Renewable barrier films based on synergy from cellulose and chitin nanomaterials

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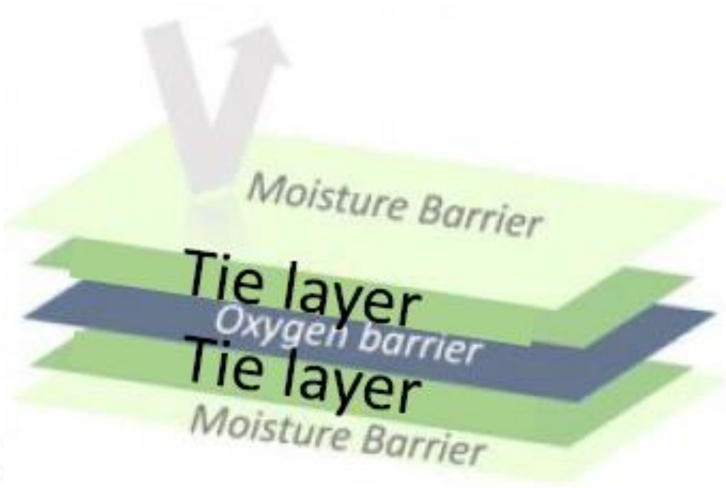
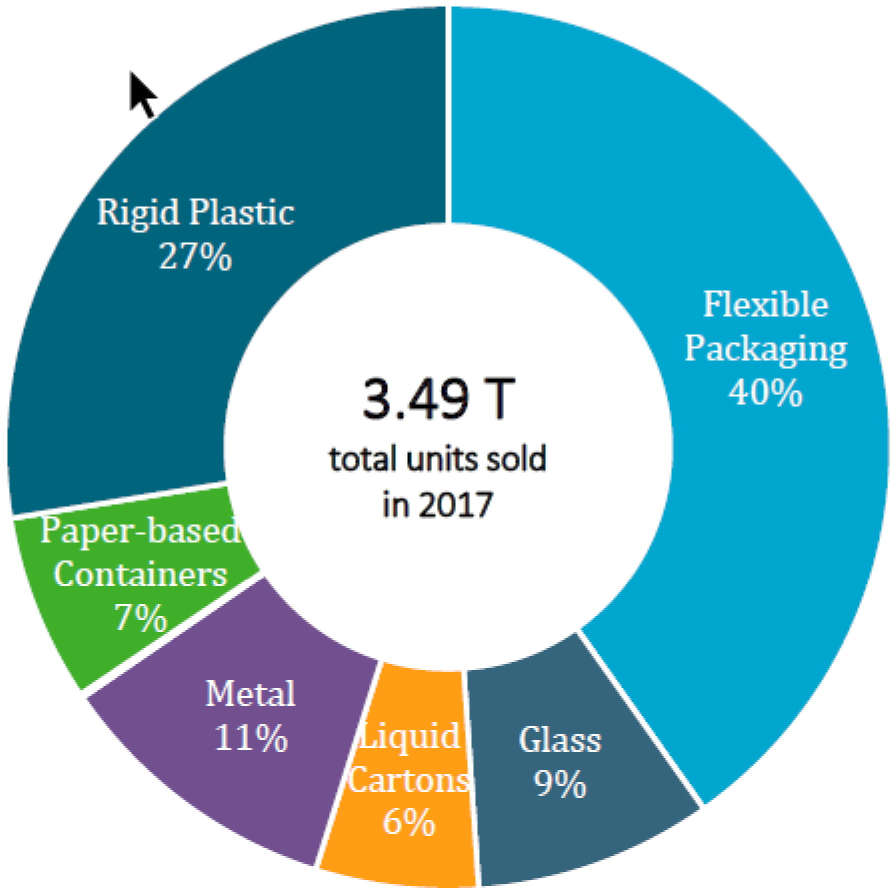
TAPPI NANO DIVISION

Functional Barriers in Packaging

Multilayer Flexible Packaging
-critical to food safety
-critical to food supply
-multimaterial by design



Global Volume share of pack types , 2017



Total 2017 market size	3.49 Tn
Total 2022 market size	3,93 Tn
Forecast Absolute Growth (2017-2022)	12.7%

Functional Barriers in Packaging

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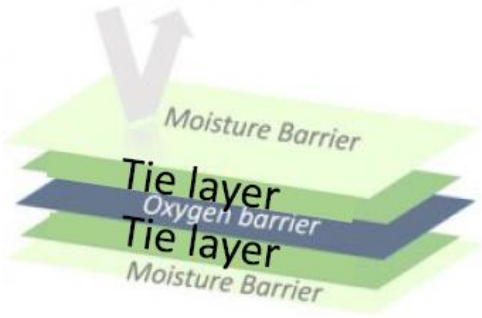
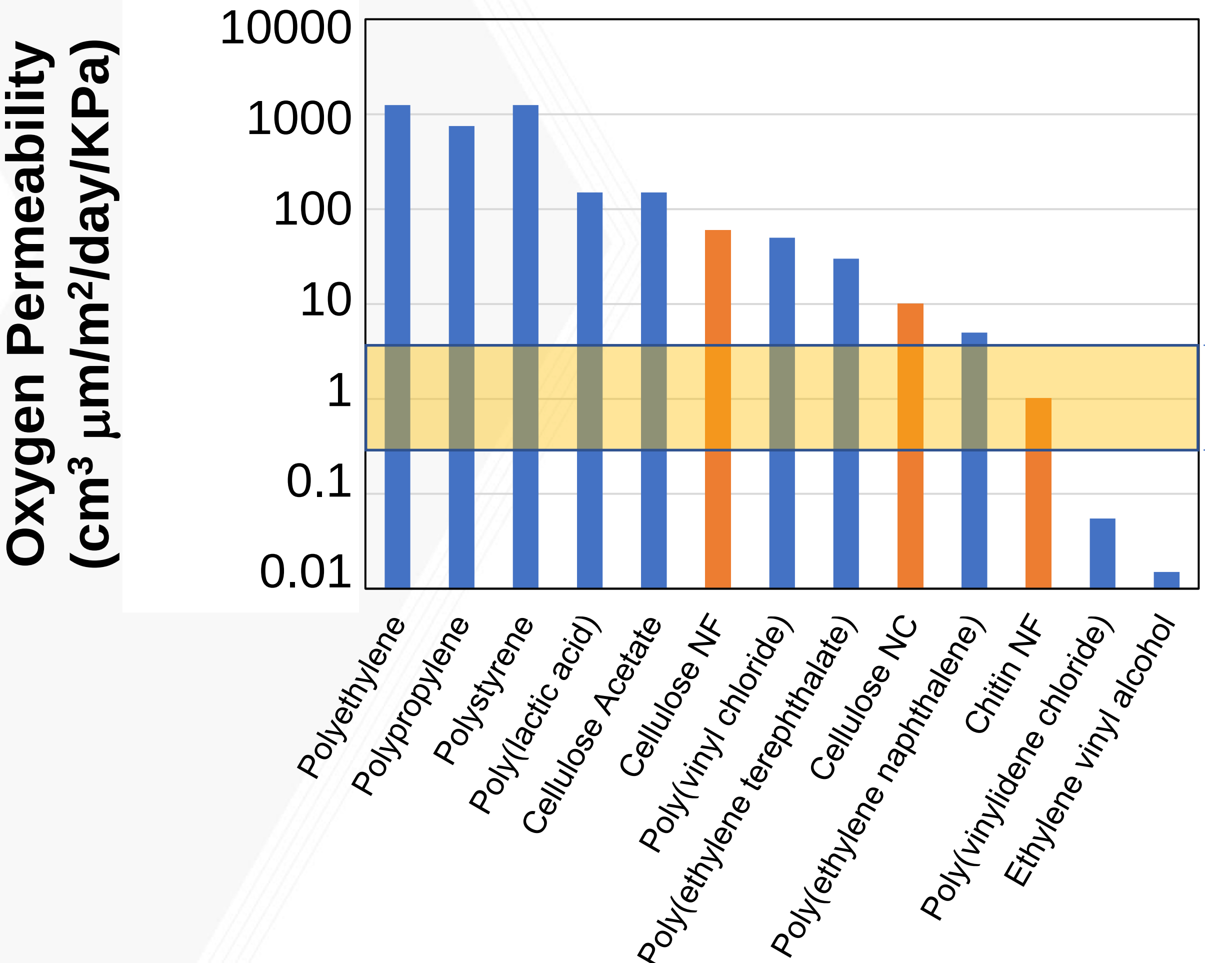




Petroleum Benchmarks (Blue)
Layers combined (sometimes metallized) to achieve
- O2 barrier
- Water vapor barrier
- Mechanical, sealing, printing, etc.

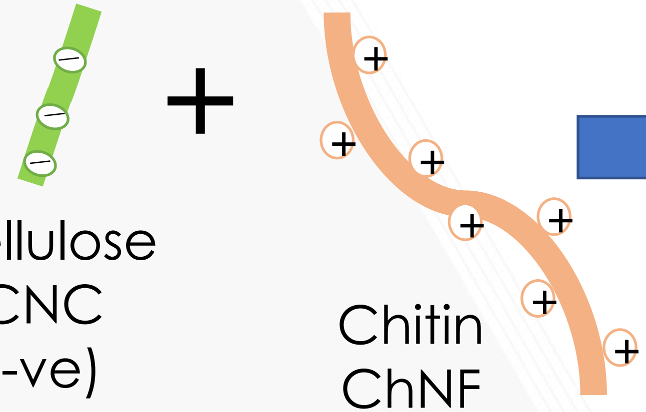
Biomass Options (Orange)
Cellulose nanofiber (CNF)
Cellulose nanocrystal (CNC)
Chitin nanofibers (ChNF)

Typical food packaging range for 1 mil thick film, 50%-80% RH

But these biomass material values are for pure materials slowly dried in lab.

