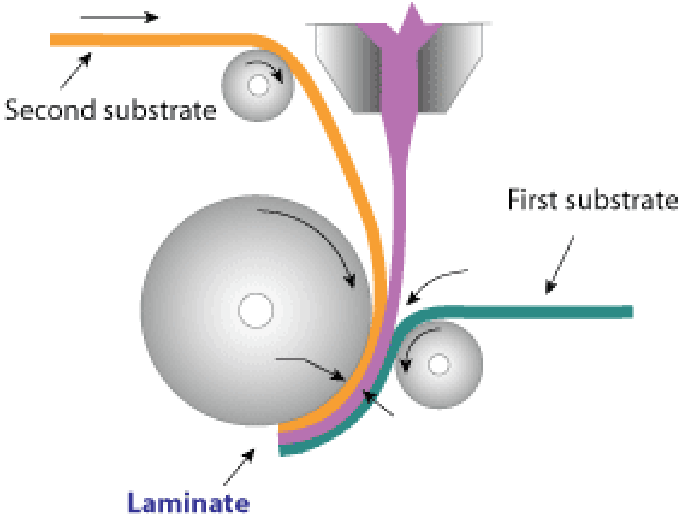

Many processes are based on extrusion:

- Extrusion coating
- Extrusion lamination
- Cast film manufacturing
- Blown film manufacturing
- Injection moulding
- Blow moulding
- Melt spinning
- Extrusion foaming

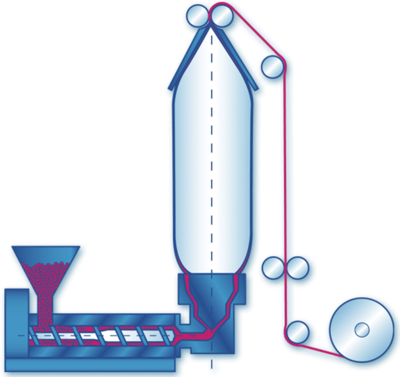
# Extrusion coating (and lamination)

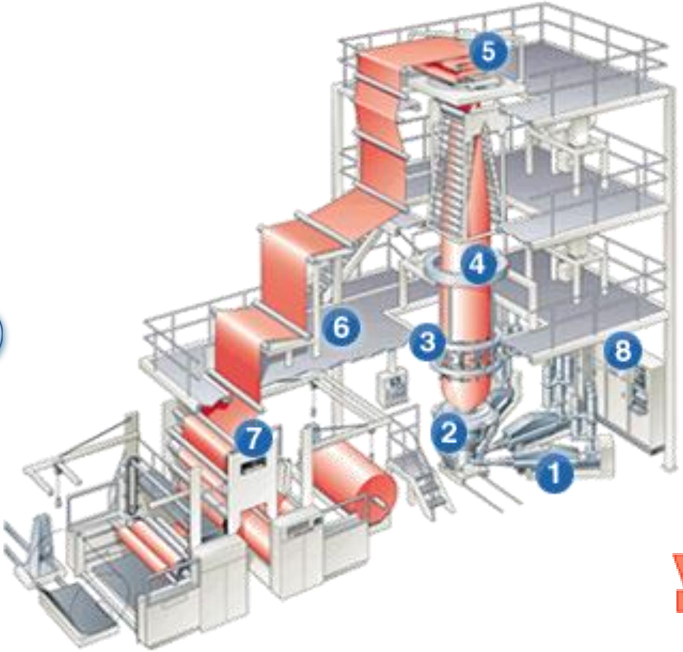
*Coating situation where molten thermoplastic film is combined with web substrate*

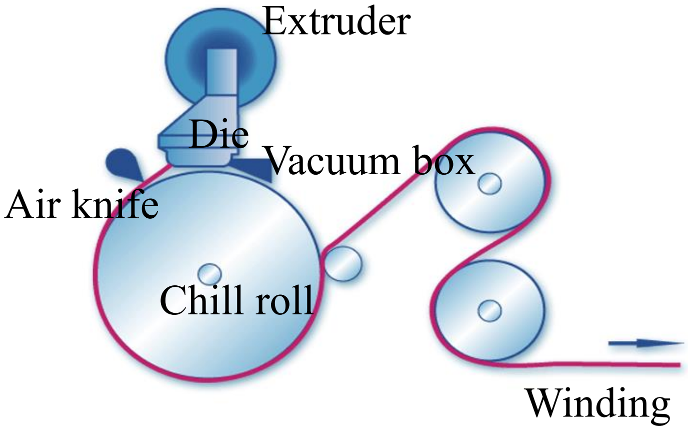


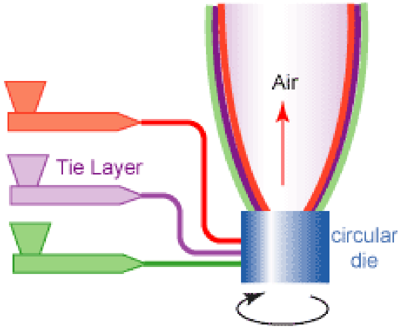


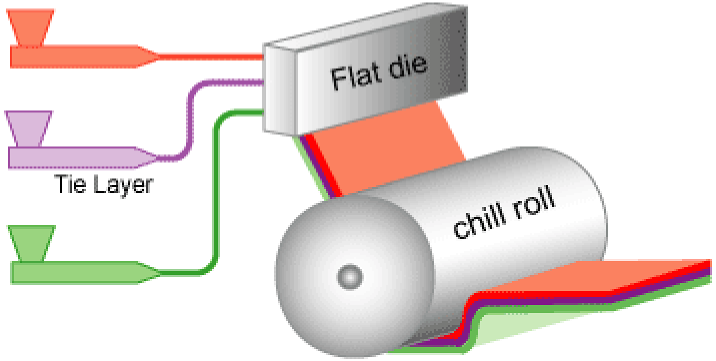
# Film manufacturing – cast and blown film





# Extrusion coating

- Extruding a high molecular weight, high melt temperature **polymer in film form onto a rapidly moving web**
- **Web (substrate)** can be, e.g. paper, paperboard, foil, plastic film
- **Co-extrusion technology provides a multilayer extrusion coated product for more demanding applications,** particularly food packaging applications, e.g. liquid packaging board (milk, juice, soup) and flexible packages
- In co-extrusion there are usually 2-4 extruders, and the polymer melts coming from different extruders are combined to the desired order before the die



# Examples of extrusion coated/laminated (multilayer) products

**Liquid packaging:** milk and juice gable top cartons, aseptic rectangular shaped drink boxes

**Flexible packaging:** snack foods, condiment packs, food, dry goods, medical packages, toothpaste type collapsible tubes, liquids, "bag-in-box"

**Paperboard packaging:** bakery boxes, microwaveable trays, frozen food boxes, detergent boxes, animal food boxes

**Industrial wraps:** drum liners, ream wrappers, composite cans, soap wrappers

**Insulation Backing**
- Foil
- LDPE
- SCRIM
- Kraft Paper

**Tarpaulins**
- LDPE
- Woven Tape Fabric
- LDPE

**Paper Snacks**
- Paper
- LDPE
- SCRIM
- Paper

SCRIM

**Gable Top Carton**
- Printing
- LDPE
- Paperboard
- LDPE

**Drink Box**
- LDPE
- Printing
- Paperboard
- LDPE
- Foil
- Coextrusion

**Snack Food Bags**
- Polypropylene Film
- Printing
- LDPE
- Metalized Film
- LDPE

**Toothpaste Tubes**
- Film
- Printing
- Coextrusion
- Foil
- Coextrusion
- Film

**Detergent Boxes**
- Film
- Printing
- LDPE
- Paperboard
- LDPE

**Ream Wrapper**
- Paper
- LDPE
- Paper

**Photo Paper**
- LDPE
- Paper
- Printing
- LDPE

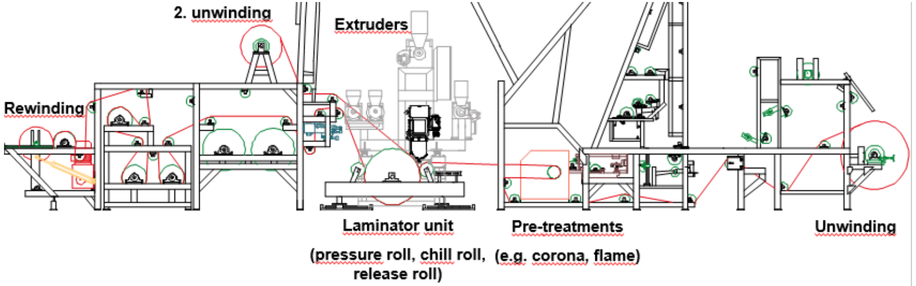
# Extrusion coating

Advantages of extrusion coating:

- tightness (barrier-properties)
  → water vapour, water, grease, aroma, gas, light
- heat sealability (i.e. closing of the package)
- suitable friction properties for converting operations
- toughness, resistance to abrasion

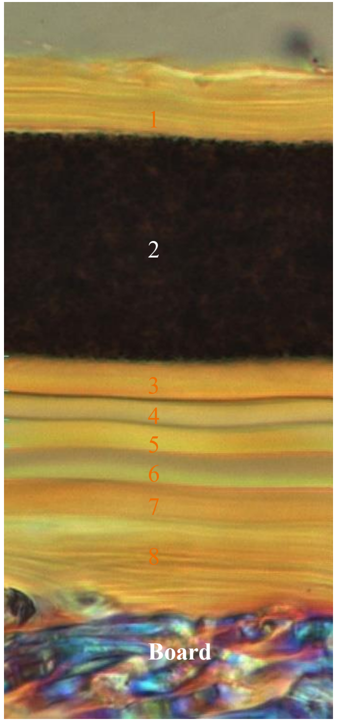
Main demands of extrusion coating:

- very high processing temperatures (can be around 300°C)
- suitable viscosity of a polymer (rhelogical properties of the polymer are very important)



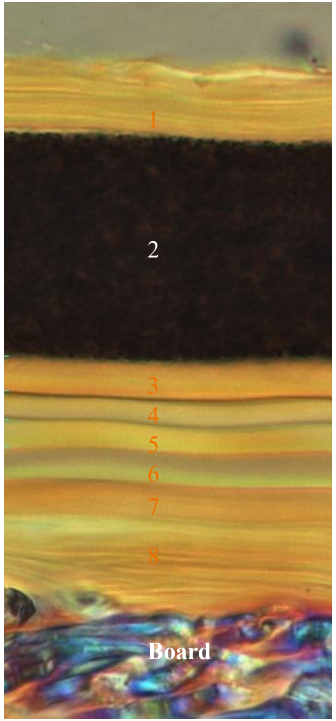
# Properties of (co)extrusion coated material

- (Co)Extrusion is used to improve the properties of a substrate, for example barrier properties of paper/board
- Material selection affects the properties of the structure
  - Adhesion
  - Friction properties
  - Uniform coating profile (both in the whole coating and single layers)
  - Barrier properties
    - Water vapour
    - Oxygen
    - Light
    - Grease
    - Aroma
  - Heat sealability
  - Printability etc.
- Co-extrusion allows thin layers and minimizes the amount of expensive special polymers
- There are less pinholes in co-extrusion coated material because of multilayer structure (vs. one layer coating)



# Advantages of co-extrusion

- **Adhesion enhancement** can occur by selection of the proper polymer bonding to the substrate or by using higher temperatures
- **Thin layers**: minimization of expensive polymer use with thinner layers of cheaper polymers as support layers around the main polymer
- **Less pinholes** in the coating enhances the barrier properties: running only one polymer with co-extrusion into a two-layer structure improves the pinhole resistance compared to a one-layer coating
- **Better heat sealability**: extruding the surface layer at a lower temperature reduces the oxidation of the polymer. Selection of the heat-sealable skin polymer can provide good heat sealing properties by using, for example, an ionomer
- **Layers containing additives and pigments**: only the surface layer needs to contain any additives to reduce cost and protect the die metal. Two dissimilar colors are also possible.
- Less manufacturing processes: machine time savings
- Polymers that are difficult to process can be run supported by other polymers
- Increase in capacity
- Combine polymers having special barrier properties as thin layers as are necessary
- Non-slip surfaces or ultra low heat seal temperatures by the selection of the skin-polymer.



