Nanocellulose Paper Barrier Coatings

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Rationale

Plastics Waste

- Only ~9% recycled
- 18 billion lbs. of plastic enters oceans annually
- 40% of plastics used for packaging

Forest Management

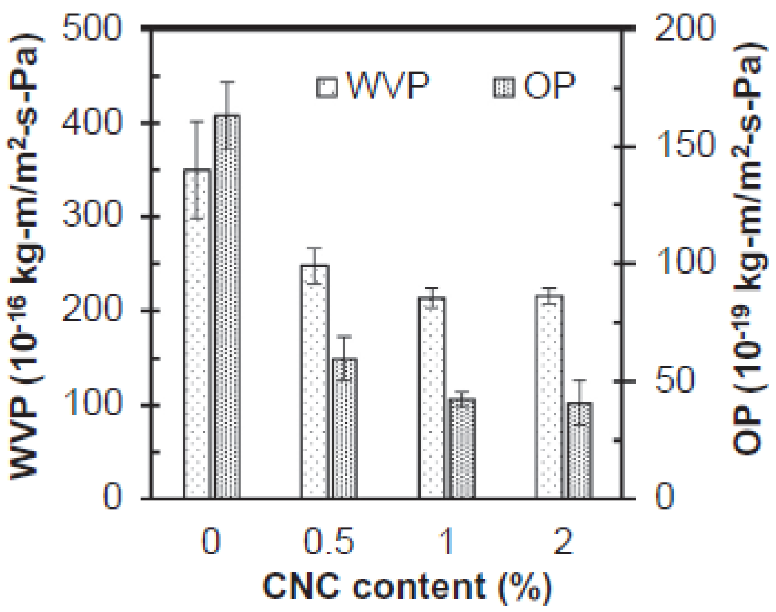
- Forest Management underfunded
- Fires are becoming increasingly expensive and impactful

Rationale

Packaging

- Packaging market is near $1 T; U.S. barrier film market is ~$4B
- Single-use packaging is driving growth
- Plastic recycle rate is ~9%; film recycle rate extremely low
- 146 million metric tons of plastic packaging

Previous Work: PLA-CNC composites

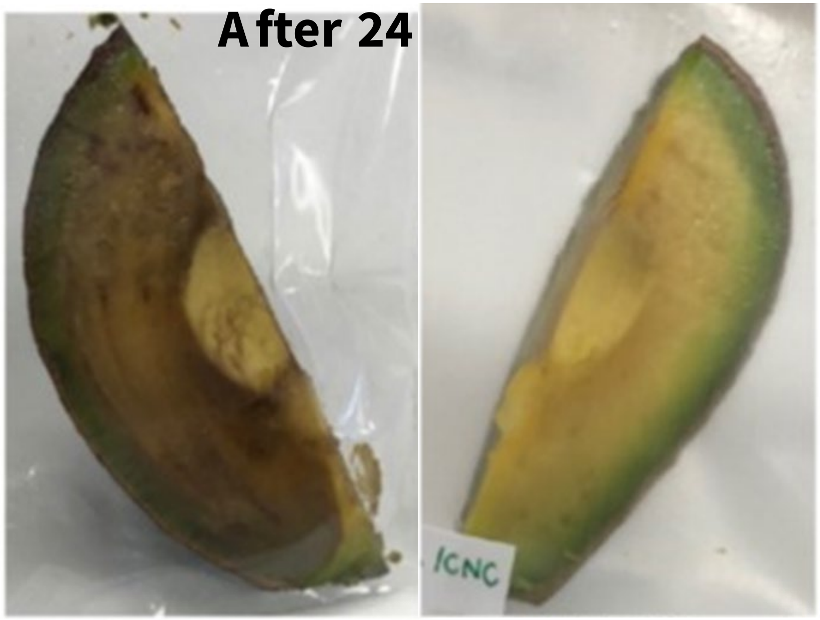


When adding CNCs to PLA

- Water vapor permeability decreased by about 40%
- Oxygen permeability decreased by about 75%

Karkhanis et al. *Composites Part A* 114 (2018) 204–211

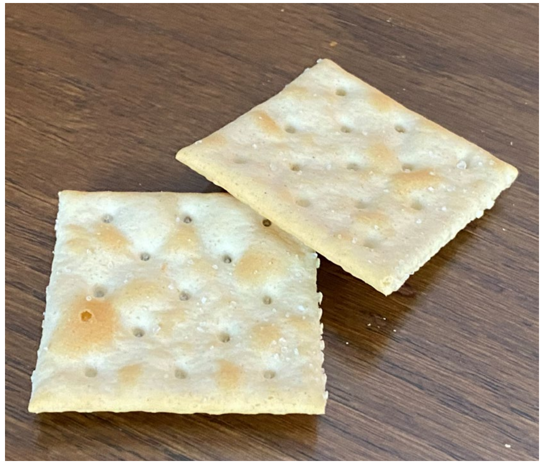
Avocados in biobased packaging After 24



PLA film PLA-CNC film

Wongthanaroj et al. *Applied Food Research* 2 (2022) 100222

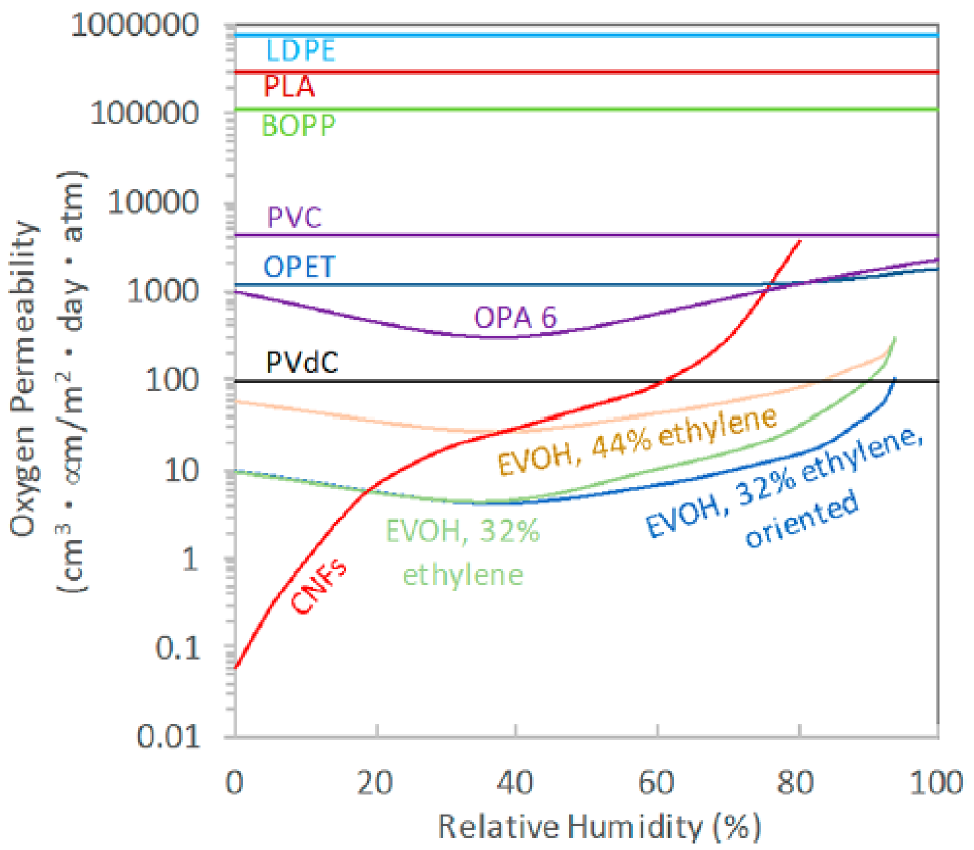
Food shelf-life testing



% RH	Shelf-life (hours)		
	PLA[1]	PLA/1% CNC[1]	Delayed time (hours) to reach CMC
10	Shelf-stable	Shelf-stable	
33	Shelf-stable	Shelf-stable	
50	Shelf-stable	Shelf-stable	
61	63.4 ± 0.6^{A}	86.1 ± 1.6^{B}	22.7
79	42.9 ± 0.7^{A}	59.9 ± 5.1^{B}	17.0
99	14.2 ± 0.2^{A}	20.1 ± 0.4^{B}	5.9