Not manufactured at scale.

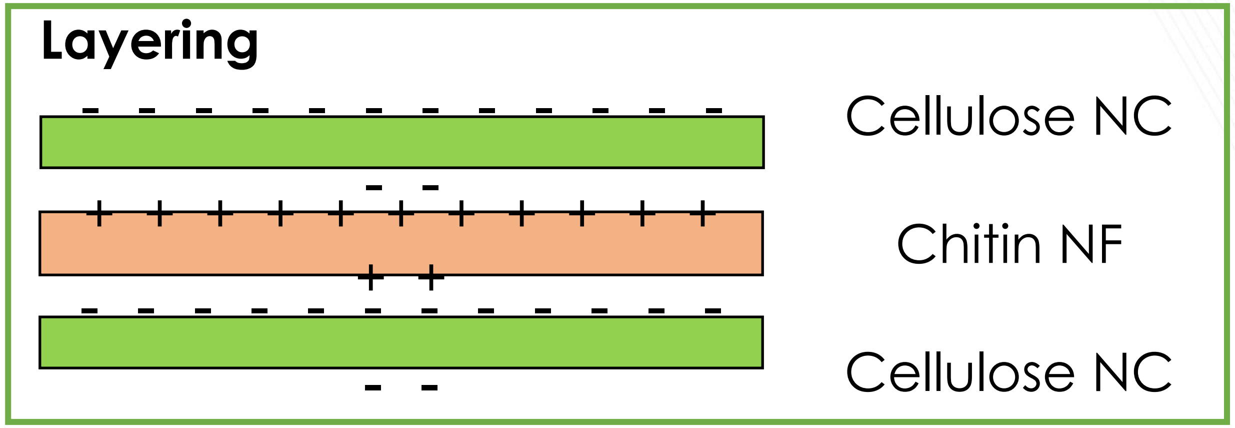
Combining CNC and ChNF



Cellulose CNC (-ve)

Chitin ChNF (+ve)

Charge stabilized suspensions



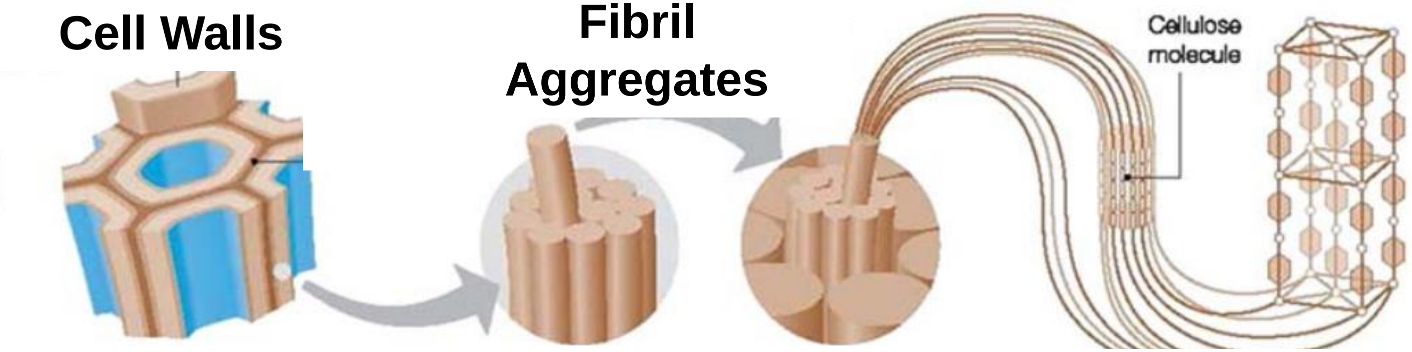
Blending

Khan et al., Carb. Polym. **2012** *90* 1601
Reinforced chitosan with CNCs

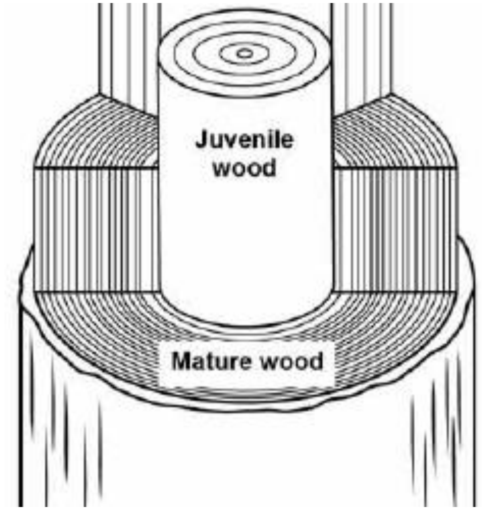
Cellulose Nanomaterials

Cell Walls

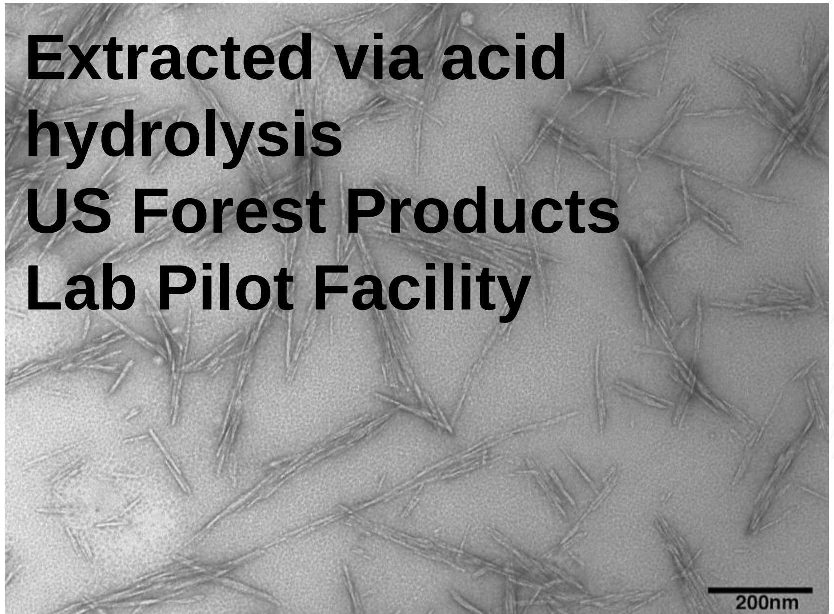
Fibril Aggregates



Fibers mm/mm | **Fibrils** mm/nm | **Crystals,** nm/Å



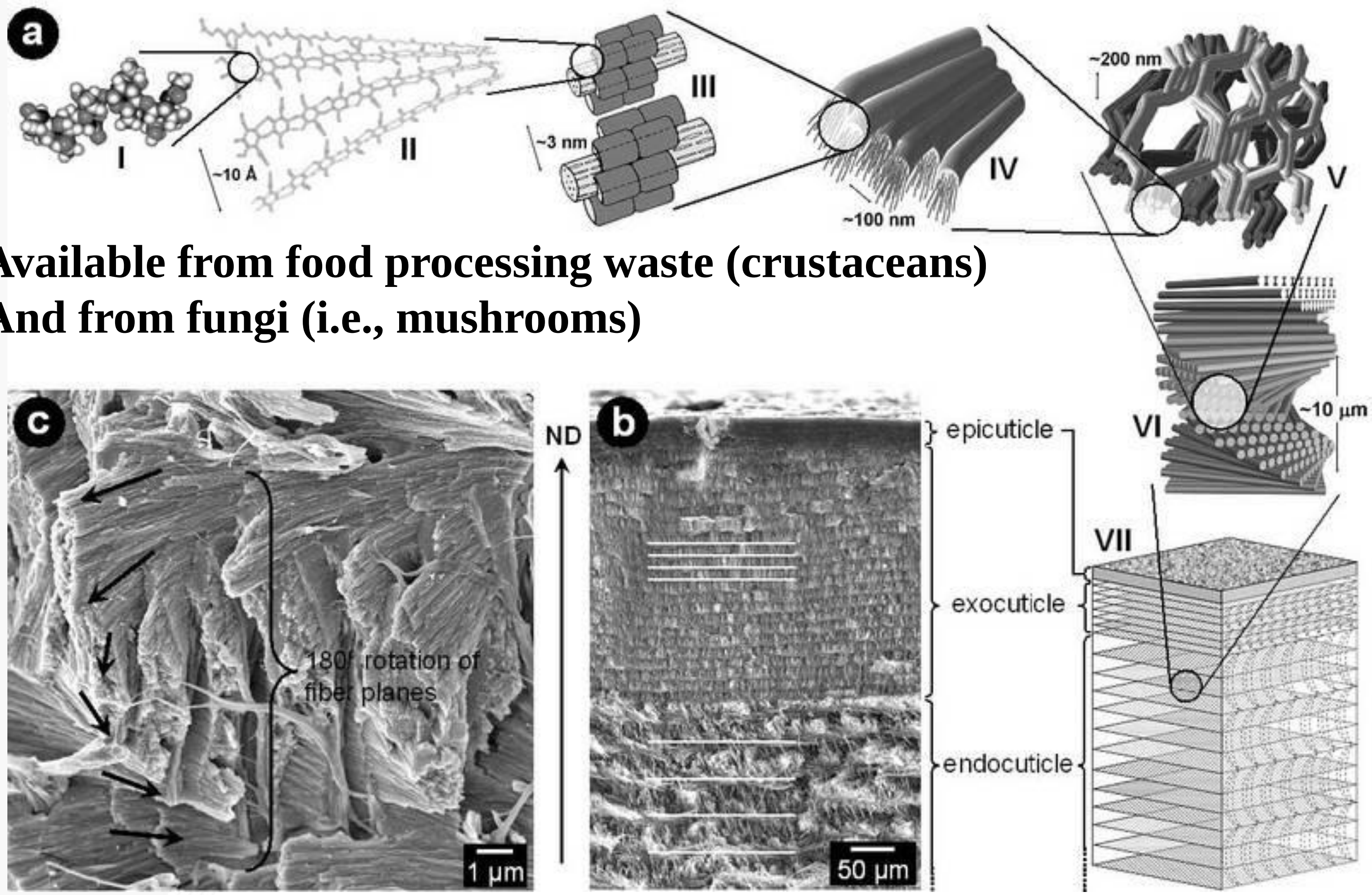
<u>Cellulose Nanocrystals</u> (CNCs)