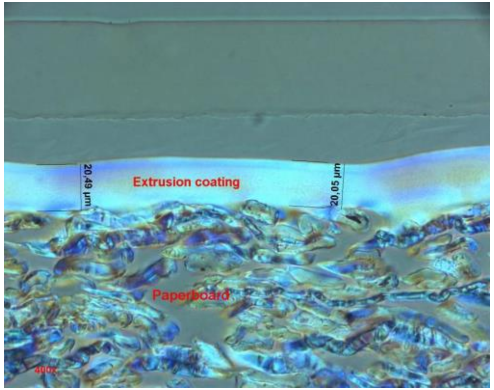
# Coat weights in extrusion and co-extrusion

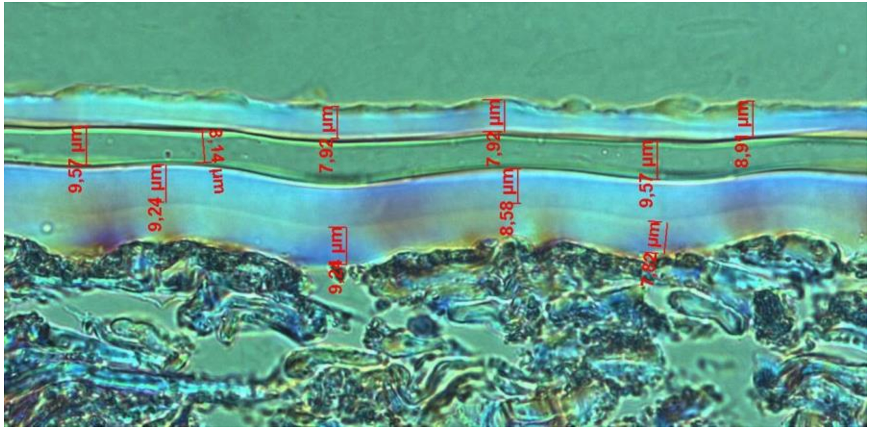
- Adjustment of coating weight:
  - Screw speed (rpm) & screw output (kg/h)
  - Line speed (m/min)

- Coat weight depends on various matters: polymer and its properties (draw down etc.), substrate, adhesion, application etc.

- In extrusion coating usually about 10-60 g/m², in multilayer structure naturally single layers can be only a few grams

- In co-extrusion can be achieved very thin layers, because there are more layers supporting each other



# Adhesion in extrusion coating

# Adhesion to various substrates including cellulosic materials

= **Adhesion is the tendency of dissimilar particles and/or surfaces to cling to one another** (vs. cohesion refers to the tendency of similar or identical particles/surfaces to cling to one another).

= The state in which dissimilar bodies are held together by intimate interfacial contact so that mechanical force can be transferred across the interface

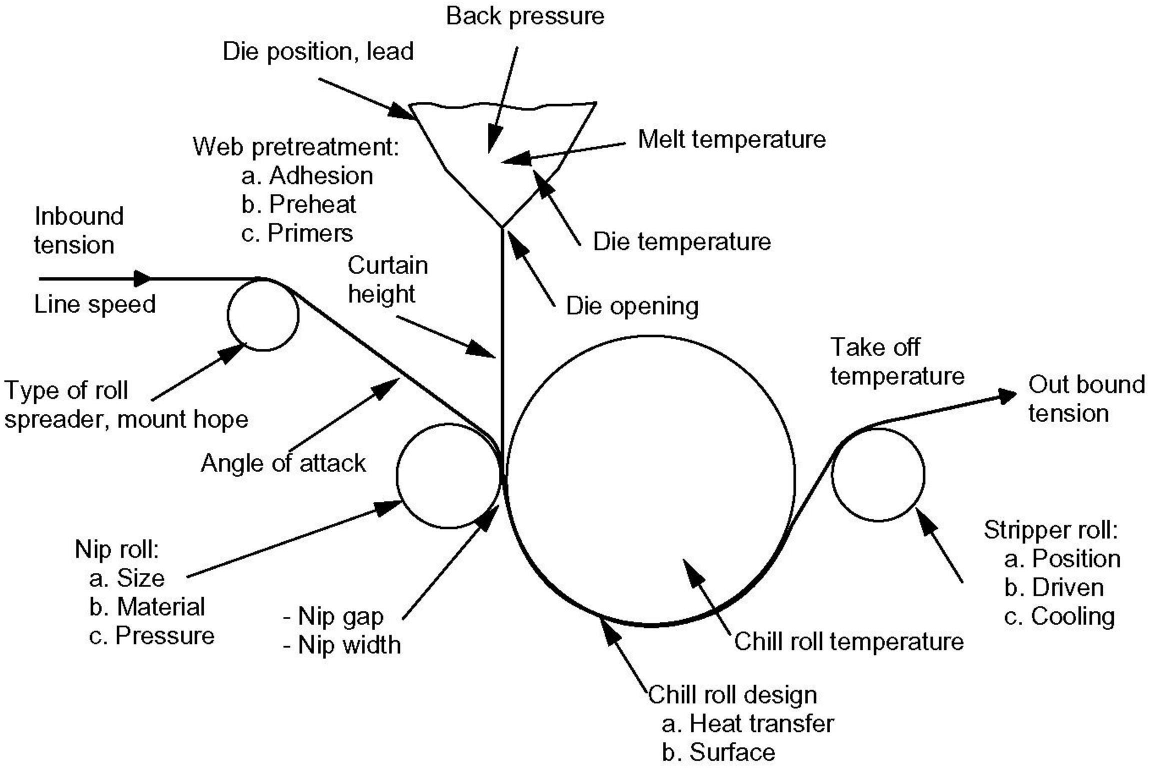
= **The force required to separate the bodies**

- The forces that cause adhesion and cohesion can be divided into several types (e.g. mechanical, diffusion, electrostatic; various adhesion theories exist)

- Adhesion is important in various interfaces:
  - between substrate and coating/adhesive
  - printing ink/glue and substrate
  - between coating layers in multilayer structures
  - sealing

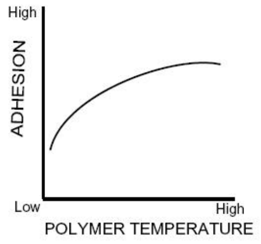
- Adhesion can be affected by various process parameters, material selection (e.g. adhesives/adhesion polymers) and surface treatments (e.g. priming, corona)

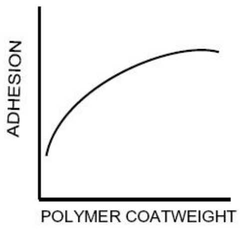
# Parameters affecting adhesion in extrusion coating

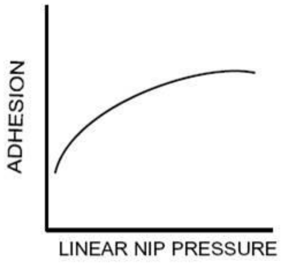


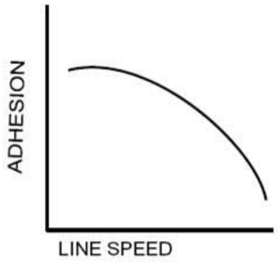
# Adhesion in extrusion coating

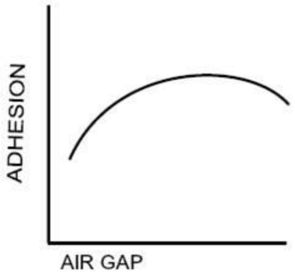
- Polymer and substrate usually differ quite a lot in **surface chemistry** → special operations are needed for adhesion
- PE and PE-based polymers **oxidize in the air** → Certain air gap is needed. Air gap depends on melt temperature, web speed and coat weight.
- The optimal time for oxidation is 100 ms. **Air gap** should not be too large, so that the melt will not cool too much and viscosity will not increase too much
- **Viscosity** must be low enough (=fluid enough) in order to have enough contact area between polymer and substrate → Adequate wetting and penetration
- The polymer **melt temperature** must be high enough to ensure oxidation and fluidity (With PE-LD about 310-330°C)
- Too high melt temperature may cause gel and polymer chain scission → The properties of the final product suffer
- The hotter the melt is when it comes into contact with the web, the better it penetrates into the web and the longer time it has to form adhesive bonds
- High **coat weight** → Heat remains better in the polymer melt
- Increasing **nip pressure** improves adhesion up to a certain point. After that, the risk for pinholes increases.
- When **web speed** is increased, adhesion becomes usually poorer, because the delay in the nip becomes shorter and, on the other hand, the time for oxidation in the air gap becomes shorter



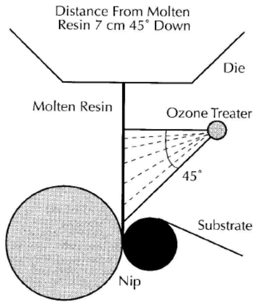



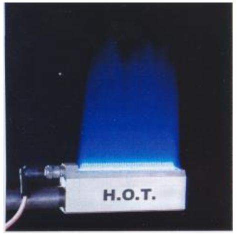



# Methods to improve adhesion

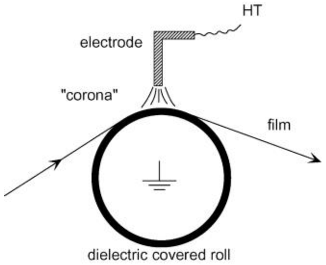
- surface treatments
- mechanical roughening
- removal of weak boundary layers (WBL)
- adhesion promoters
- favorable thermodynamics and wetting (e.g. surface energy)



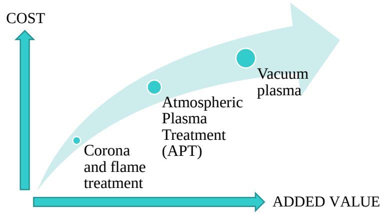




Treaments:

- **Ozone treatment of polymer** melt in the air gap
- **Corona** discharge treatment (electrical treatment of a substrate in air at atmospheric pressure)
- **Flame** treatment (Substrate is exposed to direct flame which modifies the surface of substrate)
- **Plasma** treatment (atmospheric, electrical ionisation of a gas)
- **Priming** (i.e. application of a thin layer of adhesion promoting polymer in water or solvent)