Critical moisture content of 8% represents maximum moisture acceptable for consumers

Polymer Oxygen Permeability



Wang et al. ACS Sustainable Chem. Eng. 2018, 6, 49–70

- Barrier films have orders of magnitude oxygen transmission than PLA
- Nanocellulose films have barrier properties comparable to existing barrier polymers
- But cellulose is extremely moisture sensitive

Project Goals & Objectives

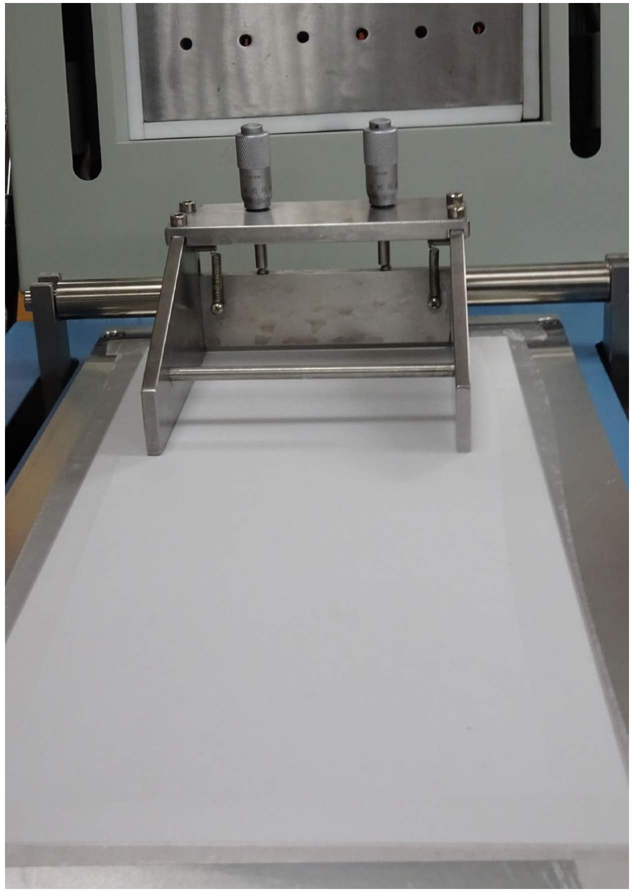
Goal

Produce biobased materials with durable oxygen and grease barriers for packaging applications

Objectives

- Evaluate effect of nanocellulose processing and formulations on paper barrier coatings
- Evaluate structure of films & relate to performance/processing
- Evaluate recyclability or biodegradability

Experimental – Coating Paper



- Doctor blade wet thickness of ~20 microns to 1.5 mm
- Coating speeds 1-100 mm/s, typically 12 or 50 mm/s
- CNCs, TEMPO-oxidized CNFs (TOCNs), mechanical CNFs
- Copy paper, Kraft paper, silicone-coated papers

Experimental - Characterization

- Oxygen transmission
  - ASTM D3985, MOCON OXTRAN 2/22
- Grease resistance
  - Oil drop method, TAPPI T559
  - Flexible film penetration, TAPPI T507
- Air permeability
  - Gurley method, T460
- Heptane transmission
  - ASTM E96 vapor cup method (developed for water transmission)

Additional experiments

- Microscopy
  - Optical, electron, AFM
- Additional air permeability tests
- Surface roughness
- Optical measurements
- Structural and chemical analyses
- Surface energy
- Mechanical properties

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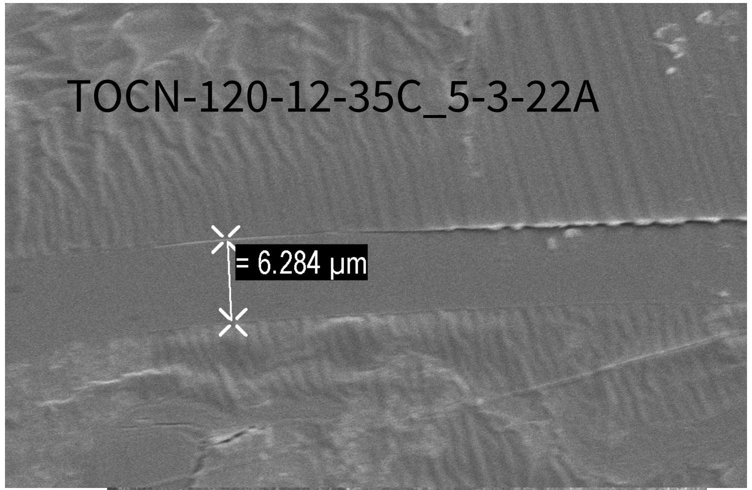
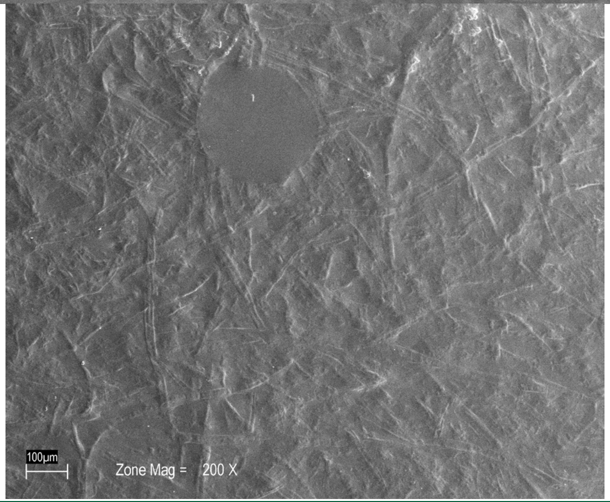
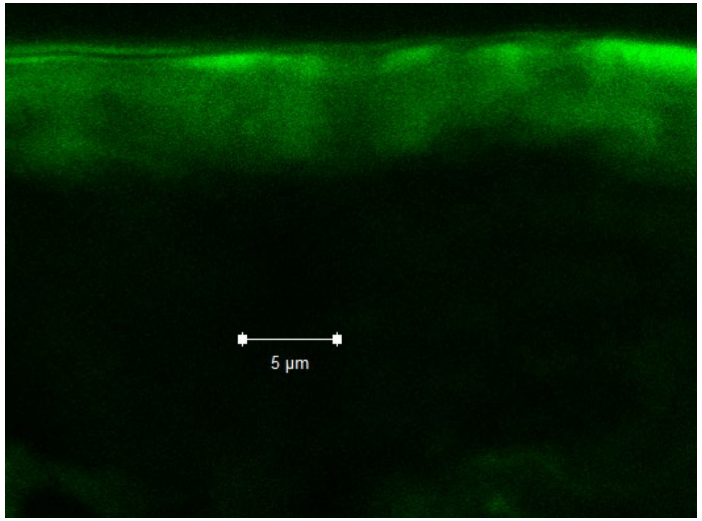
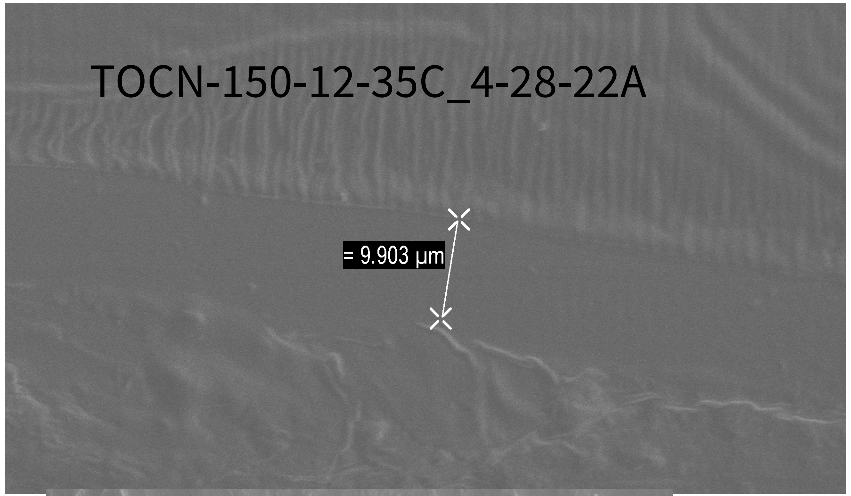
Visualizing TOCN coated papers