Extracted via acid hydrolysis
US Forest Products Lab Pilot Facility

Chitin

Hierarchical architecture in nature



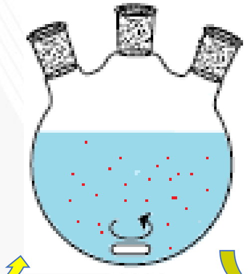
Available from food processing waste (crustaceans)
And from fungi (i.e., mushrooms)

http://www.mpie.de/index.php?id=2957&L=0

Acta Materialia 2005, 53: 4281

ChNF Processing & Optimization

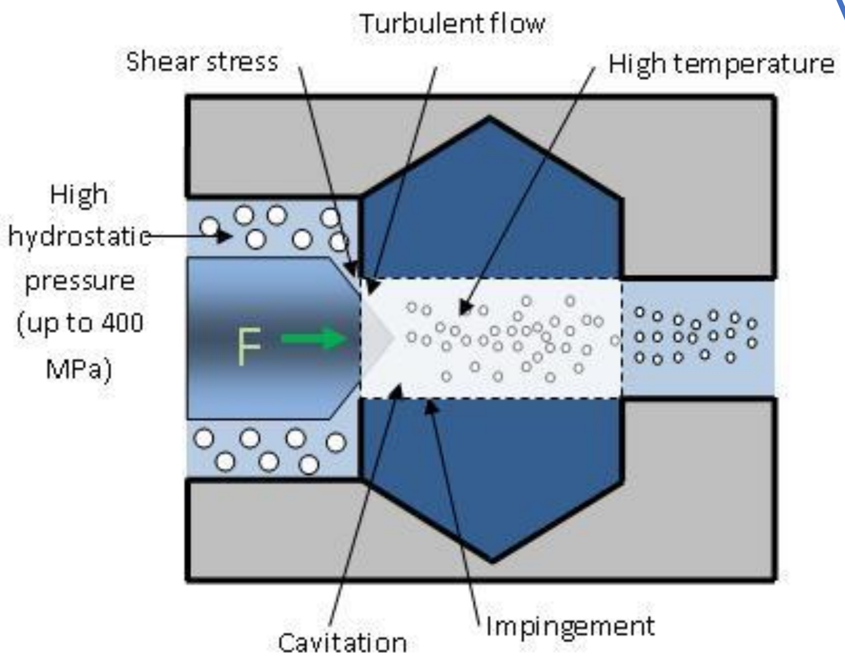
Chitin Biomass (shells or fungi)



Deproteination
Dimineralization
Deacetylation

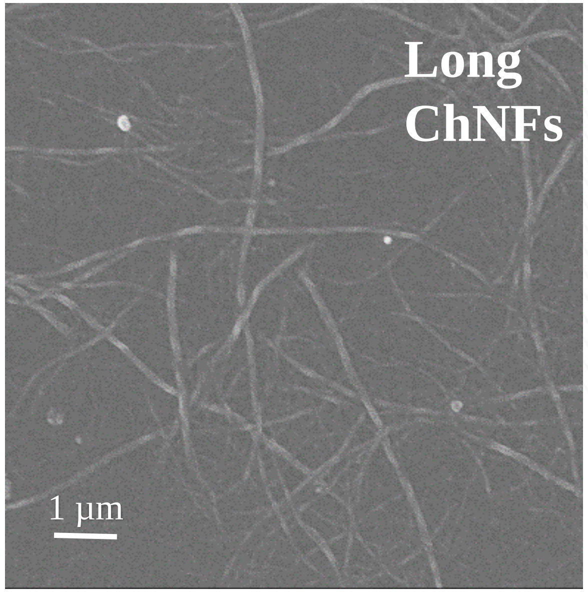
Purified chitin/water

Mechanical shearing



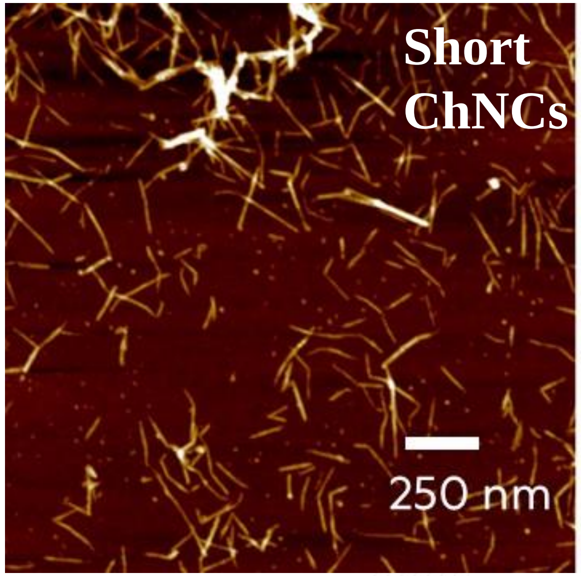
<u>size</u> and <u>charge</u> tunable via process intensity

→ control complexation with CNC



Fibers, lower charge

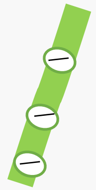
Meredith *Biomacromolecules* **2014, 2019**



Crystals higher charge

Unpublished **2019**

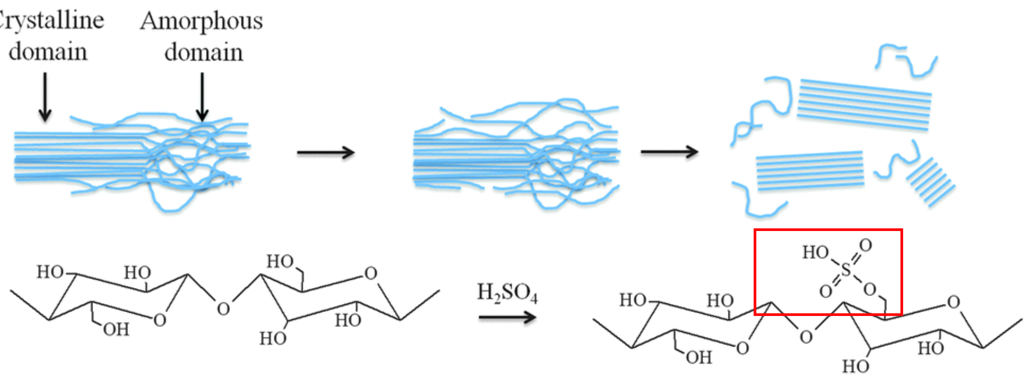
Layering materials with opposite charges



+

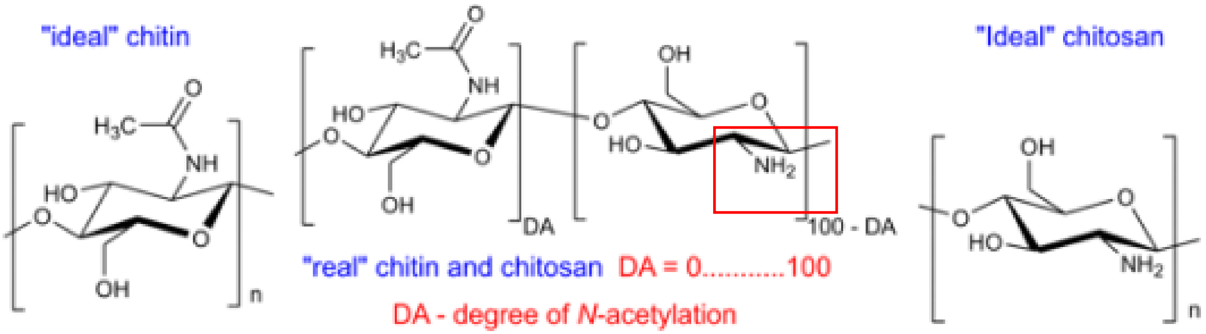
Cellulose
CNC
(-ve)

Chitin
ChNF
(+ve)



CNC sulfate half ester (-ve)