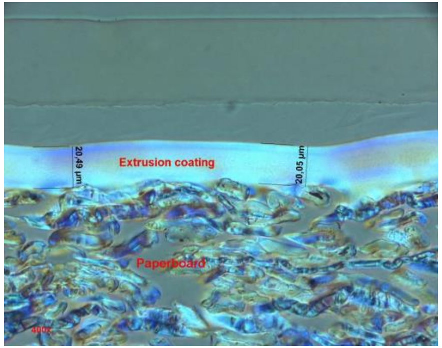

- Each method has its special use; methods can also be combined
- Each method can have several effects that improve adhesion
- An extrusion coating line may have both pre-treatment and post-treatment units
  - Pre-treatment to improve adhesion in coating and lamination
  - Post-treatment to improve e.g. printability



# Extrusion coating polymers

# Polymers in extrusion coating

- Extrusion coating and lamination aim to combine properties of different materials, e.g. paper or paperboard and thermoplastic polymer, into a same multilayer structure
- Fiber-based substrates gives:
  - Mech. properties (stiffness, strength, ”shape”)
  - Light barrier
  - Excellent printability
  - Certain barrier properties week, which restricts usage especially as a primary package for food ➔ Converting with extrusion coating / lamination
- Polymer coating/film gives:
  - Barrier properties (gas, vapours, liquid, grease… )
  - Heat sealability
  - Surface properties (food contact, outlook)



# Selection of a polymer

**Process, application & product** → Required process and end-use properties:

- Tightness (barrier-properties)
  → water vapour, water, grease, aroma, gas, light
- Heat sealability
- Suitable friction properties for converting operations
- Toughness, resistance to abrasion
- Adhesion
- Printability
- Food contact
- Appearance, clarity
- Processability (processing temperatures - in coating can be around 300°C)
- Suitable viscosity (rheological properties of the polymer are very important)
- Biodegradability, recyclability
- Price
- …

# Some important factors when selecting polymers for extrusion coating

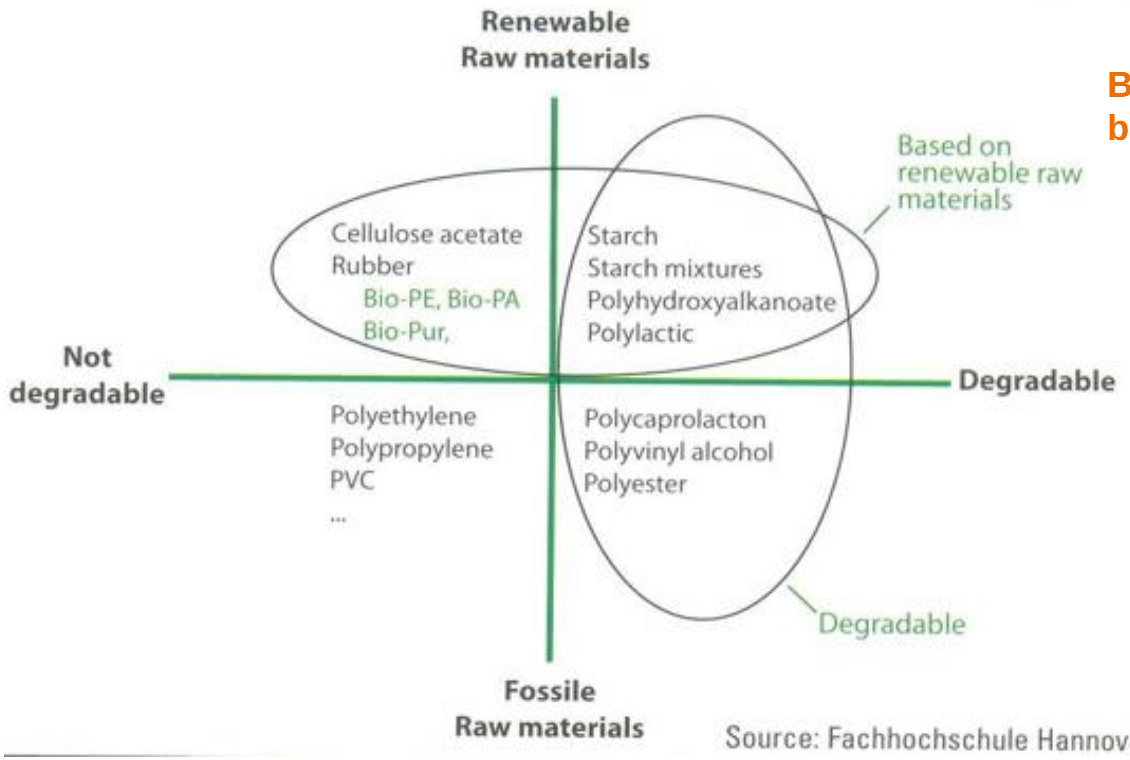
- Processability (viscosity, temperature profile)
- good draw down* (vetoresonanssi)
- low neck-in
- no edge waving
- good melt film appearance
- suitable viscosity
- good chill roll release

*how well polymer can withstand draw when it's extruded to the moving web

End products must possess various properties including:

- good adhesion
- even coating profile
- good heat sealing properties
- good barrier properties
- pinhole free coating
- no odor or taste
- good clarity

# Extrusion coating polymers

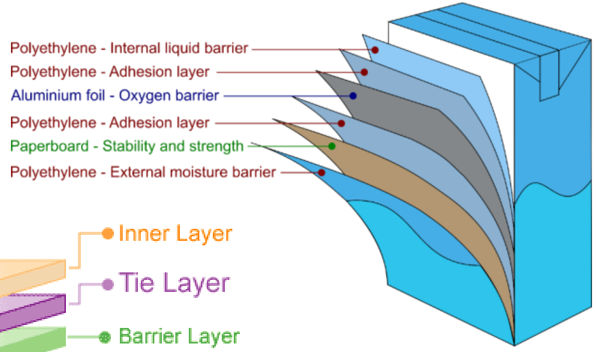


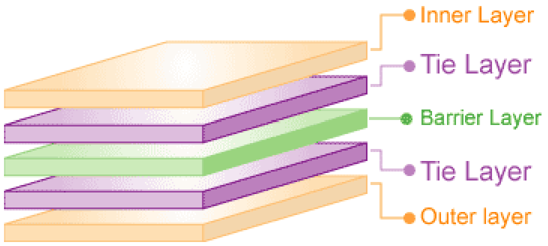

Source: Fachhochschule Hannover

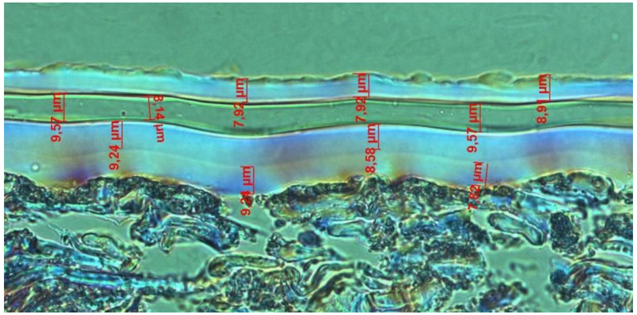
**Biopolymers are either bio-based, biodegradable or both**

# Examples of polymers used in extrusion coating (and film manufacturing)

- **Polyolefins**
  - PE (polyethylene)
    - PE-LD, PE-MD, PE-HD, PE-LLD
  - PP (polypropylene)
- **Copolymers**
  - E/VAC (ethylene vinyl acetate)
  - E/BA (ethylene butyl acrylate)
  - E/MA (ethylene methyl acrylate)
  - E/EA (ethylene ethyl acrylate)
- **Adhesives (TIE-layers)**
  - Acid copolymers (Ionomers, E/AA)
  - Grafted polyolefins (MAH grafted)
  - Modified polyolefins (e.g. Bynel, Admer)
- **Barrier polymers**
  - EVOH (ethylene vinyl alcohol)
  - Polyamide
    - PA 6, PA 66, PA 11, PA 12
- **Other special polymers**
  - PET, PVOH…
- **Biopolymers**
  - PLA, PHA, PBS, starch..



Johanna Lahti

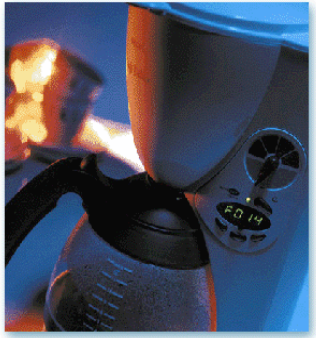
# Products from polyethylene (PE)

-Excellent WV and liquid barrier
-Good heat sealability
-Easy to process in extrusion
Etc. Etc.


# Products from polypropylene (PP)

<u>Besides extrusion coating, PP is used for :</u>

-Biaxially oriented films
-Yoghurt cups
-Trays (deep drawn)
-Blow molded bottles
-Injection molded boxes
-Plastic bags
etc.

# Bio-based (at least partially) polymers but not biodegradable

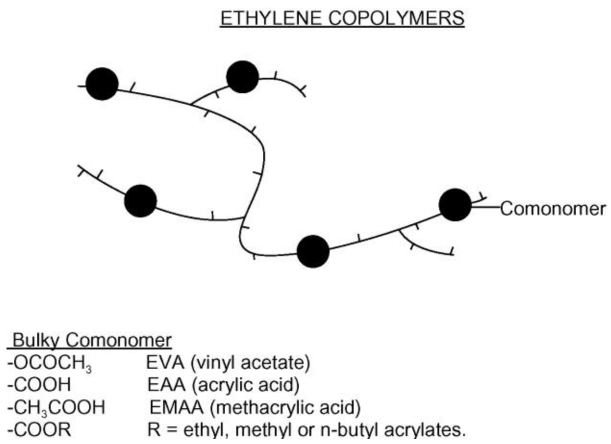
- <u>Bio-PE and Bio-PP</u>
  - Similar processability and properties as virgin PE/PP
  - Bio-PE from bio-ethanol
  - Main producers: Braskem (I'm green™), Sabic (TRUCIRCLE™)

  - Bio-PP: Neste & LyondellBasel, Borealis, Braskem

- <u>bio-based PET (Bio-PET)</u>
  - Similar processability and properties as virgin PET
  - Eastlon (FKUR)
- <u>Bio-PA</u>
  - Rilsan® (Arkema)


# Copolymers

- EVA (ethylene vinyl acetate)
  - Density 0,925-0,955
- EAA (ethylene acrylic acid)
- EMA (ethylene methyl acrylate)
- EBA (ethylene butyl acrylate)
- ….