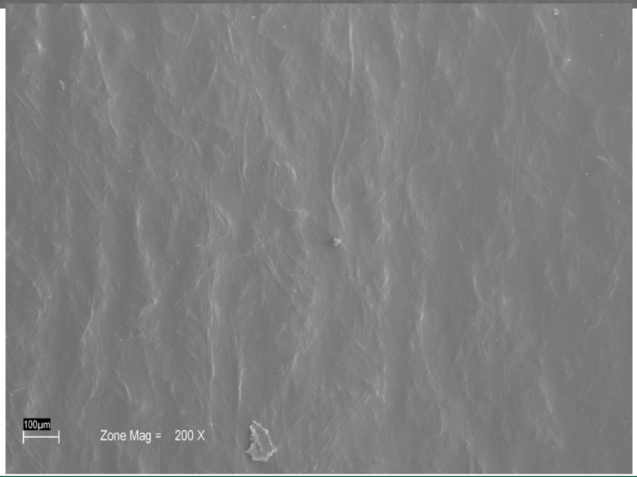






~6 g/m^2





~9 g/m^2

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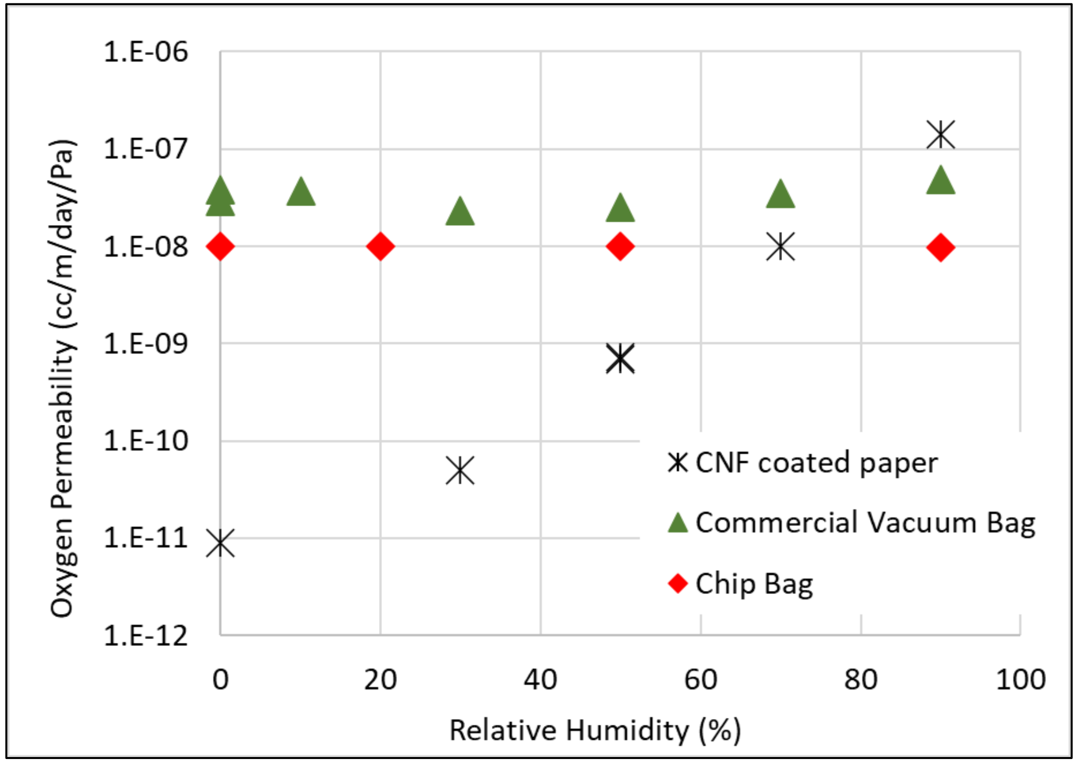
Oxygen Transmission



- ➢Nanocellulose has good vapor barrier properties, especially at low humidity
- ➢Oxygen transmission of CNF coated papers is comparable to or better than commercial barriers at ≤ 70% RH

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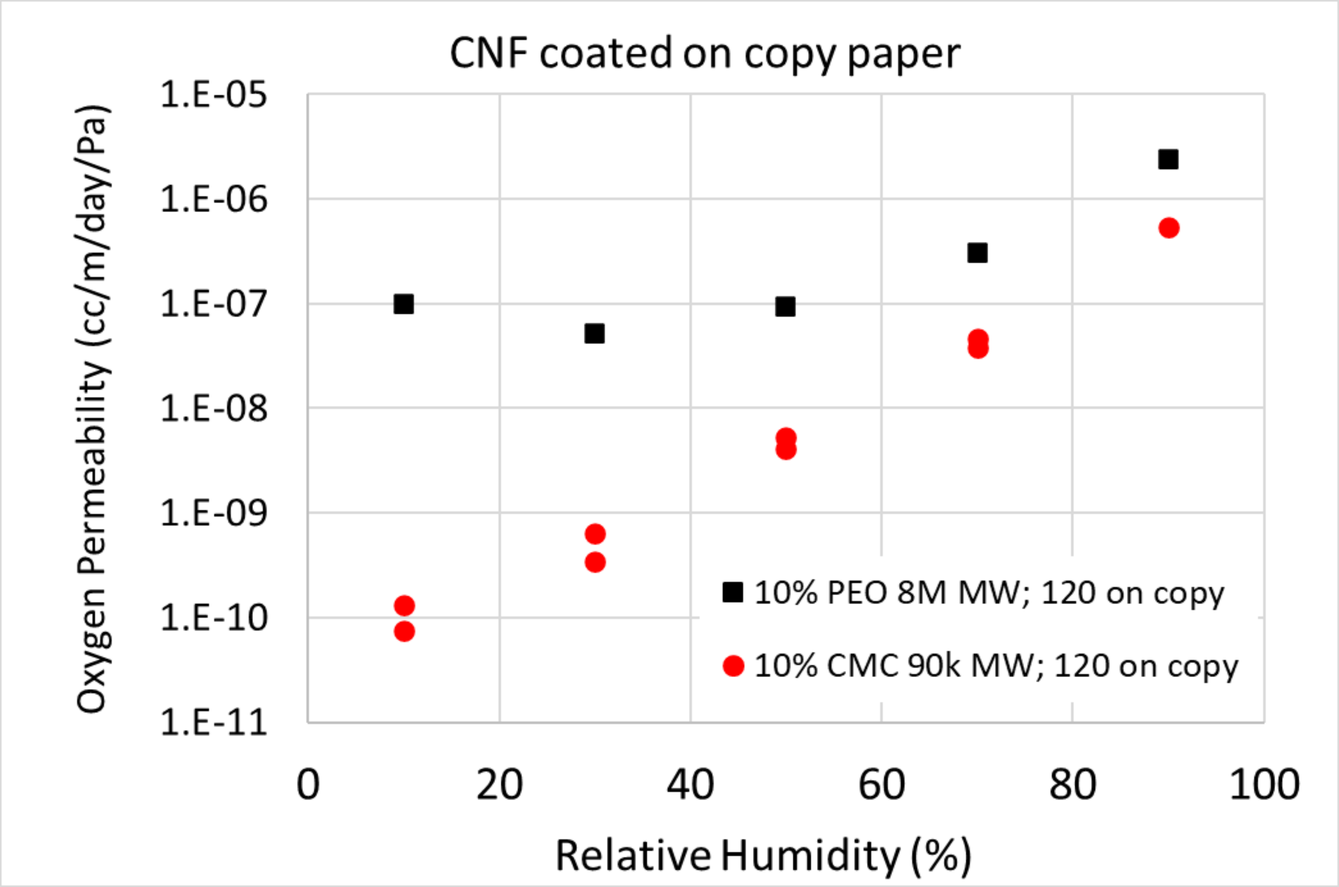
Oxygen Transmission Coated Papers