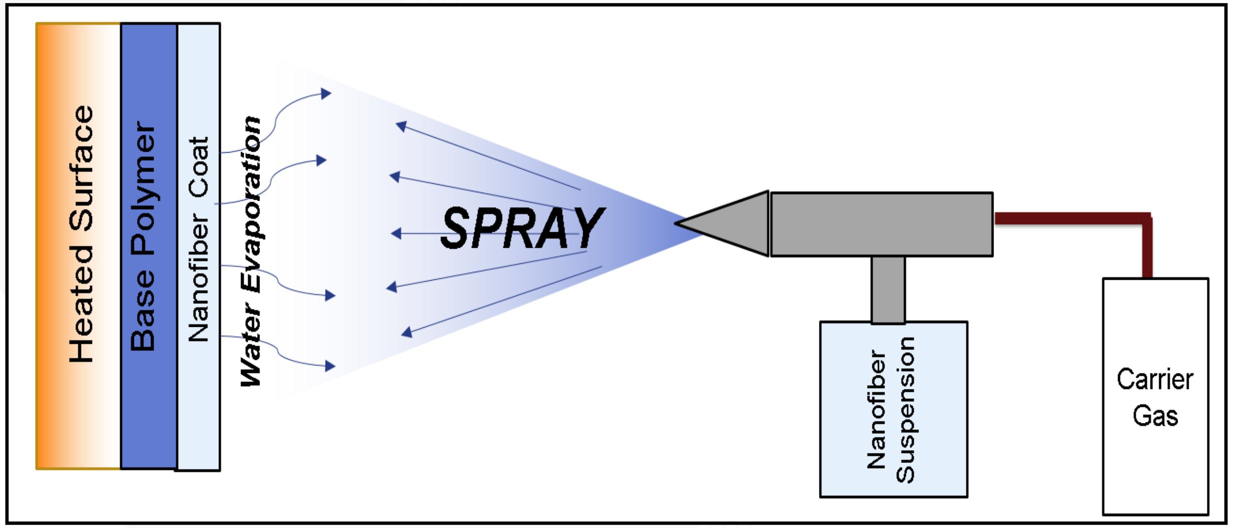
Charge stabilized suspensions

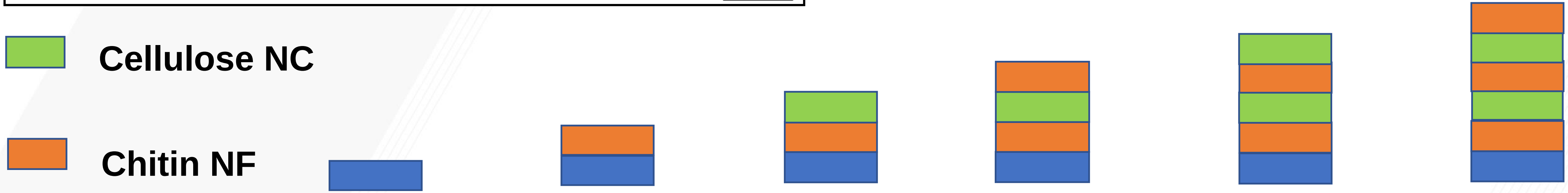


Chitin amine group(+ve)

Satam et al. 2018. Spray-Coated Multilayer Cellulose Nanocrystal—Chitin Nanofiber Films for Barrier Applications. *Sus. Chem. Eng*. 6(8) pp 10637-10644
Ehmann et al. **2014**. Design of anticoagulant surfaces based on cellulose nanocrystals. Chem. Commun., 2014,50, 13070-13072
Kumirska et al. **2011** Biomedical Activity of Chitin/Chitosan Based Materials—Influence of Physicochemical Properties Apart from Molecular Weight and Degree of N-Acetylation. *Polymers* 3, 1875-1901.

Multilayer coatings





No Layer Control

1 Layer
PLA-ChNF
PLA-CNC

2 Layers
PLA-(ChNF-CNC)$_1$

3 Layers
PLA-(ChNF-CNC)$_1$-ChNF

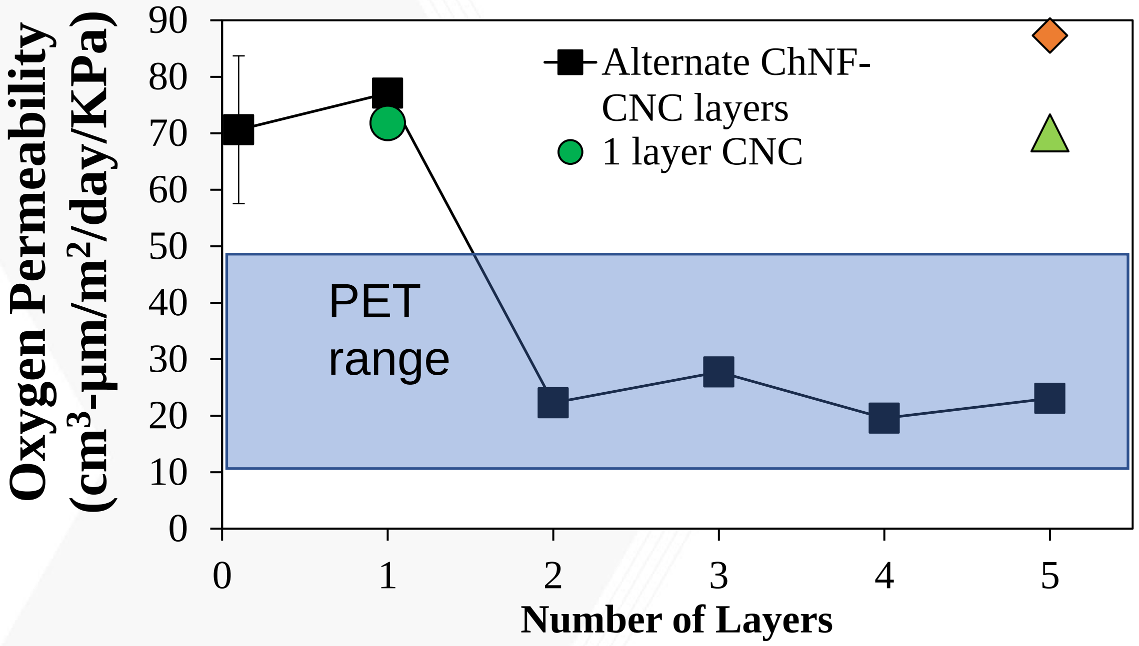
4 Layers
PLA-(ChNF-CNC)$_2$

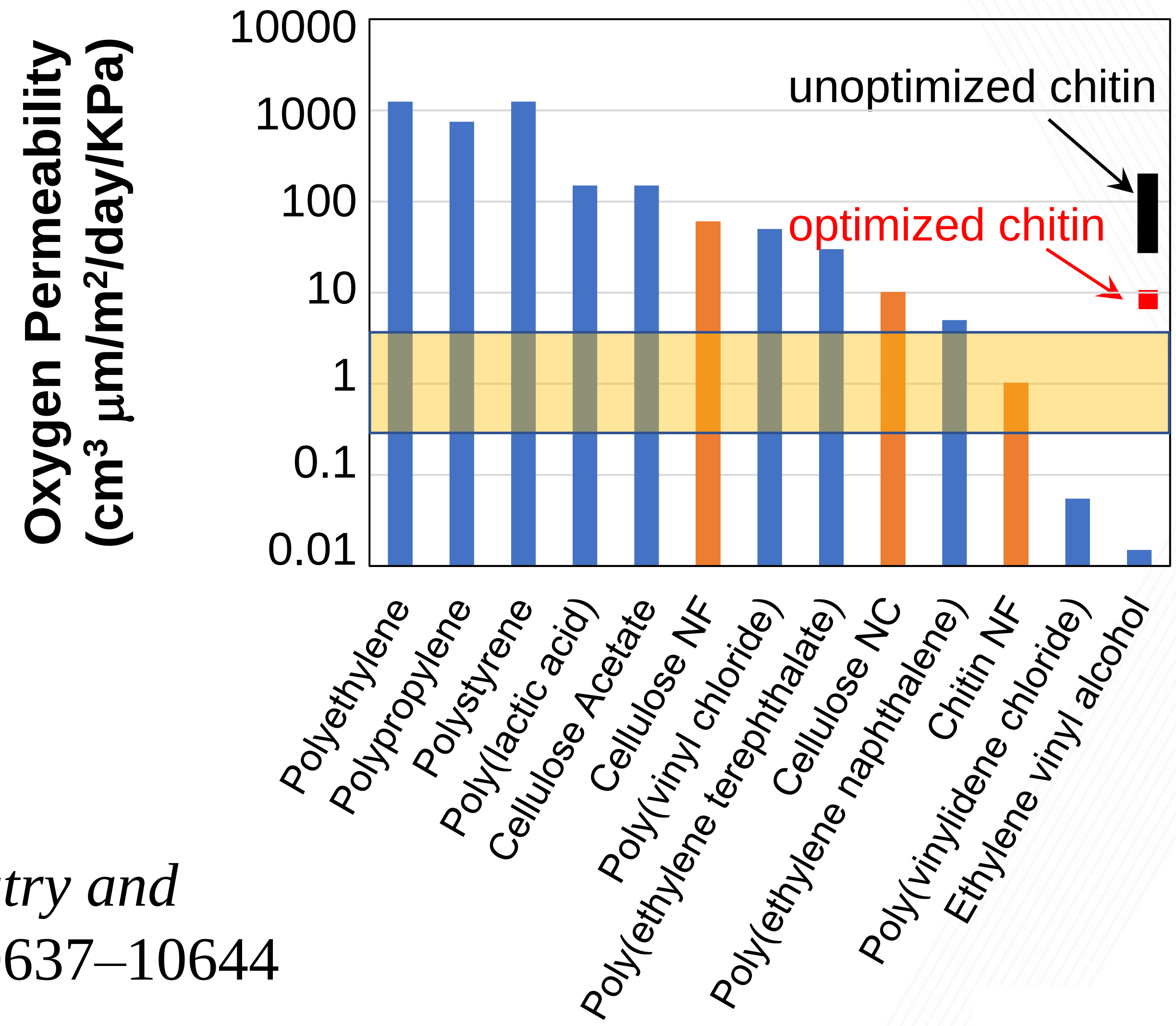
5 Layers
PLA-(ChNF-CNC)$_2$-ChNF
PLA-(ChNF/CNC)$_5$