- Polar copolymers can improve adhesion to difficult to adhere substrates
- Copolymers are used as **heat sealing layers and tie layers in coex-structures**
- Stretch film for food packaging (particularly fresh meat)

# *Adhesives*

- Acid copolymers
  - Ionomers (e.g. Surlyn)
  - E/AA (copolymer of ethylene and acrylic acid)
- Grafted polyolefins
- Chemically modified polyolefins

Table 8.11.2 ATTRIBUTES OF ETHYLENE COPOLYMERS

| MATERIAL | EMA | IONOMER | EAA | EVA |
|---|---|---|---|---|
| PROCESSING RANGE (°C) | 150-326 | 165-305 | 176-305 | 240 max. |
| Thermal stability | Excel. | Good | Good | Poor |
| Moisture sensitivity | No | Yes | No | No |
| **ADHESION TO:** | | | | |
| BOPP/PP | Good | Poor | Poor | Fair |
| PAPER | Good | Excellent | Excellent | Good |
| PET/PETG | Good | Poor | Poor | Fair |
| PC (polycarbonate) | Good | Poor | Poor | Fair |
| PVC (rigid) | Good | Poor | Poor | Fair |
| ALUMINIUM FOIL | Poor | Excellent | Excellent | Poor |

- Extrusion coating process generally requires two different resins – one gives **adhesion to the substrate**, and the other provides **interply adhesion** in coextrusion (tie layers in multilayer structures)
- Adhesives give also heat sealability

# Barrier polymers

- Most used barrier polymers:
  - Ethylene vinyl alcohol (EVOH)
  - Polyamide (PA) (also bio-based PA)
- To improve especially **<u>oxygen barrier</u>**
- Barrier polymers are moisture sensitive and when exposed to moisture, they loose their barrier property ➔ used in coex-structures with polyolefins
- Usually **need an adhesive layer** in polyolefin coex-structures

| **Plastic** | **$O_2TR$ (cm$^3$/m$^2$/d)** |
|---|---|
| E/VA | 5000 |
| PE-LD | 3500 |
| PP<br>Oriented | 1800<br>500 |
| PE-HD | 1300 |
| PET<br>Oriented | 80<br>40 |
| PA-6<br>Moist | 25<br>120 |
| EVOH<br>moist | 0.2 – 2<br>30 - 50 |

Ref: Paper and paperboard converting


*Excellent barrier against oxygen, nitrogen, carbon dioxide and helium
*Excellent transparency and high gloss

# Modified Atmosphere Packaging

Ham

***Tray***
PS // PE/ Tie / EVOH / Tie / PE
***Lid***
PET// PE / Tie / EVOH / Tie / PE

Pre-baked bread


***Bottom Web***
PA / EVOH / PA / Tie / PE
***Top Web***
OPP// PE / Tie / EVOH / Tie / PE

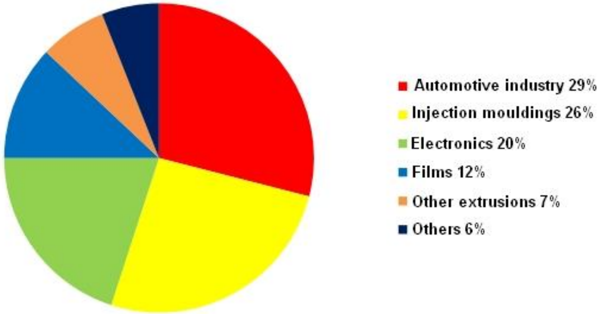
Red Meat

***Tray***
PP / Regrind/ Tie / EVOH / Tie / PP
***Lid***
PA / EVOH / PA / Tie / PE

Fresh Pasta

***Tray***
PS / Tie / EVOH / Tie / PE
***Lid***
PET// PE / Tie / EVOH / Tie / PE

# Polyamide Film: Applications




Polyamide widely used for food packaging

- meat, poultry
- cheese
- processed food

due to its combination of

- oxygen barrier
- flavor and aroma barrier
- good mechanical properties
- high transparency
- thermoformability
- thermal stability

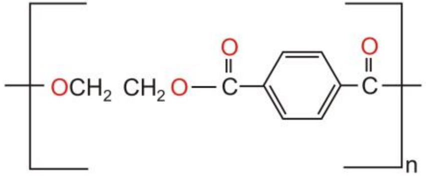
# Polyethylene Terephthalate (PET)

- The most used and most important polyester, also bio-PET available

- The most used synthetic fiber

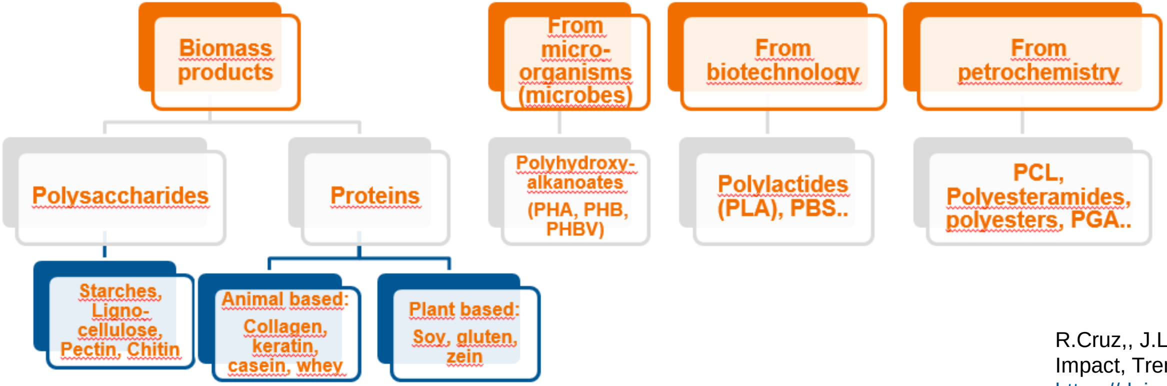
- Good heat resistance (60 – 235 °C) → ovenable packages, boil-in-bag packages, retortable packages..

- Used in bottles, containers, food packings, fibers, films, electronic insulators, clothing fibers, etc.




# Bio-based polymeric materials for packaging

- The use of bio-based materials in packaging decreases the dependence on fossil fuels.
- **Wood based biomass** that is available in a large scale offers attractive “green” polymers.
- Also **biopolymers** that are based on agricultural or other waste streams offer interesting alternatives for traditional petroleum-based polymers.
- Can be processed into **films and coatings** to be used in packaging applications as mono materials or combined with fibre-based materials (paper, paperboard)




R.Cruz,, J.Lahti, et al, Bioplastics in the Food Industry: Environmental Impact, Trends and Regulatory Aspects, Foods 2022, 11(19), 3087; https://doi.org/10.3390/foods11193087

*foods*

MDPI

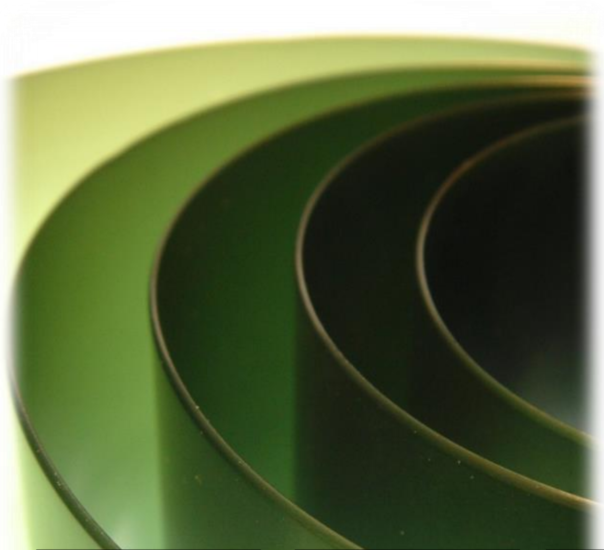
*Review*

# Bioplastics for Food Packaging: Environmental Impact, Trends and Regulatory Aspects

**Rui M. S. Cruz [1,2,*], Victoria Krauter [3,*], Simon Krauter [3], Sofia Agriopoulou [4], Ramona Weinrich [5], Carsten Herbes [6], Philip B. V. Scholten [7], Ilke Uysal-Unalan [8,9], Ece Sogut [8,10], Samir Kopacic [11], Johanna Lahti [12], Ramune Rutkaite [13] and Theodoros Varzakas [4]**

https://doi.org/10.3390/foods11193087

# Sustainable film solutions with VTT

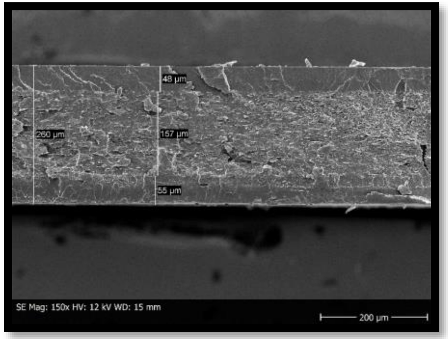


VTT provides easy-access material development, piloting and demonstration facilities with world class material experts and unlimited material possibilities, including biopolymers, biocomposites and multilayer structures.

Film processing services include:

- ✓ Pilot-scale roll-to-roll cast film processing and (co)extrusion coating, 500 mm wide
- ✓ Laboratory-scale cast film processing, 100 mm wide
- ✓ Blown-film processing (1-layer), die 60 mm
- ✓ Biaxial orientation of thick plastic sheets, for 80 * 80 mm samples
- ✓ Experience in versatile materials and applications

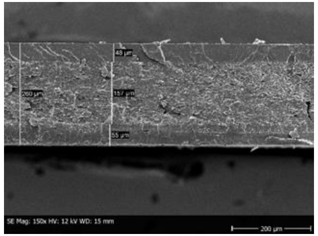
For polymer processing we have also twin-screw compounding and injection moulding in lab- and pilot-scale




# PlasCo – Tailorable piloting environment for thermoplastic materials

- Wet coating (i.e. dispersion coating or priming) on various substrates: bar and gravure coating
- Extrusion coating
- Monolayer cast film extrusion (thickness range 10-700 µm)
- Multilayer extrusion coating and casting up to 5 layers
- Two 35 mm single screw extruders with 30 L/D ratio, different screws available
- On-line compounding with twin-screw extruder
- Sheet die with width of 550 mm
- Surface treatment (corona, plasma)
- Machine directional orientation (MDO)
- On-line thickness measurement for precise profile adjustment
- Chill roll with temperature range of 15-95°C
- Chill roll unit has two individually working nip rolls with adjustable pressure
- Position of the chill roll is adjustable and horizontal air knife can be used
- 3 and 6 inch cores for winding, line tension adjustable
- Main customer groups: Packaging, plastics, pulp & paper and construction industry, SME:s and start-ups





YouTube-> VTT PlasCo
https://youtu.be/rvhvqcr-jNo

# PLASCO – Tailorable piloting environment for thermoplastic materials

**Heat sealable fluid package**

- Multilayer co-extrusion
- Bio-based
- Heat-sealable
- Excellent barrier

**Bio-based and biodegradable coating**

- Monolayer cast film extrusion
- Wet coating + plasma treatment
- Bio-based & biodegradable
- Heat-sealable

**Lidding for thermoformed food package**

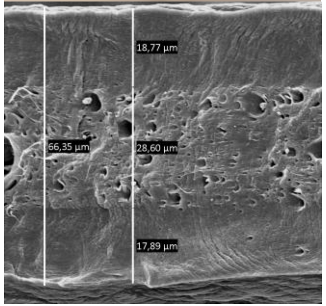
- Multilayer co-extrusion
- Bio-based and compostable
- Heat-sealable

**Substrate film for printed electronics**

- 4.5x MDO film & annealing
- Compostable
- Monolayer cast film extrusion
- Heat stable bio-based film with high crystallinity