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Gurley Air Permeability –TAPPI T460

- ➢ Want a test for permeabilities above our MOCON limitations
- ➢ Standard Gurley method is better suited for high permeability

Copy paper > ~1 g/m2 TOCN coat > release paper ~2g/m2 TOCN coat > commercial films > thick CN films/coat

	Copy paper	~1 g/m2 TOCN coat	release paper	~2g/m2 TOCN coat	commercial films	thick CN films/coat
Gurley time (100 mL)	15 s	~1,000 s	40,000 s - ∞	∞		
MOCON OTR (cc/m2/day)	EXCEEDS MAXIMUM OTR →				20 - 50	0.01 - 500

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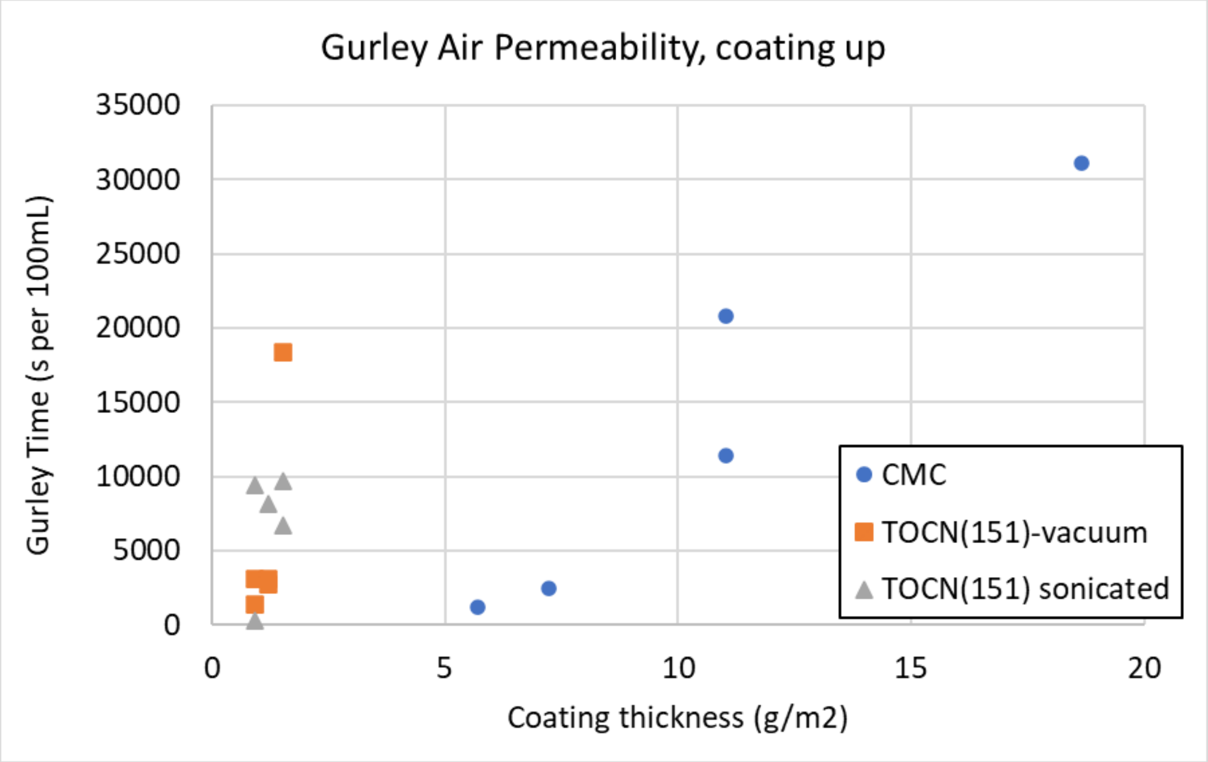
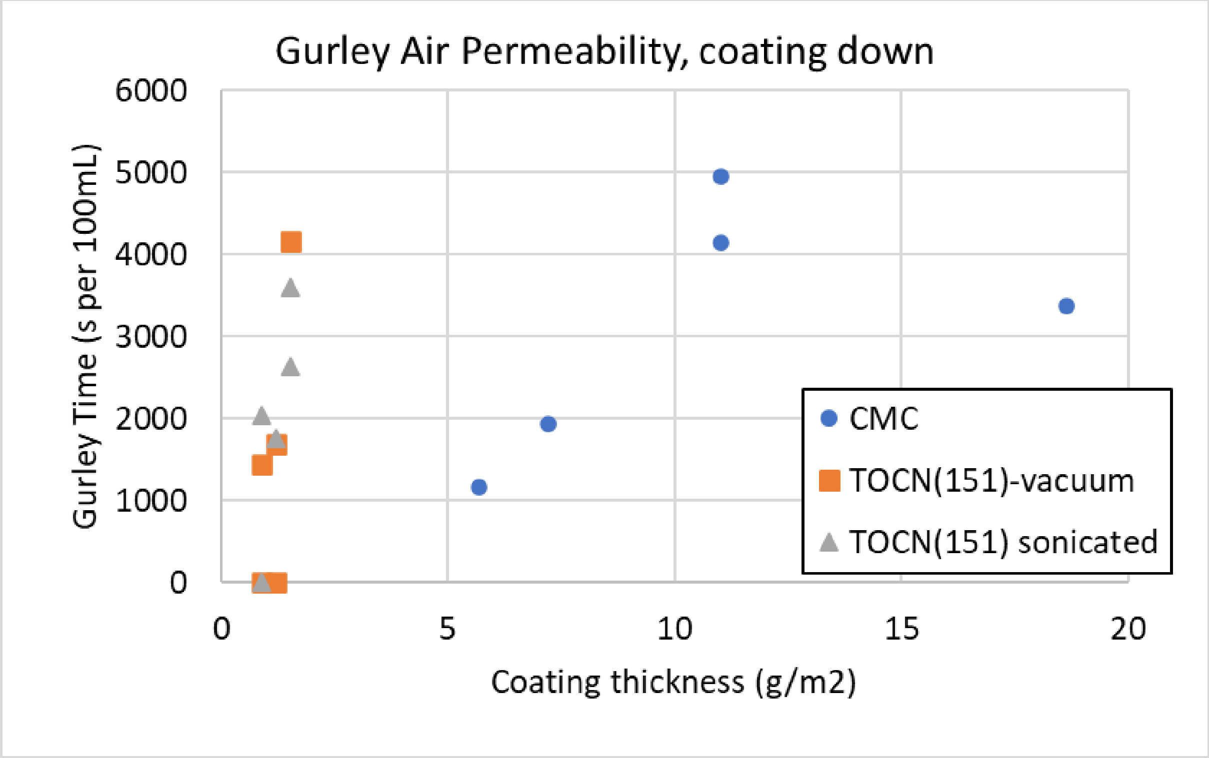
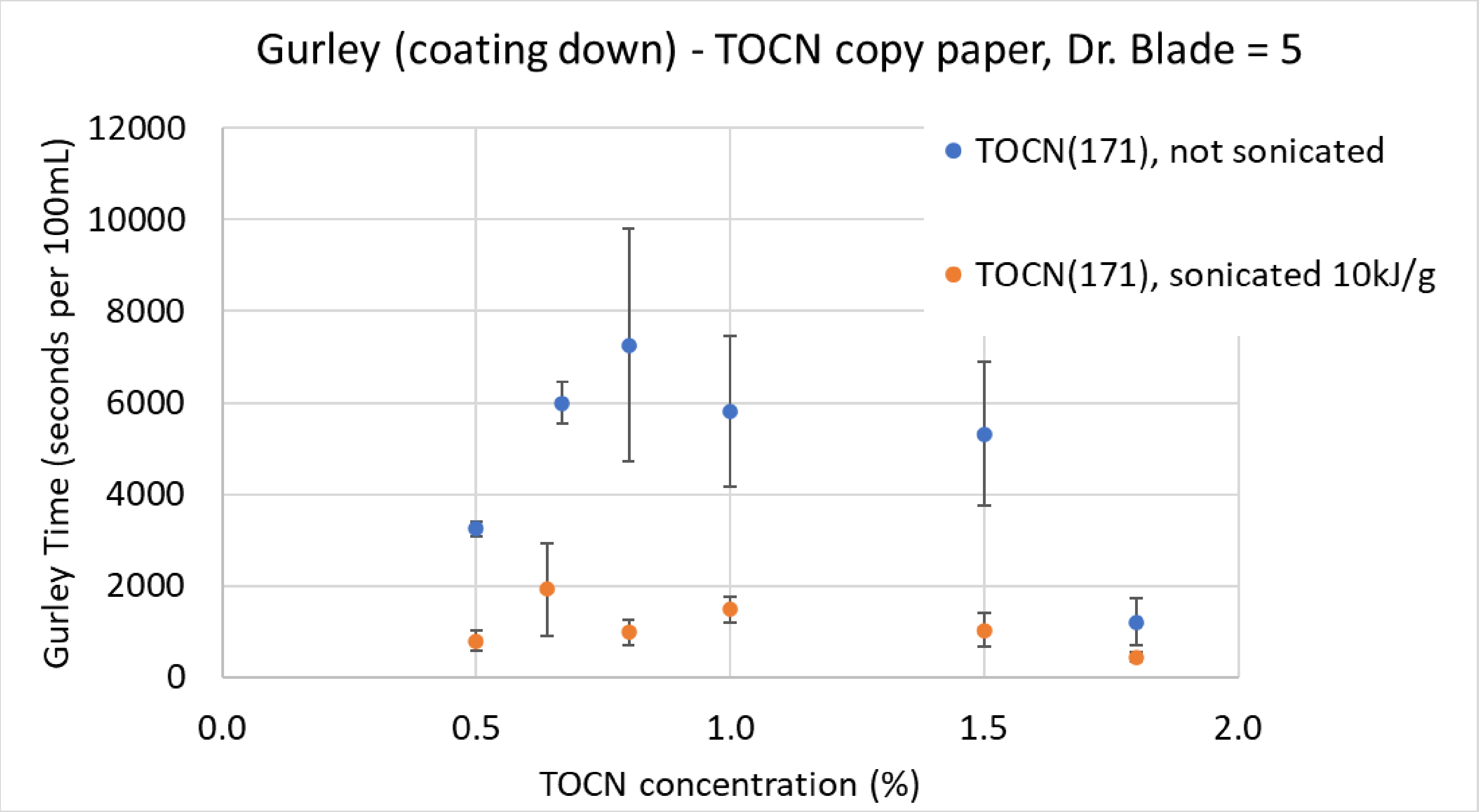
Air Permeability