- Substrate: poly(lactic acid) (PLA) film

Satam et al. 2018. Spray-Coated Multilayer Cellulose Nanocrystal—Chitin Nanofiber Films for Barrier Applications. *Sus. Chem. Eng*. 6(8) pp 10637-10644

Barrier Properties: O_2





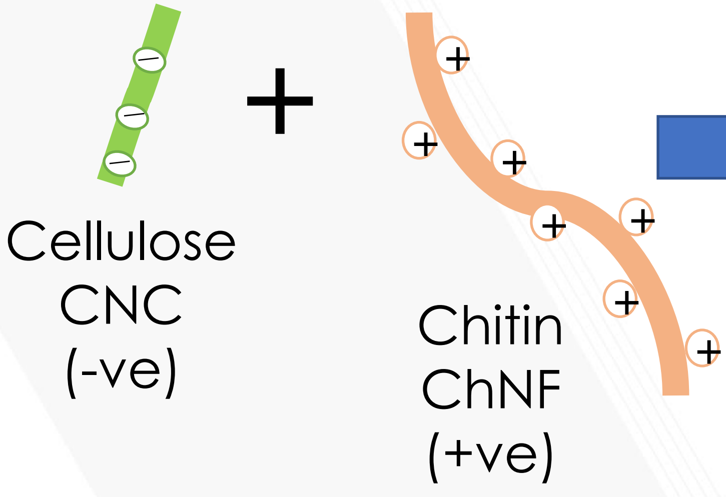
Cellulose NC

Chitin NF

PLA

ACS Sustainable Chemistry and Engineering, **2018**, *6*, 10637–10644

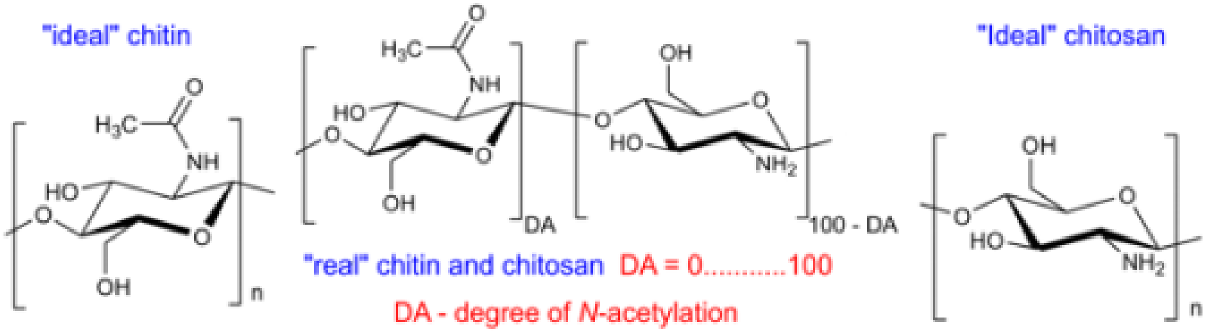
Layering materials with opposite charges



Charge stabilized suspensions

Optimizing ChNF Charge / Size

- Optimize preprocessing: control size and charge of chitin
- Optimize deposition: controls alignment and density
- Utilize crosslinking: diminish H2O sensitivity and WVTR



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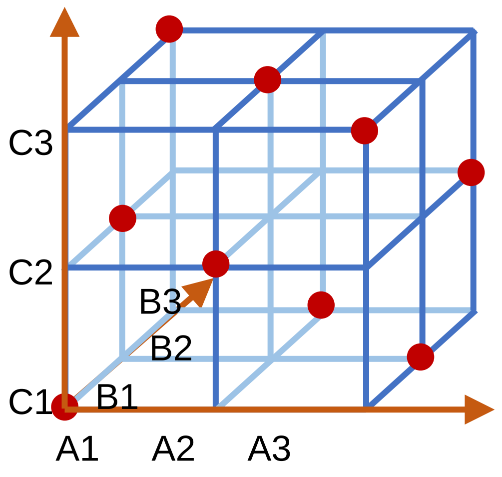
Systematic studies of ChNF preparation

- 3-factor, 3-level: 27 (3^3) -> 9
- Test cases are dispersed uniformly
- Objectives:
  - Find optimized conditions
  - Find coupling among the factors
  - Find the contribution of effect of each factor



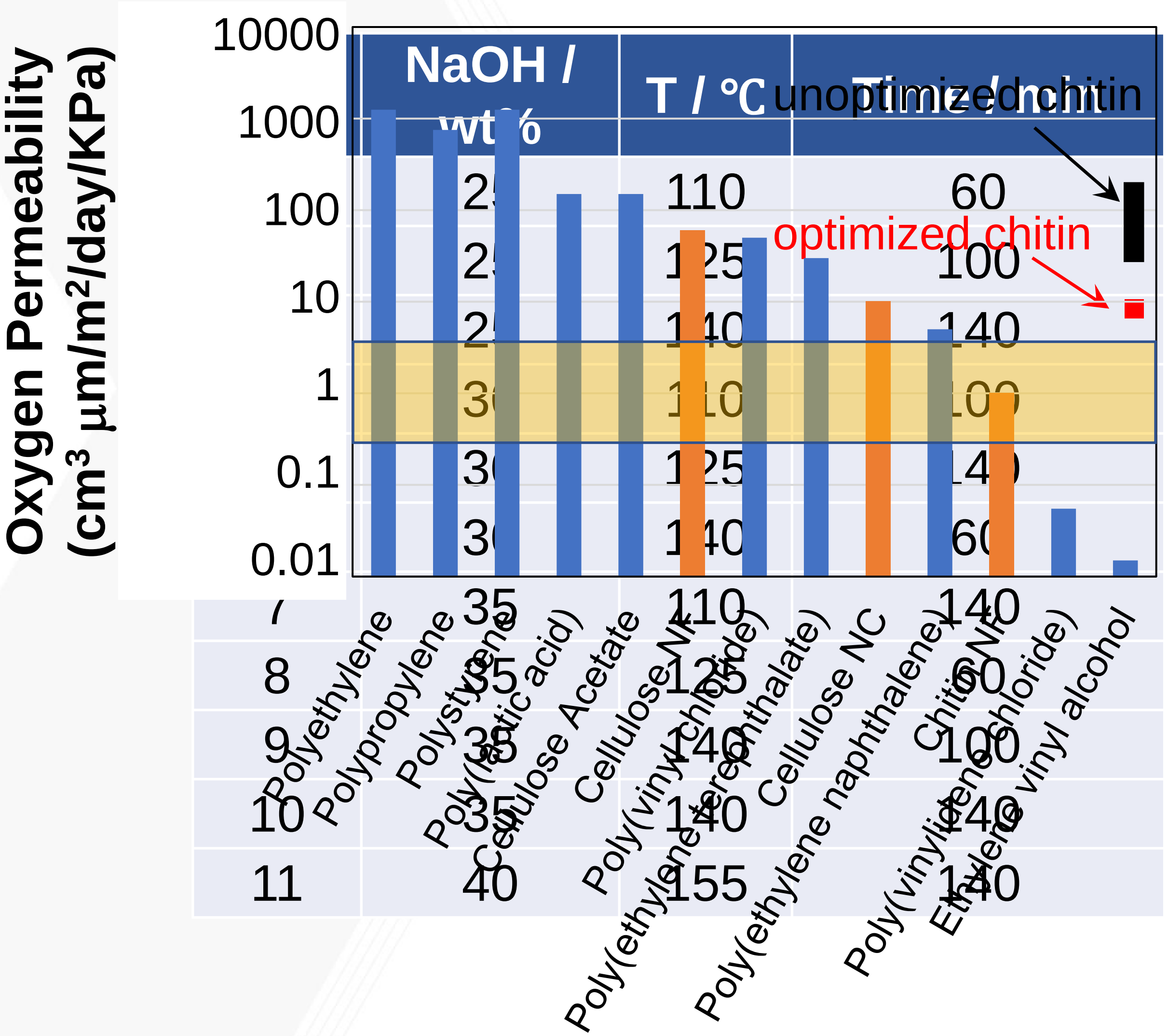
#	factor A	factor B	factor C	Name	c(NaOH)	Temperature	time
1	1	1	1	Or1-1	25 wt%	110 ℃	60 min
2	1	2	2	Or1-2	25 wt%	125 ℃	100 min
3	1	3	3	Or1-3	25 wt%	140 ℃	140 min
4	2	1	2	Or1-4	30 wt%	110 ℃	100 min
5	2	2	3	Or1-5	30 wt%	125 ℃	140 min
6	2	3	1	Or1-6	30 wt%	140 ℃	60 min
7	3	1	3	Or1-7	35 wt%	110 ℃	140 min
8	3	2	1	Or1-8	35 wt%	125 ℃	60 min
9	3	3	2	Or1-9	35 wt%	140 ℃	100 min