**Bio-based and biodegradable blend film**

- On-line compounding
- Studying effects of blending
- Bio-based & biodegradable

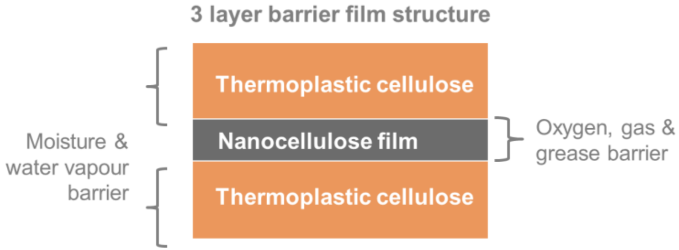



**Recycled film with virgin surface layers**

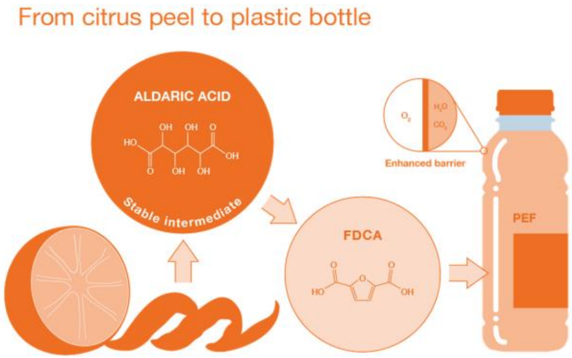
- On-line compounding
- Multilayer cast film extrusion
- Viscosity analysis of different layers
- Impurities of recycled material remain in middle layer

# Thermoplastic polymers and cellulose-based materials as coatings and films @VTT

- In addition to commercial polymers, VTT has its own developments, e.g.
  - ThermoCell (thermoplastic cellulose)*
  - PGA (poly(glycolic acid))
  - PHA (polyhydroxy alkanoate)
  - PEF (polyethylene furanoate)
  - Nanocellulose (NFC, MFC), regenerated cellulose
- Bioruukki pilot lines (in Espoo) for producing cellulose materials and cellulosic films and coatings



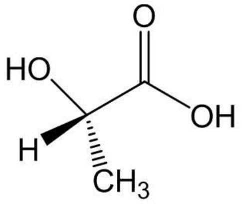



*In industrial testing with Arla Foods, Paulig and WIPAK*

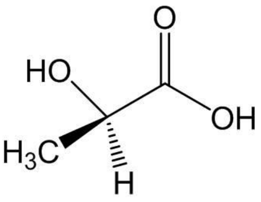


https://doi.org/10.1039/D0GC02293D

- PLA, Poly(lactic acid)
  - Derives from lactic acid polymerisation
  - High crystallinity (mainly L-lactic) and amorphous (L- and D-lactic) grades
  - Biodegradable
  - Disposable tableware, take-away coffee cups, food packaging, medical industry..
  - Glossy, transparent or slightly yellowish
  - Moderate oxygen and moisture barrier
  - Producers e.g. NatureWorks (Ingeo®), Total Corbion (Luminy®)



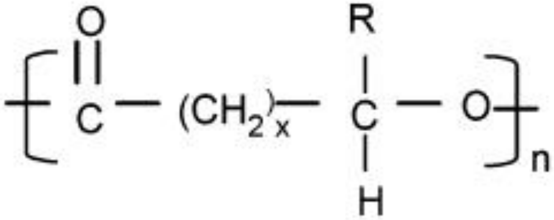

L-lactic acid



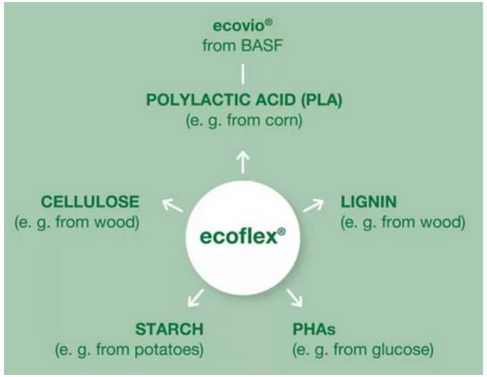

D-lactic acid

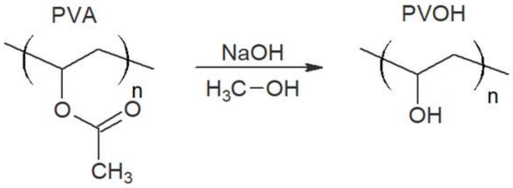

- Alifatic polyesters → PHA (polyhydroxy alkanoate), PHB (polyhydroxy butyrat), PHBV (polyhydroxy butyrat valerate)
  - Made by fermentation from sugars
  - Biodegradable
  - PHAs have rather high melting point (140-180ºC) and it resembles PP in properties
  - Rigid, brittle, challenging processability due to slow crystallisation rate and poor thermal stability, narrow processing window
  - Properties can be tailored by modifying the polymer structure or by using additives (nucleating agents, plasticisers, blending)
  - PHB is rather stiff, but it can be softened using valerate (PHB/V)
  - PHBs most studied group (homopolymer)
  - PHBV, copolymer with varying content of hydroxy valerate, which can be used to tailor the properties (e.g. easier processing, softness)

  - Producers e.g. Danimer Scientific, Tianjin Green Biomaterials, TianAn Biologic Materials, Biomer, Natureplast, Kaneka, Helian Polymers, Gruppo Maip, Ercros, …



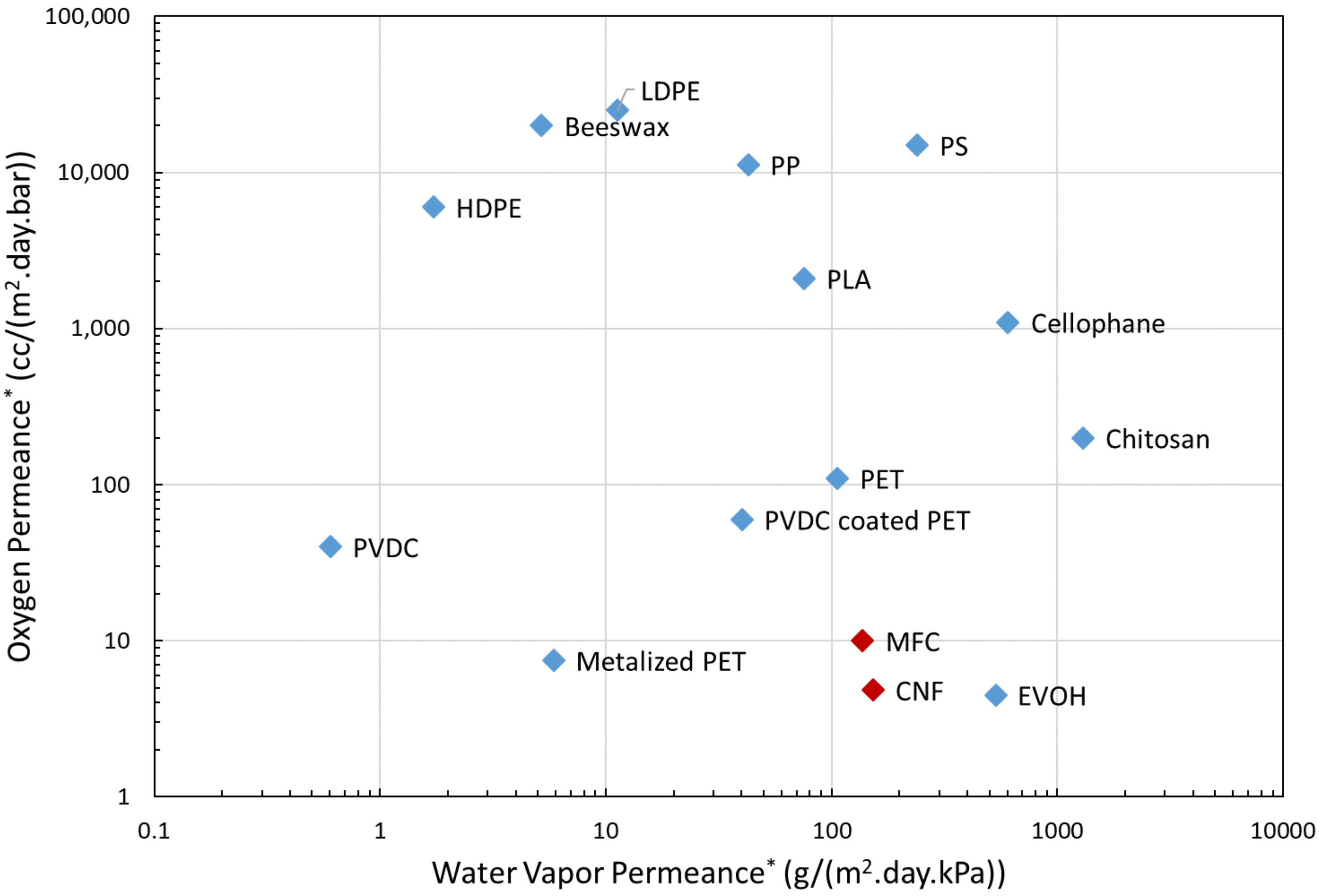
- Thermoplastic starch (TPS)
  - Biodegradable
  - e.g. Mater-Bi by Novamont
- PBS, poly(butylene succinate)
  - Bio-based & biodegradable also available by PTT MCC Biochem
    - Good processability, adhesion and heat sealability, barrier against oil and grease
  - Co-monomer PBSA (polybutylene succinate-co-adipate)
- PGA, Poly(glycolic acid)
  - Biodegradable, from fossil resources
  - Excellent barrier properties
  - Main producer Kureha
- PBAT Poly(butylene adipate-co-terephtalate)
  - Biodegradable
  - Main producers: BASF (Ecoflex®), Novamont (Mater-Bi)
  - Frequently blended with other polymers like PLA (-> BASF ecovio® - PBAT, PLA)
- PVOH, Polyvinyl alcohol
  - Biodegradable, good barrier properties and sealability
  - Producers: Aquapak Polymers, Kuraray, Nippon-Gohsei
- PEF, Poly(ethylene fuaronate)
  - Similarities to PET: very good barrier and mechanical properties. Lower melting temperature so as high processing temperatures are not needed as with PET
  - Degradable
  - Main producer Avantium
  - Also VTT has developed a technology to produce PEF



- Lignin is the second most abundant biopolymer on earth, after cellulose.
- As a coating material it is very promising with its many benefits compared to the synthetic and bio-based coatings currently used
- It has e.g. excellent anti-corrosion, anti-bacterial, anti-icing, and UV-shielding properties
- The polyphenolic chemical structure of lignin with aromatic rings provides antioxidant activity.
- Lignin has also shown antibacterial and radical scavenging functions, which could be exploited in active packaging.

https://clicinnovation.fi/project/susbinco-sustainable-binders-and-coatings/
Ruwoldt, J. et al., Functional surfaces, films, and coatings with lignin – a critical review, doi: 10.1039/d2ra08179b;
Hult, E-L. et al. https://doi.org/10.1016/j.indcrop.2013.08.013