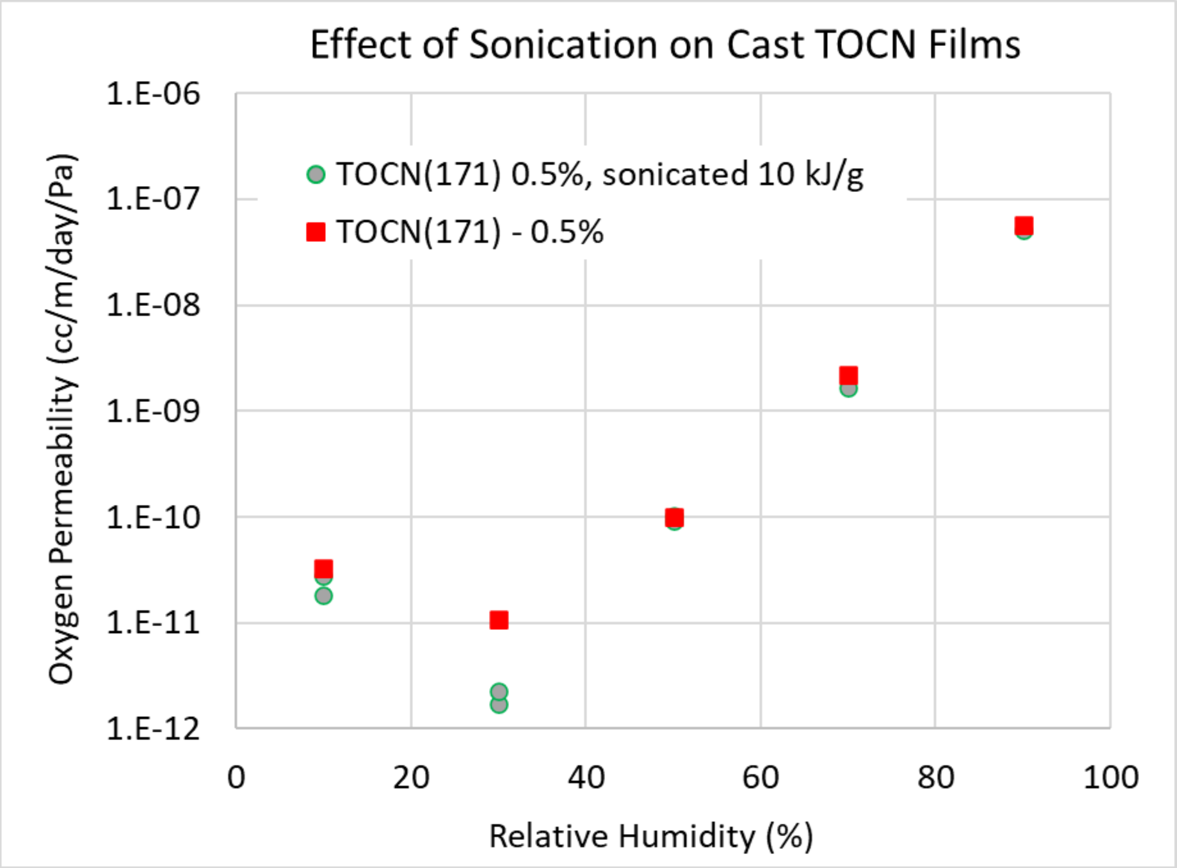
- TOCNs reached high air resistance at lower weights than carboxymethyl cellulose (CMC)
- CNF coating side up shows very high resistance to air at low coating levels

TOCN: Sonication & Concentration



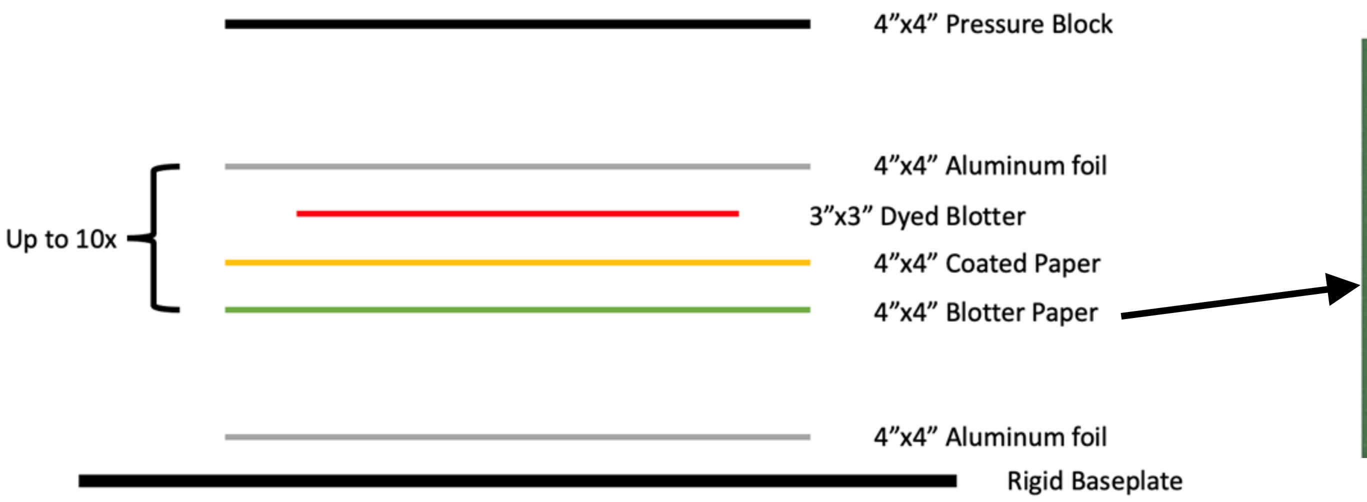
- Sonication of TOCN(171) resulted in increased air permeation
- Was not observed for TOCN (151)
- There appears to be an effect of concentration