Systematic studies of ChNF preparation

ChNF	pH	DA / %	Viscosity at the lower limit of shear rate / cP	Size of fibers / nm	
				Length	Diameter
Or1-1	3.07	88.8±1.4	67 (10.00 s^{-1})	417±298	5.3±1.5
Or1-2	3.16	88.8±3.1	31 (25.12 s^{-1})	392±268	7.5±3.1
Or1-3	3.12	93.1±0.8	60 (15.85 s^{-1})	287±181	4.9±2.4
Or1-4	3.15	93.7±1.9	118 (10.00 s^{-1})	360±234	3.7±1.2
Or1-5	3.27	85.7±1.5	22 (25.12 s^{-1})	205±104	5.5±1.4
Or1-6	3.12	93.4±1.0	34 (15.85 s^{-1})	260±209	4.5±2.2
Or1-7	3.26	86.5±1.1	47 (15.85 s^{-1})	224±115	3.5±1.3
Or1-8	3.21	89.0±0.8	24 (25.12 s^{-1})	294±160	4.5±2.0
Or1-9	3.32	84.1±1.7	18 (25.12 s^{-1})	169±97	4.5±2.2
Or1-opt	3.24	75.1±1.5	28 (25.12 s^{-1})	176±96	2.1±1.0

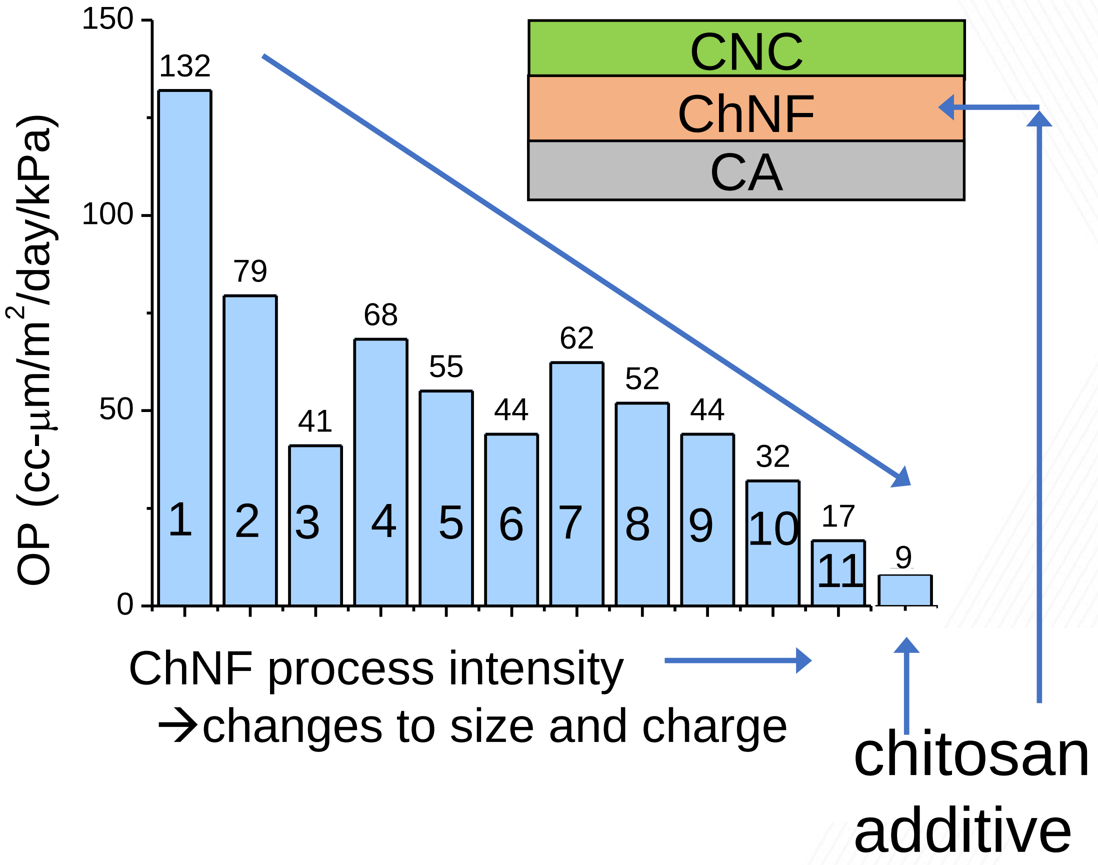
Or1-1 through Or1-9 →

Multilayer ChNF and CNC: Shows importance of processing

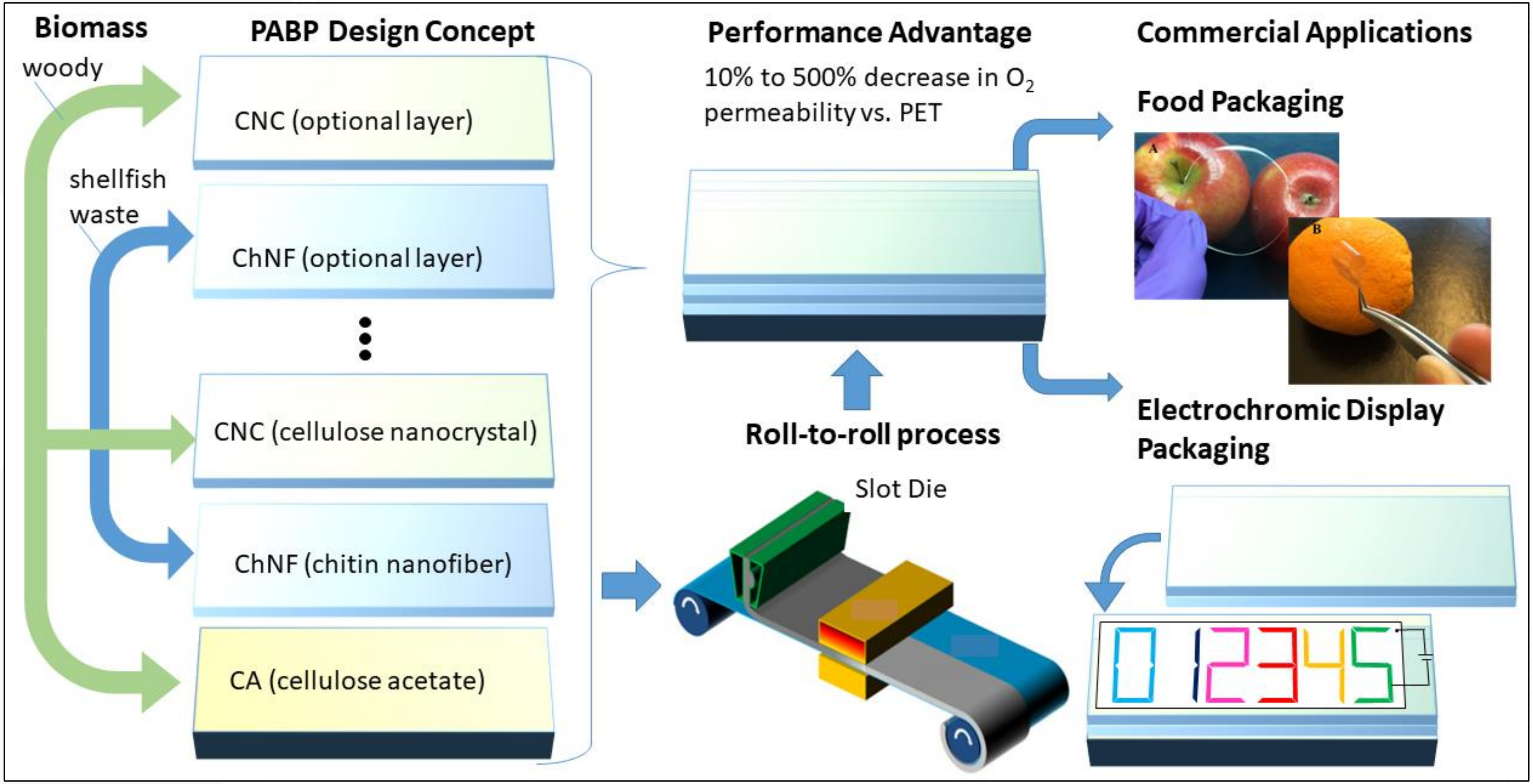


	NaOH / wt%	T / °C	Time / min
[illegible]	25	110	60
[illegible]	25	125	100
[illegible]	25	140	140
[illegible]	30	110	100
[illegible]	30	125	140
[illegible]	30	140	60
7	35	110	140
8	35	125	60
9	35	140	100
10	35	140	140
11	40	155	140

Sprayed ChNF or ChNC + CNC on cellulose acetate (CA)



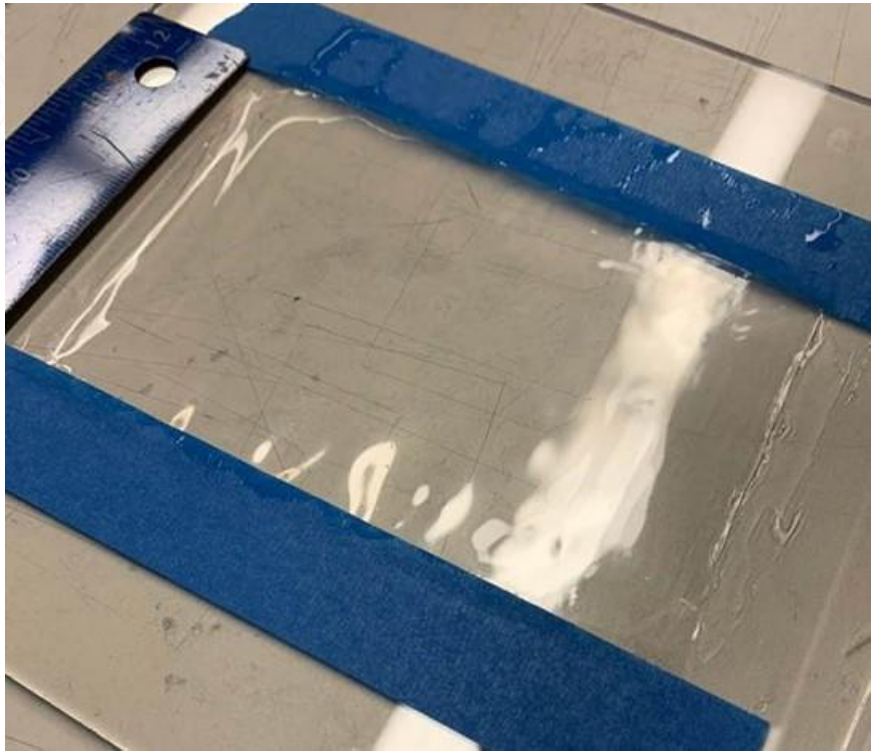
Scalability of Deposition: Spray to Roll Coating