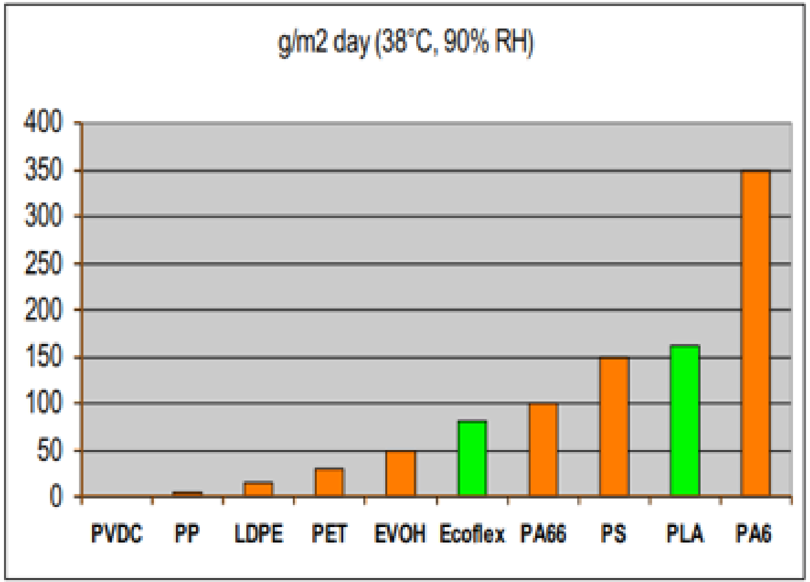

Oxygen Permeance* (cc/(m².day.bar))
100,000
10,000
1,000
100
10
1
LDPE
Beeswax
PP
PS
HDPE
PLA
Cellophane
Chitosan
PET
PVDC coated PET
PVDC
MFC
Metalized PET
CNF
EVOH
0.1
1
10
100
1000
10000
Water Vapor Permeance* (g/(m².day.kPa))

## Oxygen (OTR)

| | cc micron/m2 day bar |
|---|---|
| LDPE | 200.000 |
| PS | 100.000 |
| PP | 70.000 |
| PLA | 16.000 |
| PET | 2.000 |
| PA6 | 800 |
| PVDC | 100 |
| EVOH | 25-50 |

| | |
|---|---|
| (peach) | Low barrier |
| (yellow) | Medium barrier |
| (cyan) | High barrier |

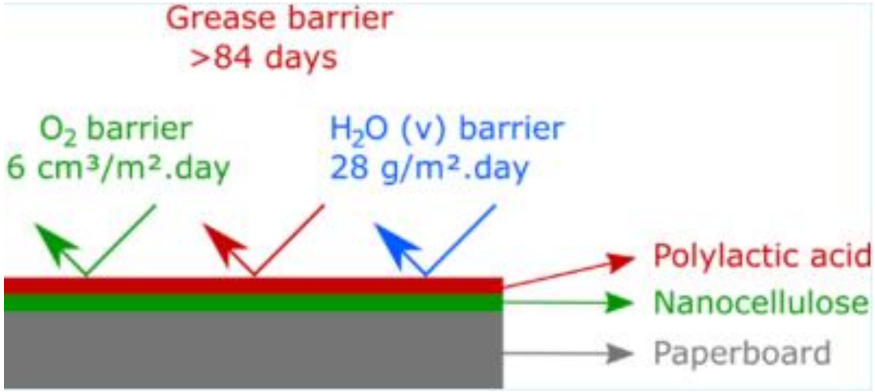
## Water vapour (WVTR)



# Barrier improvement

- There are many ways to improve barrier:
  - ✓ Waxes
  - ✓ Metallisation
  - ✓ Thin coatings like ALD, SiOx, etc.
  - ✓ Polymer selection
  - ✓ Cellulosic coatings and films
- Coextrusion technology provides multilayer structures
- Nanocellulose/MFC provides improved $O_2$-barrier properties
- On the other hand, NC/MFC layers can be protected with extrusion coating – PLA provides WV-barrier

→ **Bio-based multilayer packaging structure**

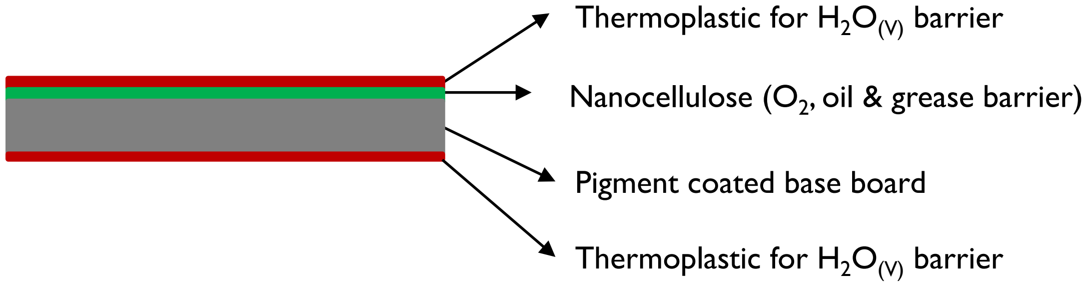



Koppolu, R. et al. 2019,
Koppolu, R. et. al. 2023

# Case study: Biodegradable multilayer packaging paperboard with barrier properties comparable to existing state of the art

# Case - Biodegradable multilayer packaging paperboard with barrier properties comparable to existing state of the art

- Target to 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

Ref. Lahti, J. et al. 18th TAPPI European PLACE conf. 2022

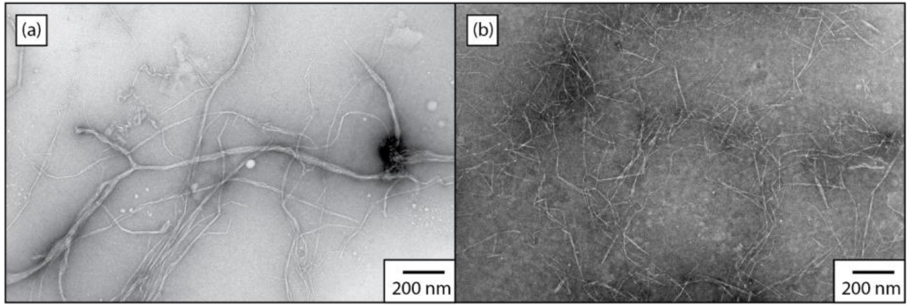
# Nanocellulose – A promising biomaterial

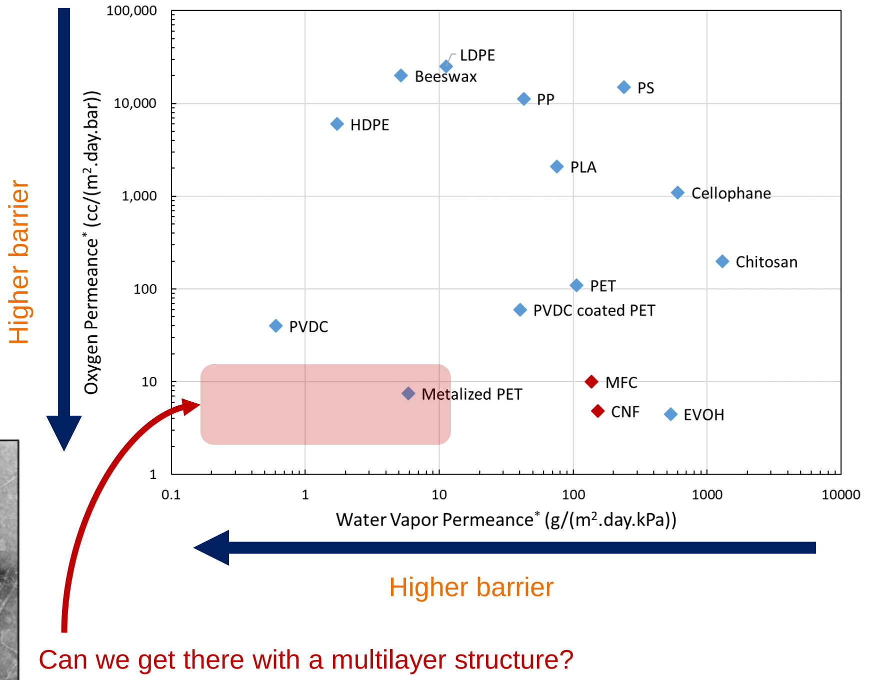
(a) Microfibrillated Cellulose (MFC) from University of Maine, USA