TOCN Sonication



No effect of sonication was seen in oxygen permeability for cast TOCN films

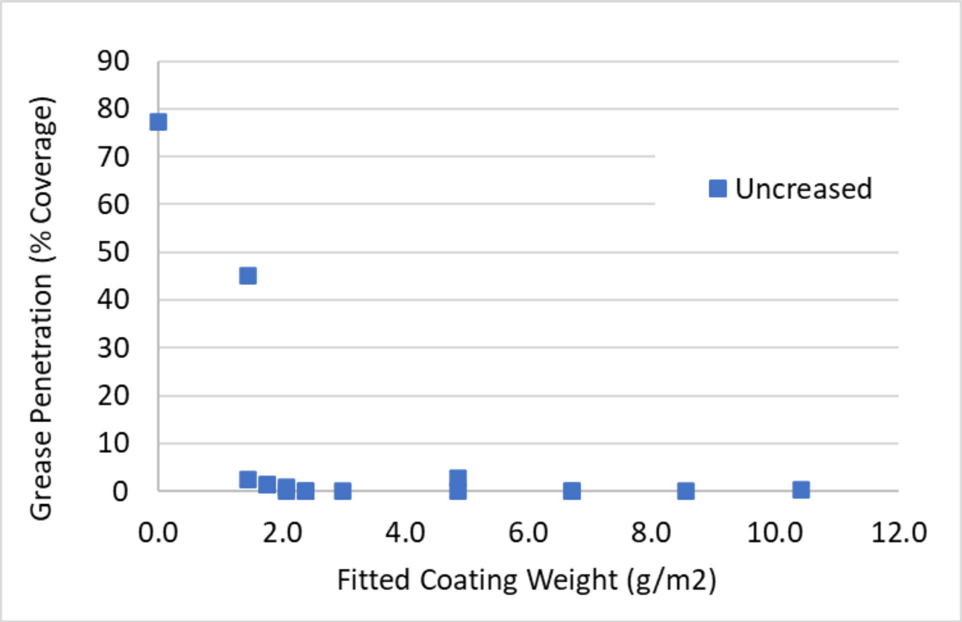
Grease Penetration – TAPPI T557

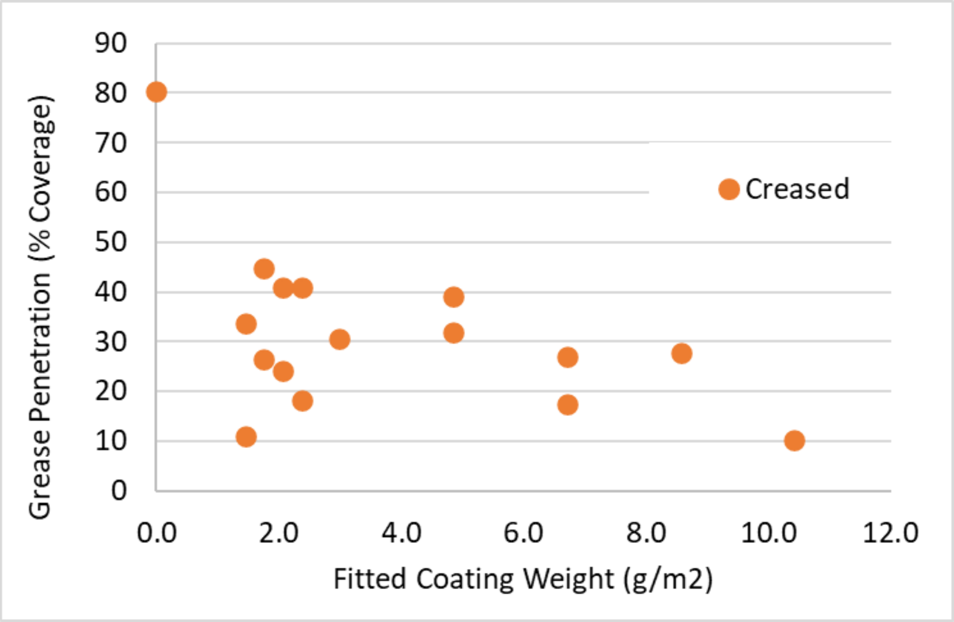


- Test metric is the percent coverage of oil stain on the receiving blotter paper
- Creased paper samples are also tested

Grease Penetration

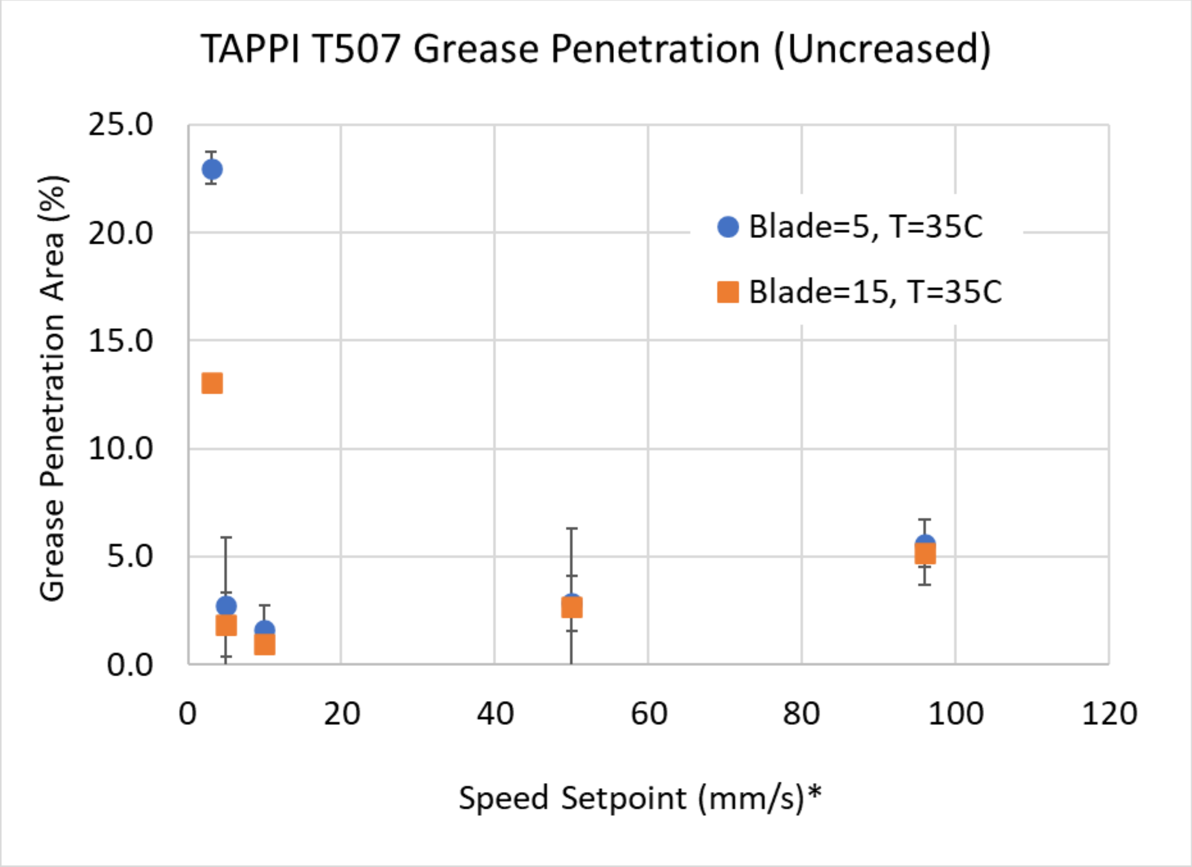
TEMPO-Oxidized CNFs on Copy Paper





- 2 g/m^2 of TOCNs gives a good grease barrier to coated papers
- Creasing of TOCN coated paper results in significant grease penetration even up to 10 g/m^2