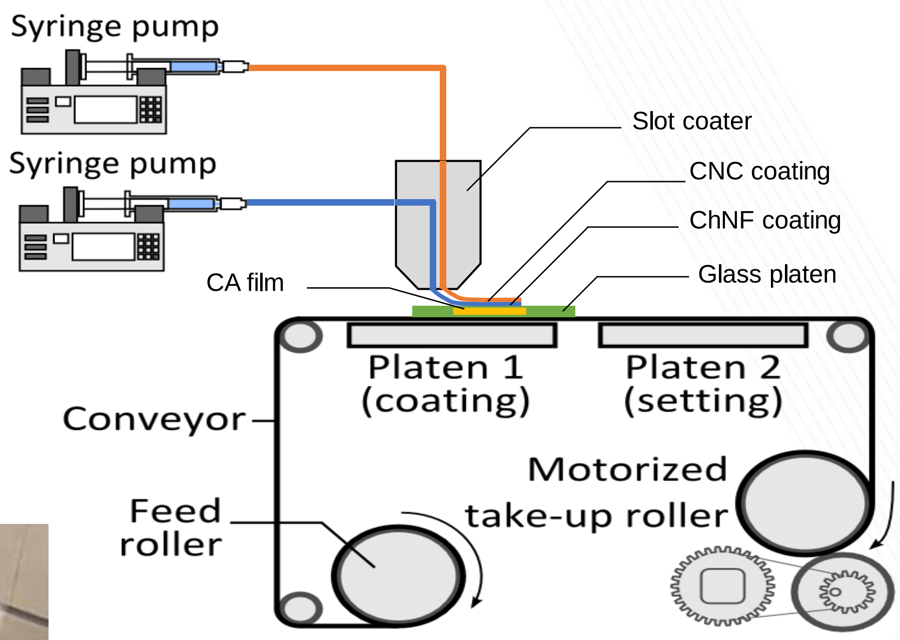


C. Meredith
M. Shofner
T. Harris
J. Reynolds

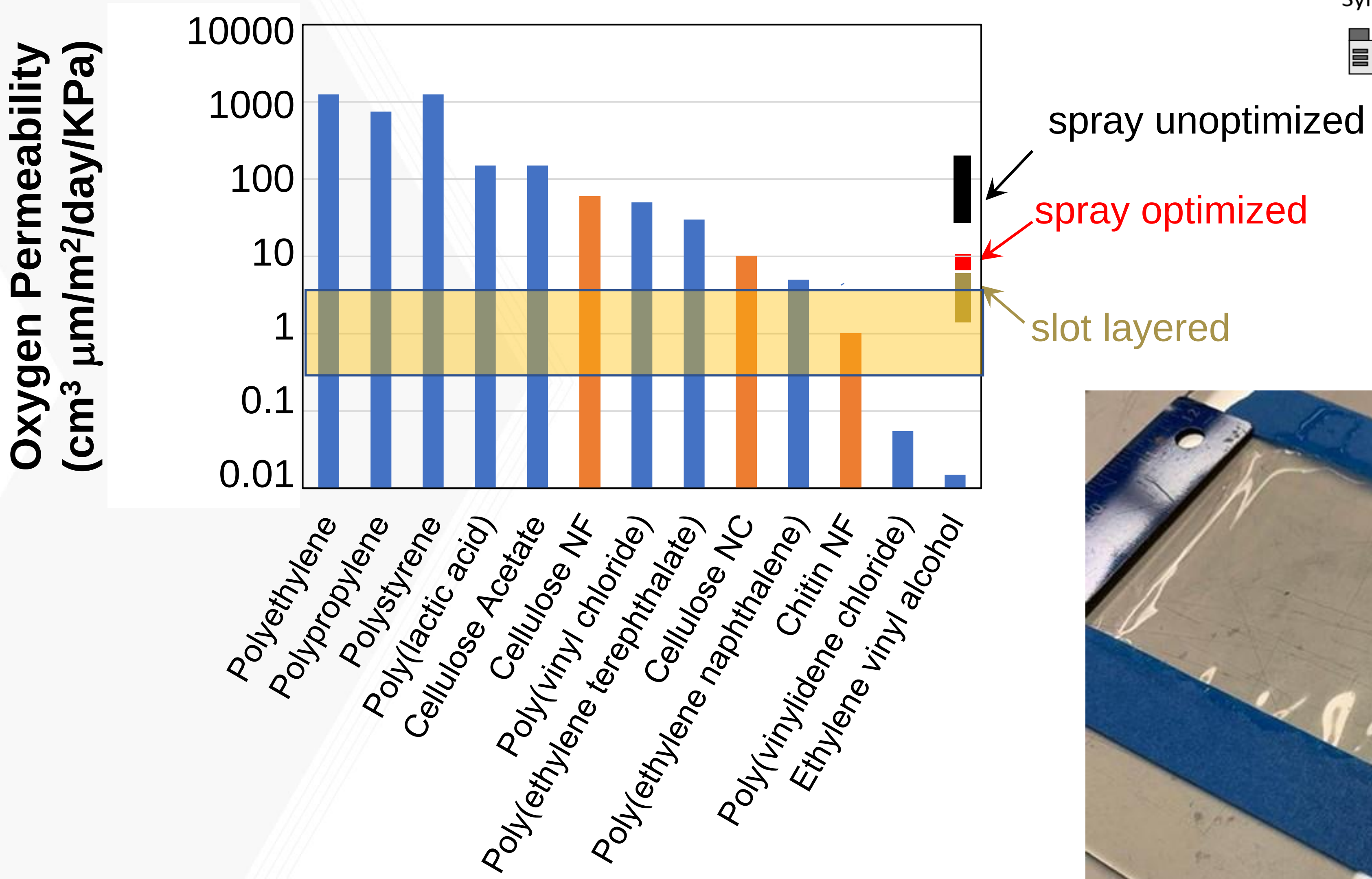
Dual die coating – CA-ChNF-CNC

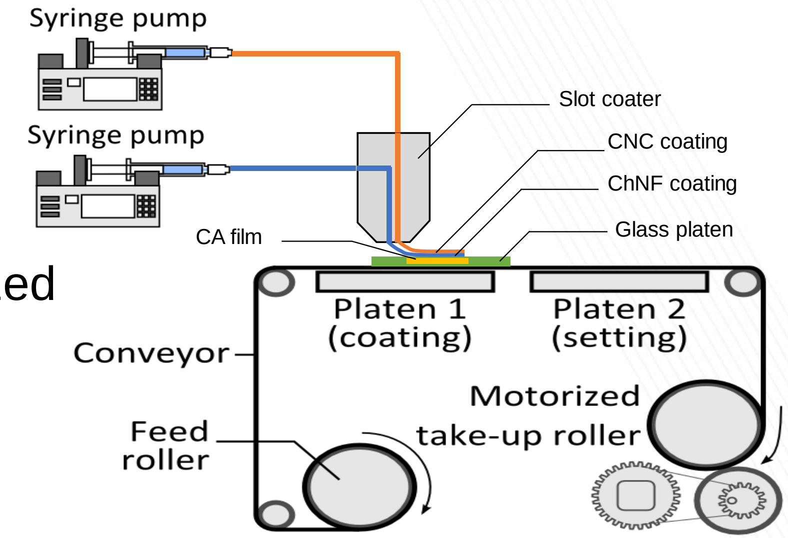
with Tequila Harris (ME)