- 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



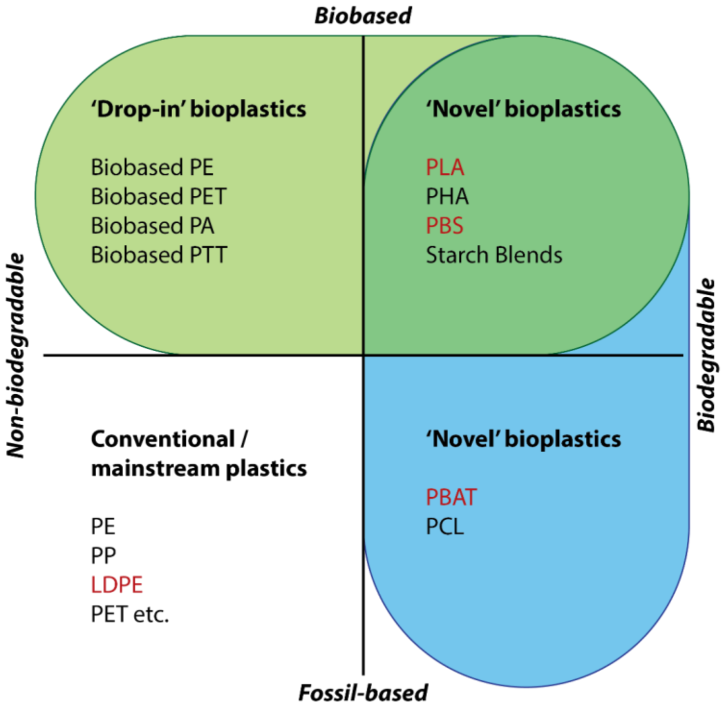




*All values for 10 µm films at 23 °C / 50 % RH

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

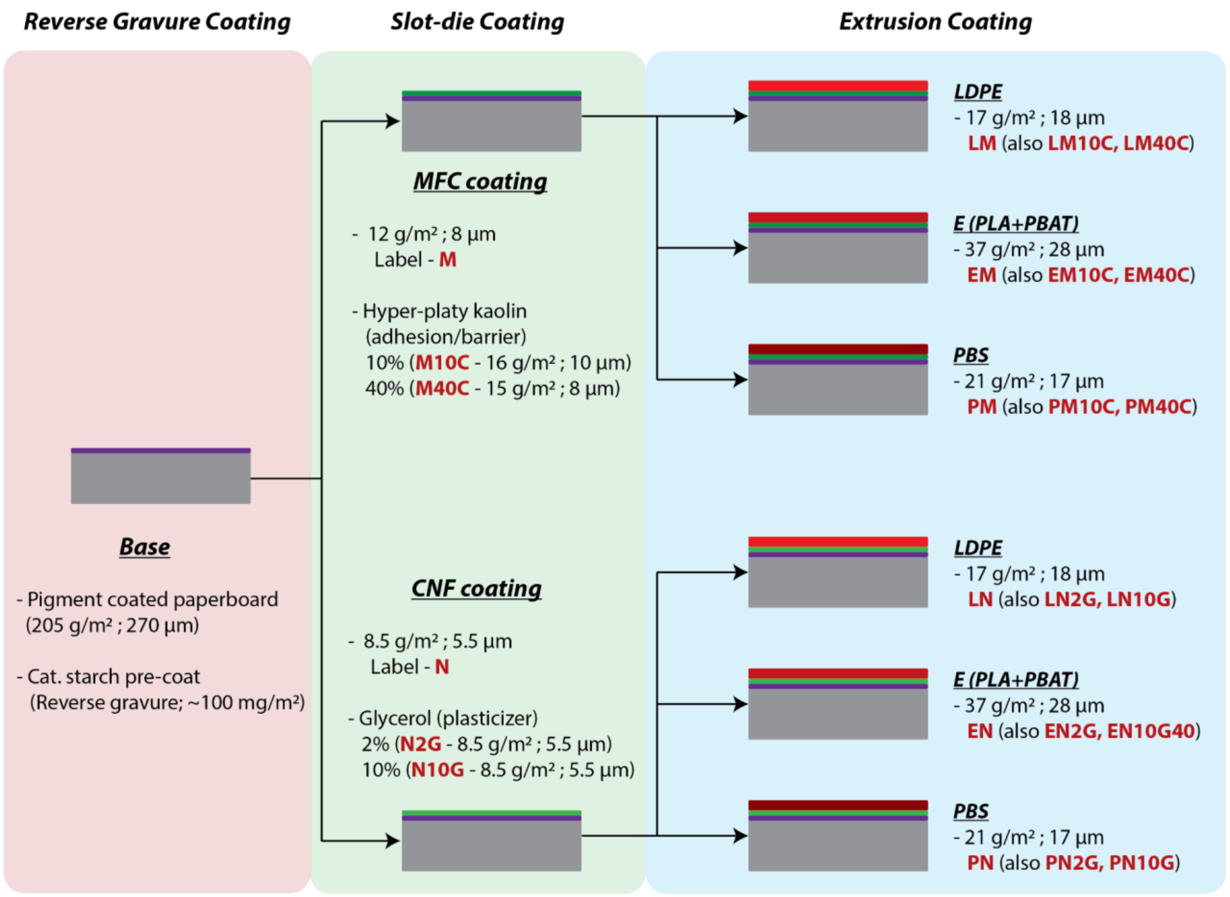
# Biodegradable thermoplastics

- Over 90% of the total mass of plastics produced are thermoplastics
- Processed via injection moulding, blow moulding, thermoforming, and cast extrusion
- Barrier against e.g. 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)

# Sample setup



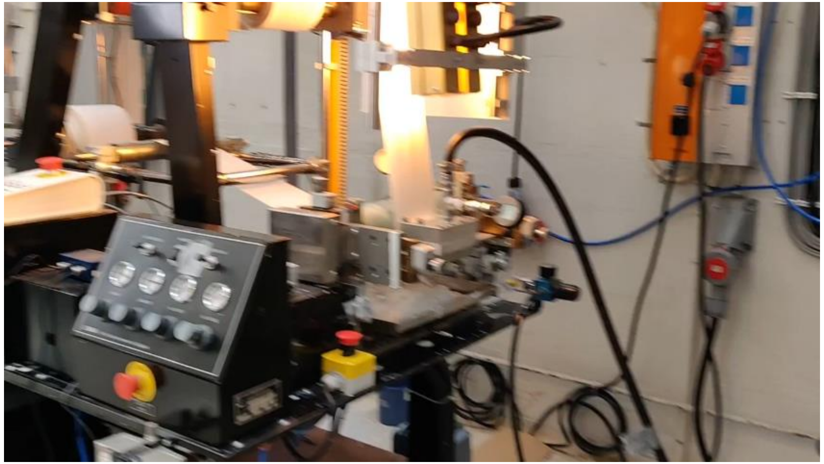

Both MFC & CNF have 5 % CMC (Finnfix 4000G, CP Kelco) added on dry nanocellulose as rheology modifier

- 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

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

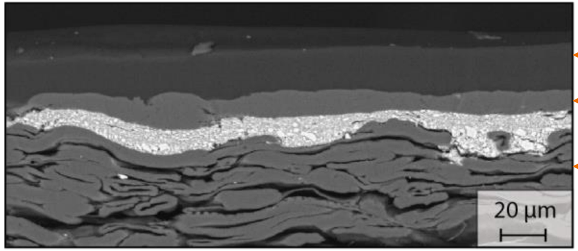


- 300 mm max. web width, 50 m/min max. line speed
- Custom fitting of slot-die (100 mm wide)
- Nanocellulose coating – 100 mm wide & ~ 5 m/min line speed

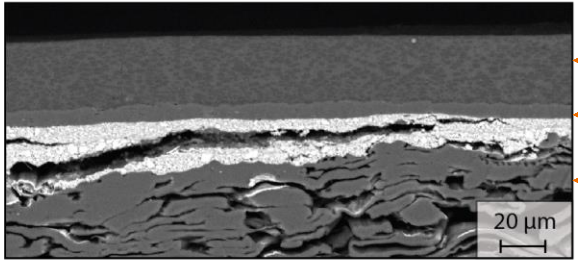
*Pilot scale extrusion coater at Tampere University*


- 500 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)

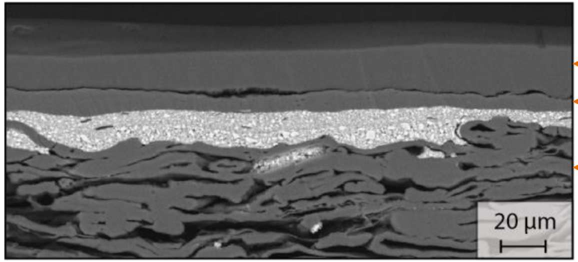
# SEM cross-sections




LDPE
MFC
Baseboard



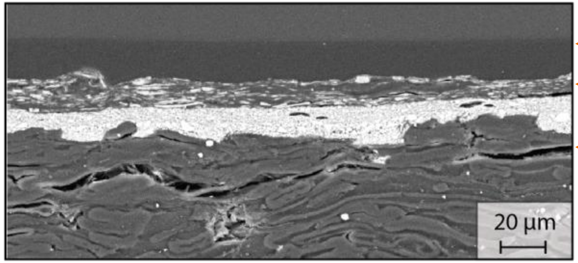

E (PLA+PBAT)
MFC
Baseboard




PBS
MFC
Baseboard

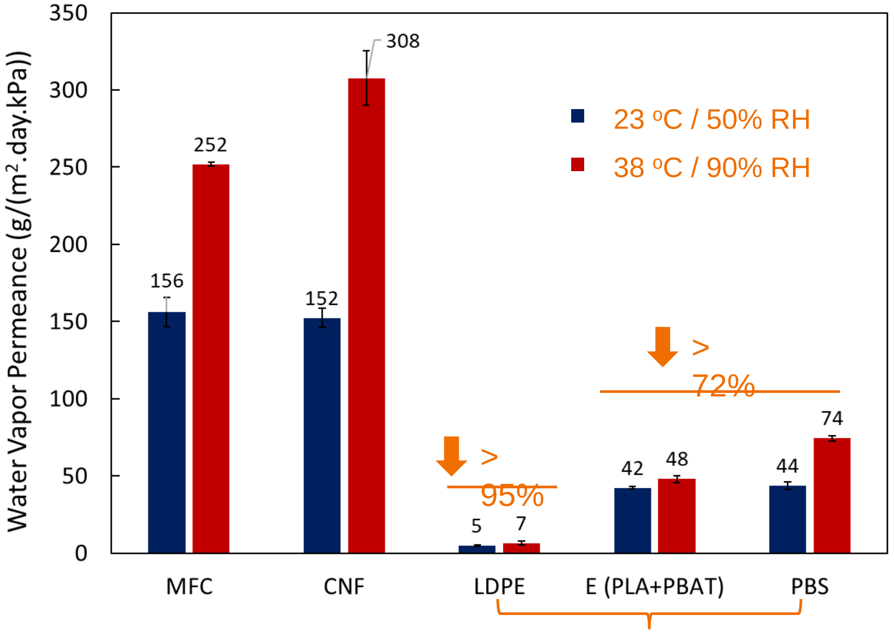
- PBS does not have sufficient adhesion with nanocellulose
- Blending kaolin into MFC improves adhesion with PBS
- Plasma treatment/ultra-thin pigment coating on nanocellulose might also improve adhesion with thermoplastics

PM40C – Improved adhesion at PBS/MFC interface




PBS
MFC + 40% kaolin
Baseboard

# Water vapour barrier




Similar values for multilayer samples

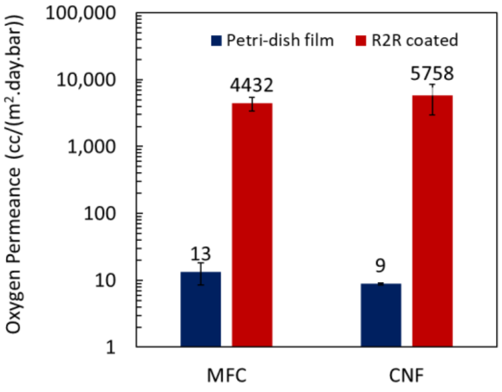
- Water vapor <u>permeance </u>(WVP) measured at two conditions:
  - 23 ºC / 50 % RH & 38 ºC / 90% RH
- Extrusion coated top layer influences the water vapor barrier for multilayer coated samples
- Over 95% reduction in WVP with LDPE as top layer
- Over 72% reduction in WVP with E (PLA+PBAT)/PBS top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

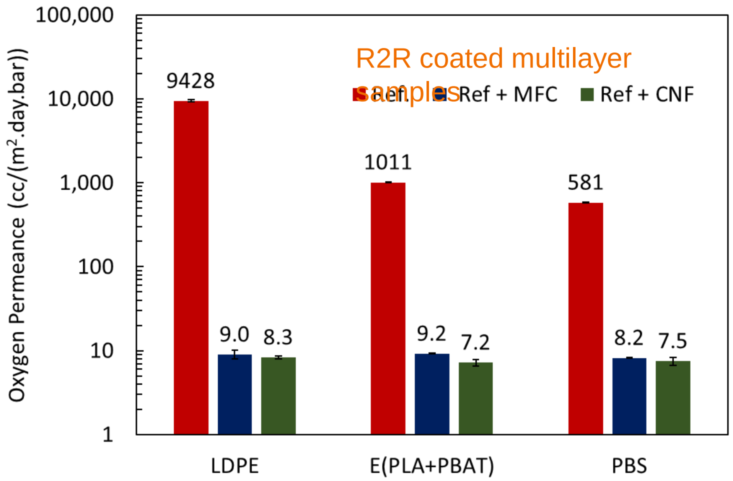
WVP measured according to ASTM E96/96M-10; Desiccant method

# Oxygen barrier

## (Influence of extrusion coating)

- Oxygen permeance (OP) measured at 23 $^{o}$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!