Coating Speed



Blade setting 5: ~40 microns wet; coating ~1 g/m2
Blade setting 15: ~150 microns wet; coating ~2 g/m2

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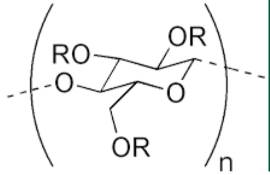
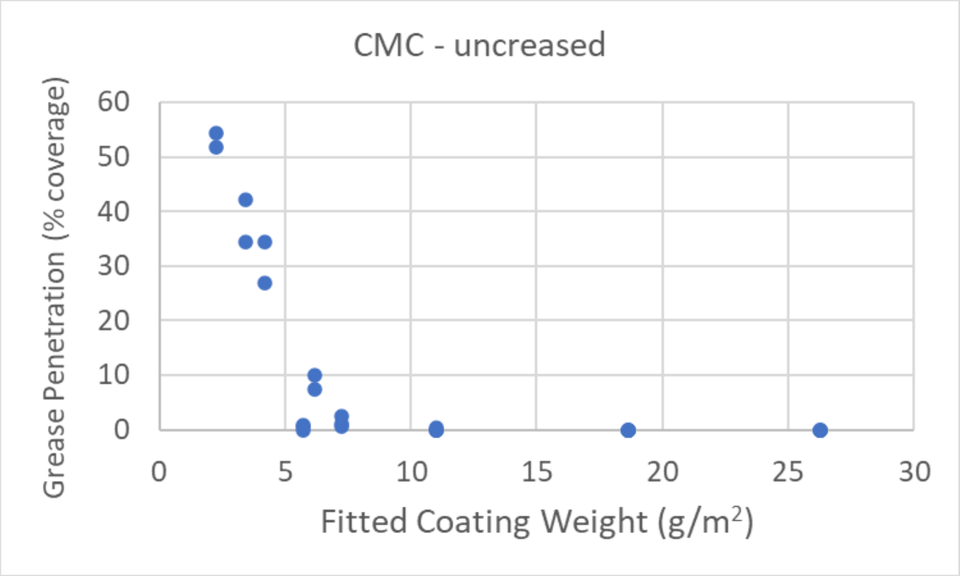
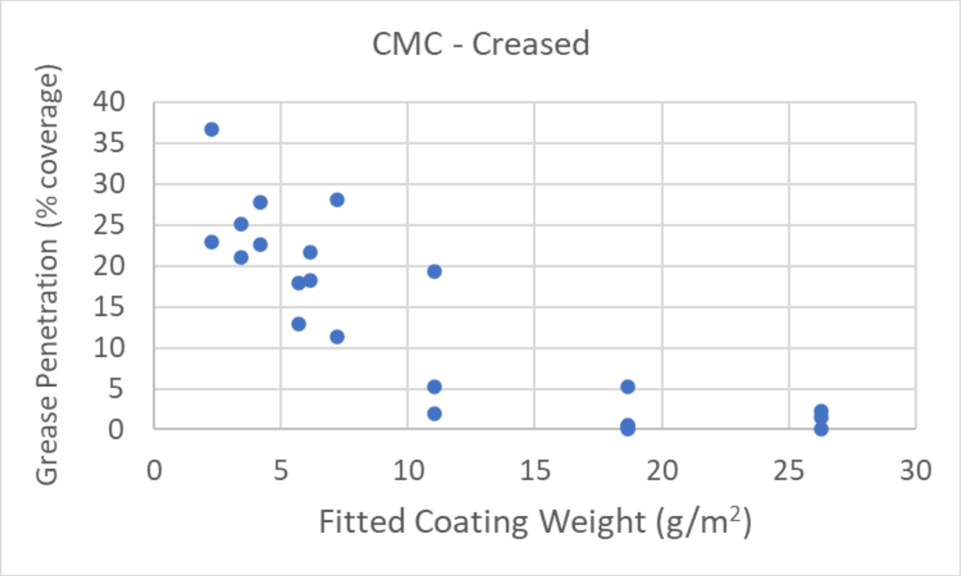
Carboxymethyl Cellulose



R = H or CH_2CO_2H

Grease penetration of CMC-coated copy papers

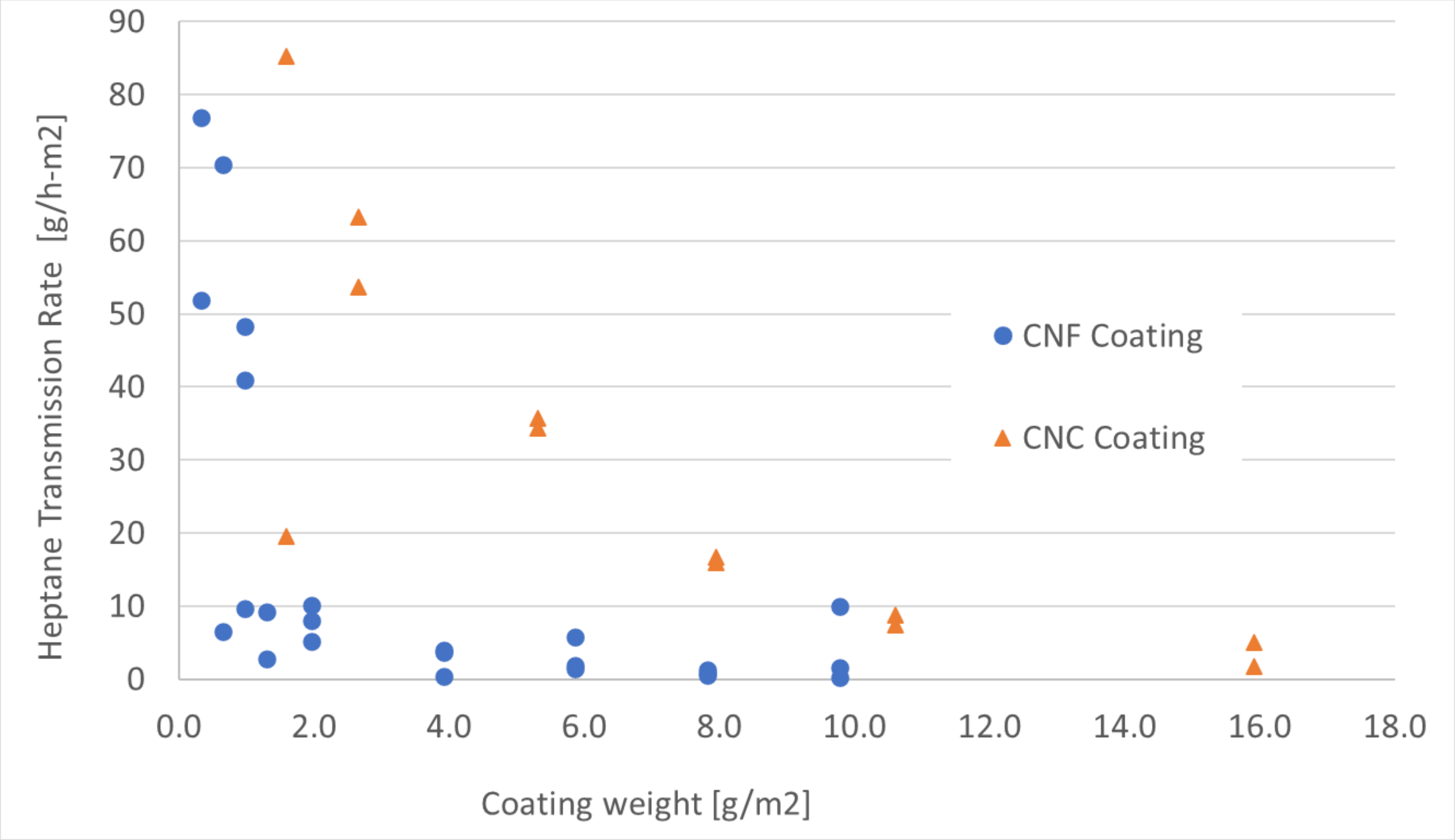




- >5 g/m^2 of CMC coating is needed to get zero grease penetration of coated papers
- Paper coated with nearly 20 g/m^2 had near-zero grease penetration upon creasing