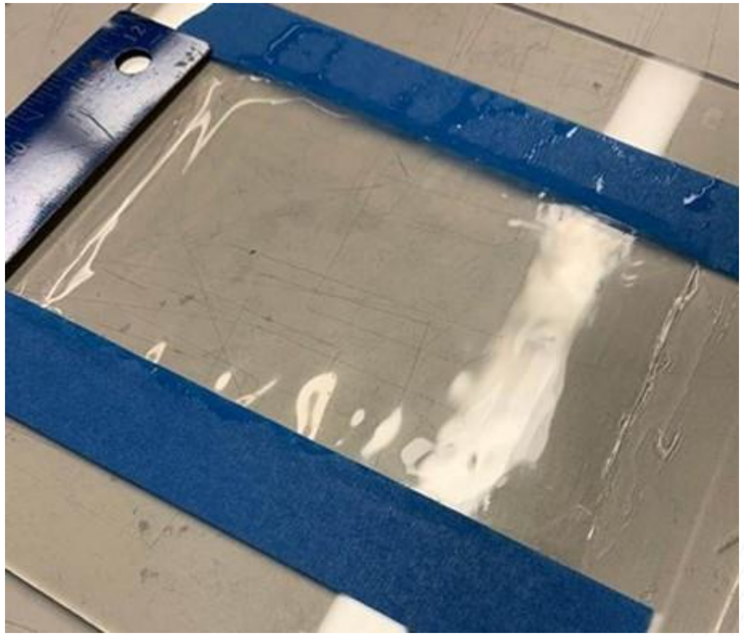




Slot-die coating





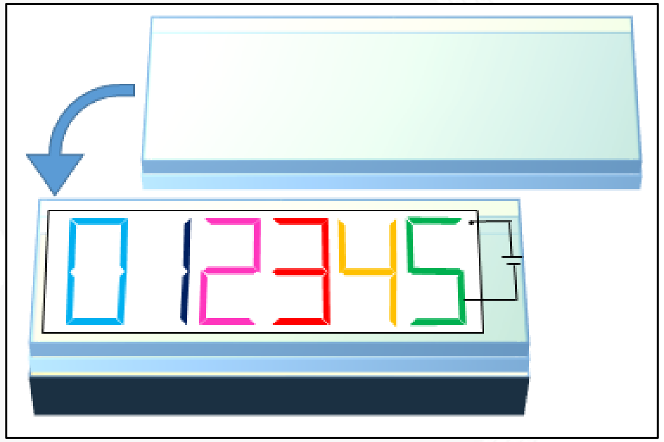


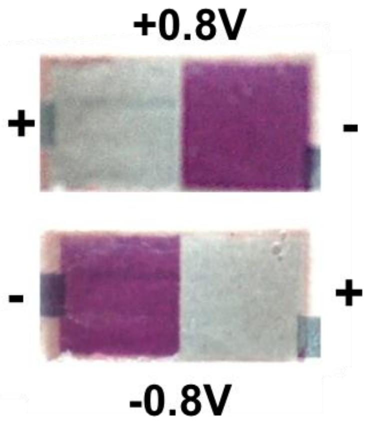
Encapsulating Electrochromic Devices

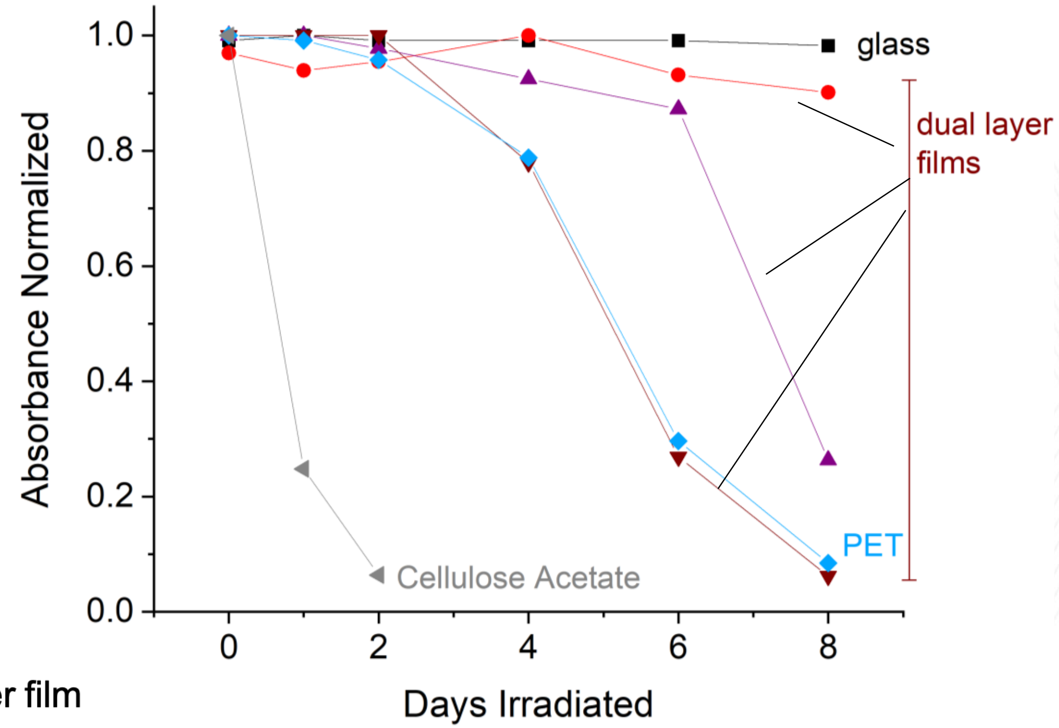
Performance of ECDs packaged in CNC/ChNF/CA barriers is near 3M FTB and better than PET.

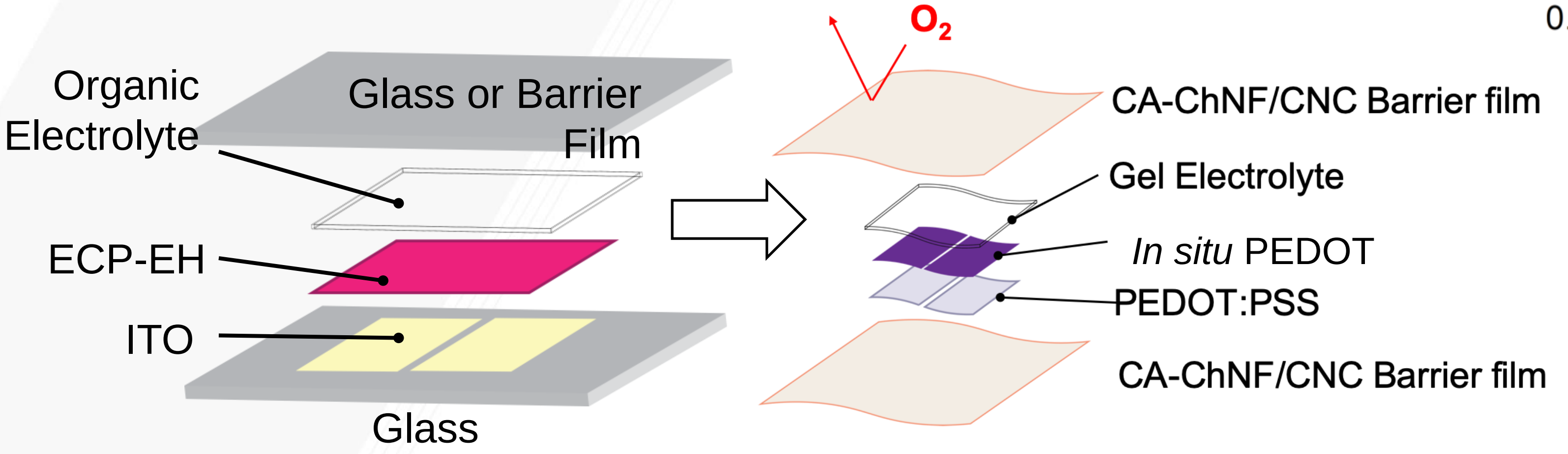
w/John Reynolds, CHEM@GT

Photostability



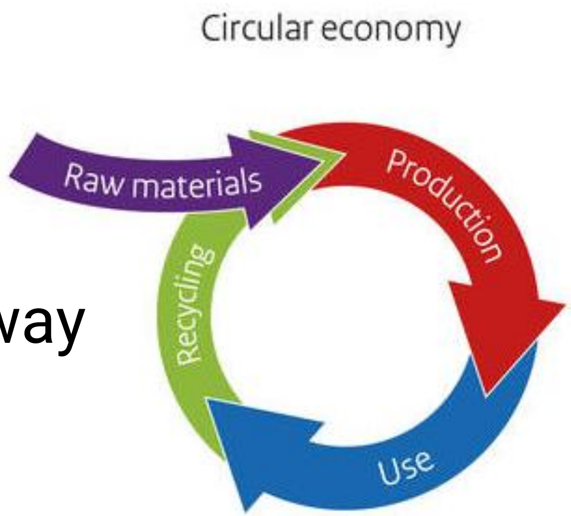


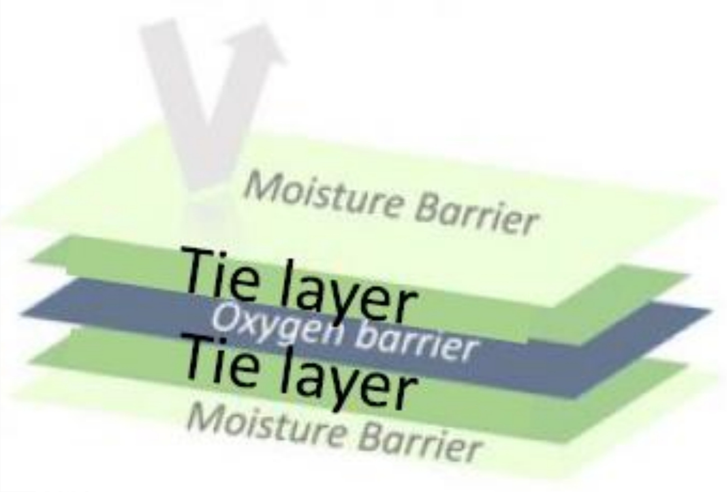




Conclusions

- Hybrid biomass-derived materials are a promising approach to circular functional barrier packaging
  - Allows renewable sourcing of some or all layers
  - Optimization towards O_2 and water targets
  - Compatible with layering or blending
  - Potentially biodegradable with food waste – study under way
    - Chitin-cellulose have been industrially composted together





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