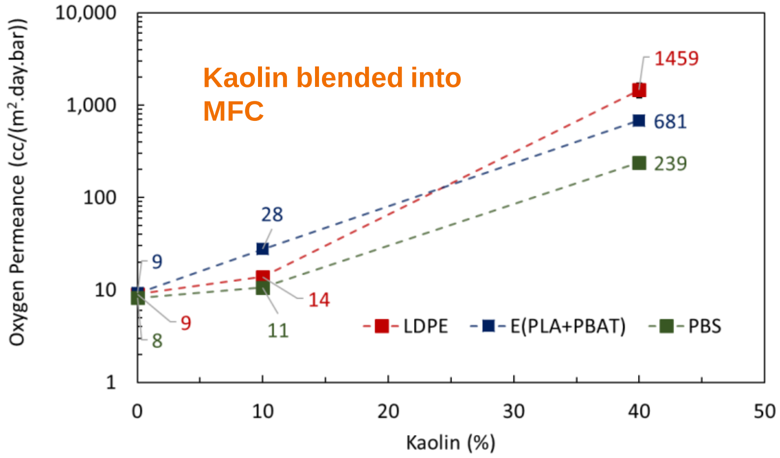



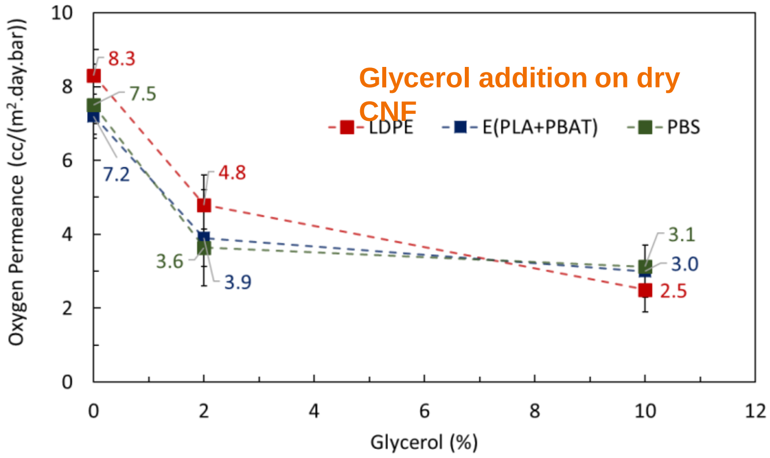

OP measured according to ASTM D3985-05 (coulometric sensor)/F3136-15 (dynamic accumulation)

# Oxygen barrier

## (Influence of kaolin/glycerol additives)

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



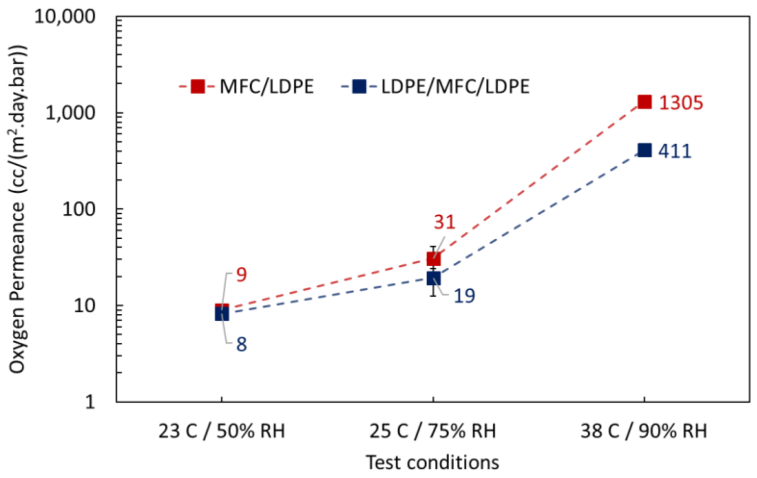

- ➢ 10% kaolin blend has similar OP as pure MFC coating
- ➢ A small % of pigment can be blended into nanocellulose to aid adhesion without compromising Oxygen barrier

- ➢ 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

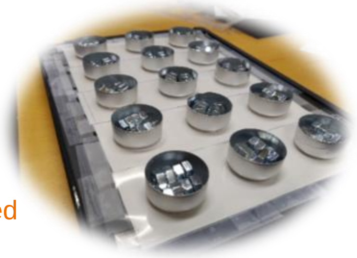
## (Influence of relative humidity/double-sided extrusion coating)



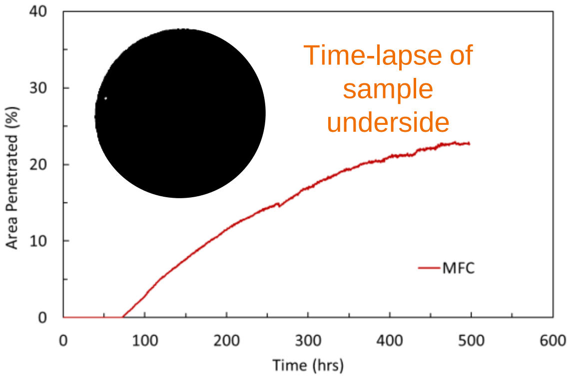

- Oxygen barrier gets worse at higher temperatures and relative humidities
- Backside extrusion coating LDPE protects nanocellulose to an extent → Yet, falls short of required OP value for certain applications
- Water vapor might be seeping in through along the cross-section
- Sealing the cross-section/sandwiching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

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

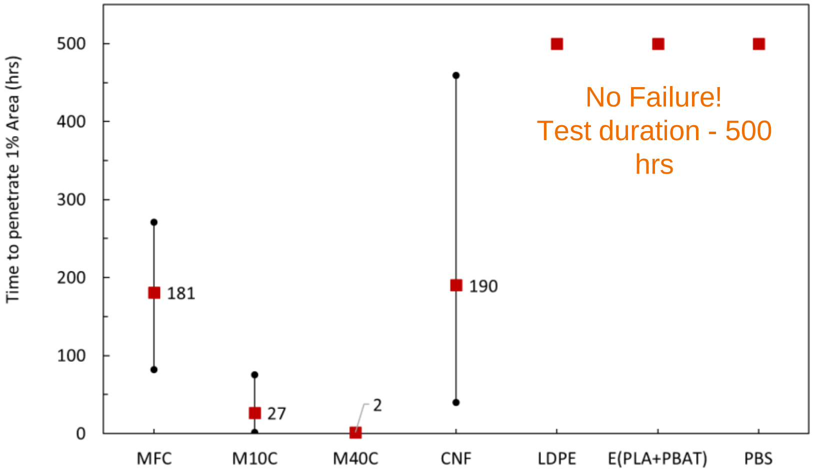
# Grease barrier



- The samples were placed on top of a scanner with coated side facing up; olive oil & 50 g weights placed on the coated side

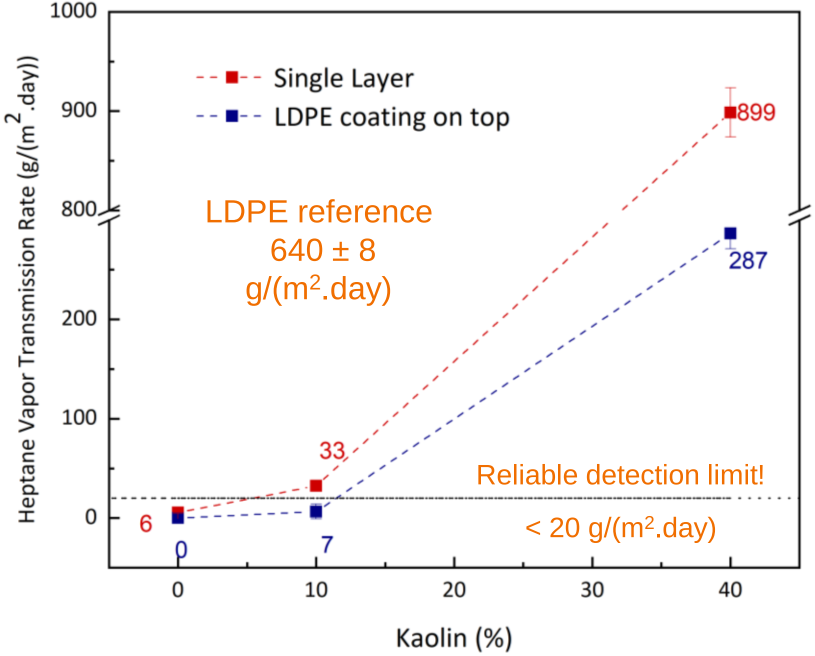



- Underside of the samples scanned at regular intervals. Test temperature: 40 ºC
- Time for oil to penetrate 1% of the area is reported
- Sensitive to coating defects
- Kaolin negatively affects grease barrier; No influence of glycerol
- No failure for extrusion coated samples even after 500 hrs.




Grease barrier measured according to ASTM F119-82

# Mineral oil barrier



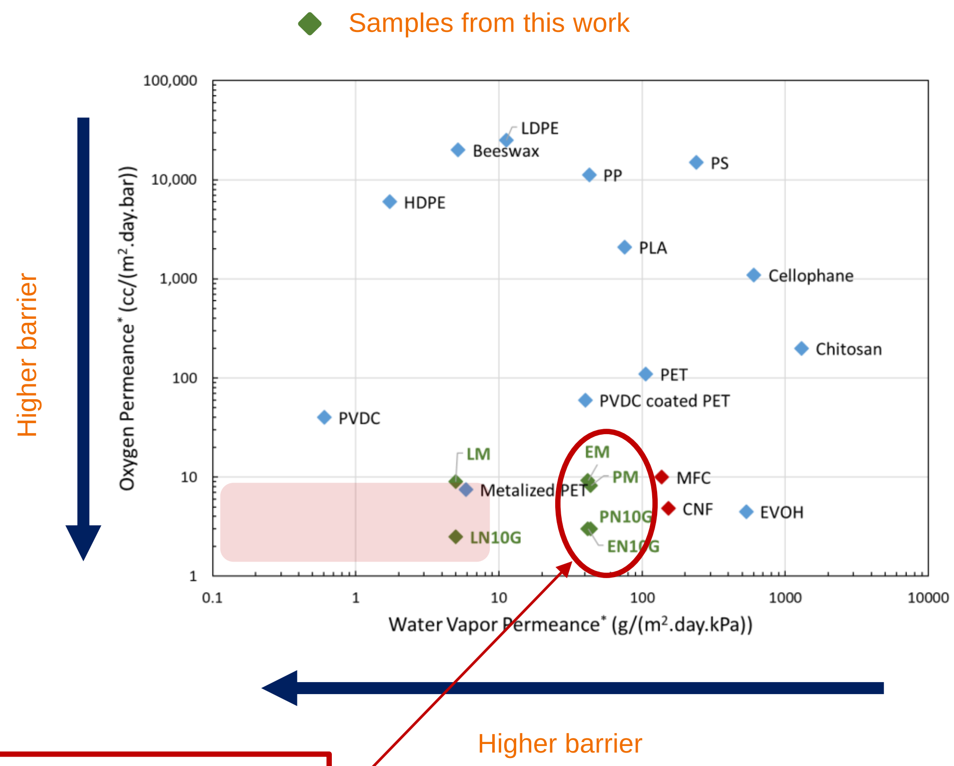

Kaolin blended into MFC

- 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 are 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 of the case

- 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 ºC / 50% RH

# References and more information

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*Lists of polymers (producers & trade names) are not considered complete. Information collected from various sources e.g. company web-sites.*
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# beyond
## the obvious

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