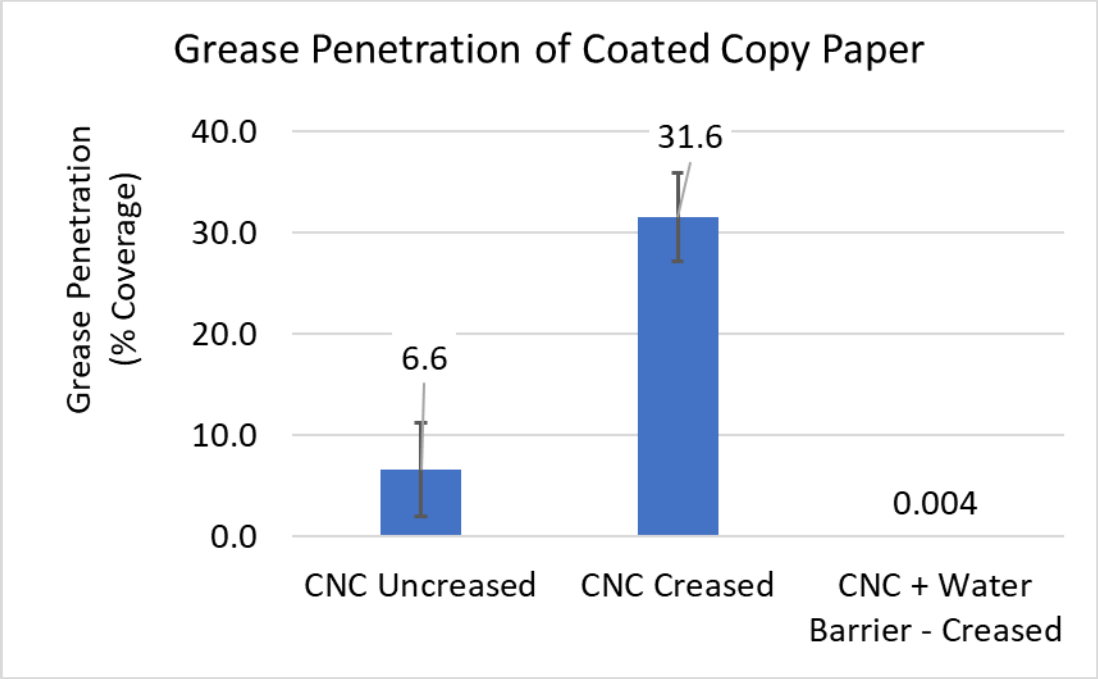
Heptane Transmission

$$Transmission\ Rate = \frac{\Delta Mass}{time * Area}$$



Water Barrier Coating

- Applied multiple coatings to same sheet
- First coating CNCs
- Second coating a proprietary waterborne biobased water barrier coating
- Each layer dried separately
- Performed creased grease test
- Tested Oxygen transmission of creased samples



- ➢ Synergy with waterborne barrier coatings
- ➢ Creased grease penetration was very low for multi-layer coatings

Water Barrier Coating

Oxygen Transmission Rate (cc/m²/day)				
RH (%)	Oxygen Barrier Only		Water + Oxygen Barrier	
	Uncreased	Creased	Uncreased	Creased
70	n/a	>2000		127
90	n/a	>2000		710

Light scattering

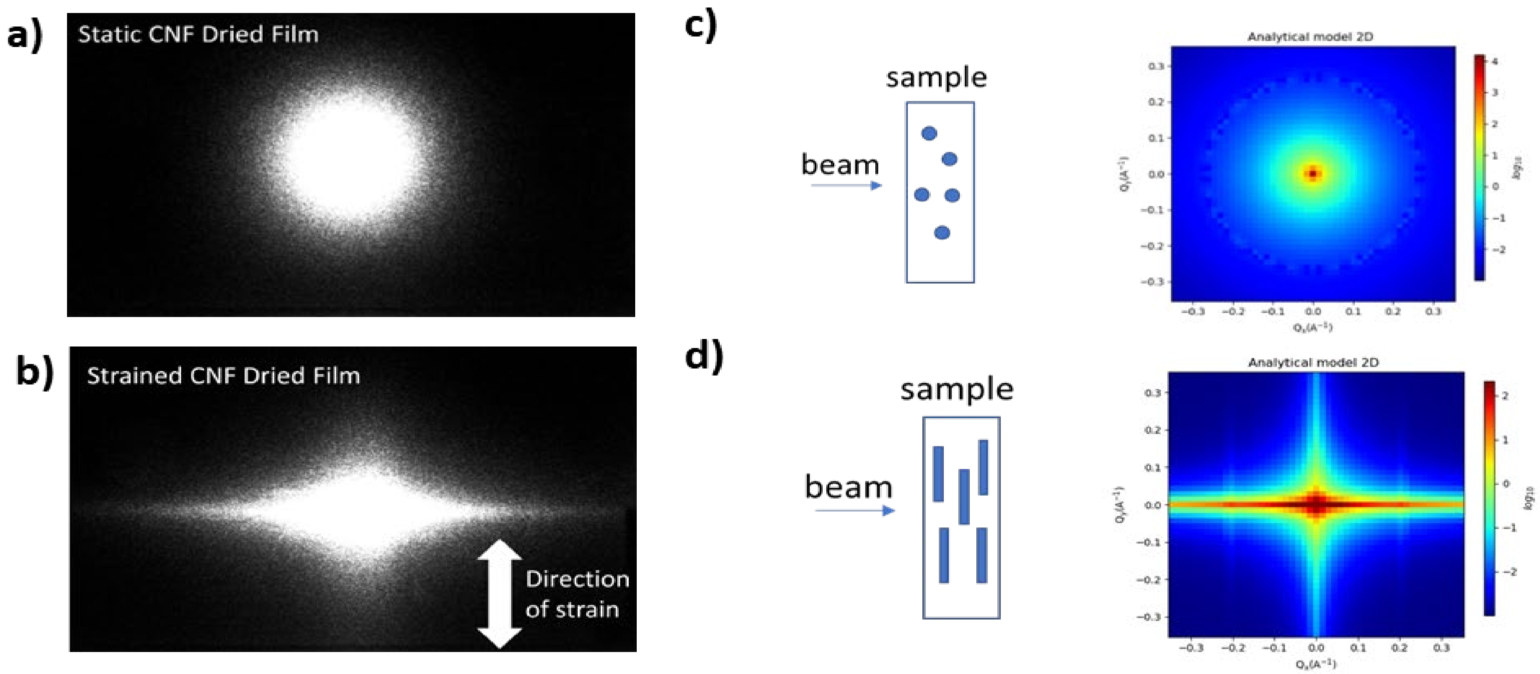


Figure 7: Effect of alignment on scattering from CNF films. Light scattering pattern from CNF film with (a) random alignment, (b) preferred orientation. Modeled scattering patterns from (c) randomly oriented spheres and (d) aligned cylinders whose size is similar to CNMs.

Preliminary Light Scattering

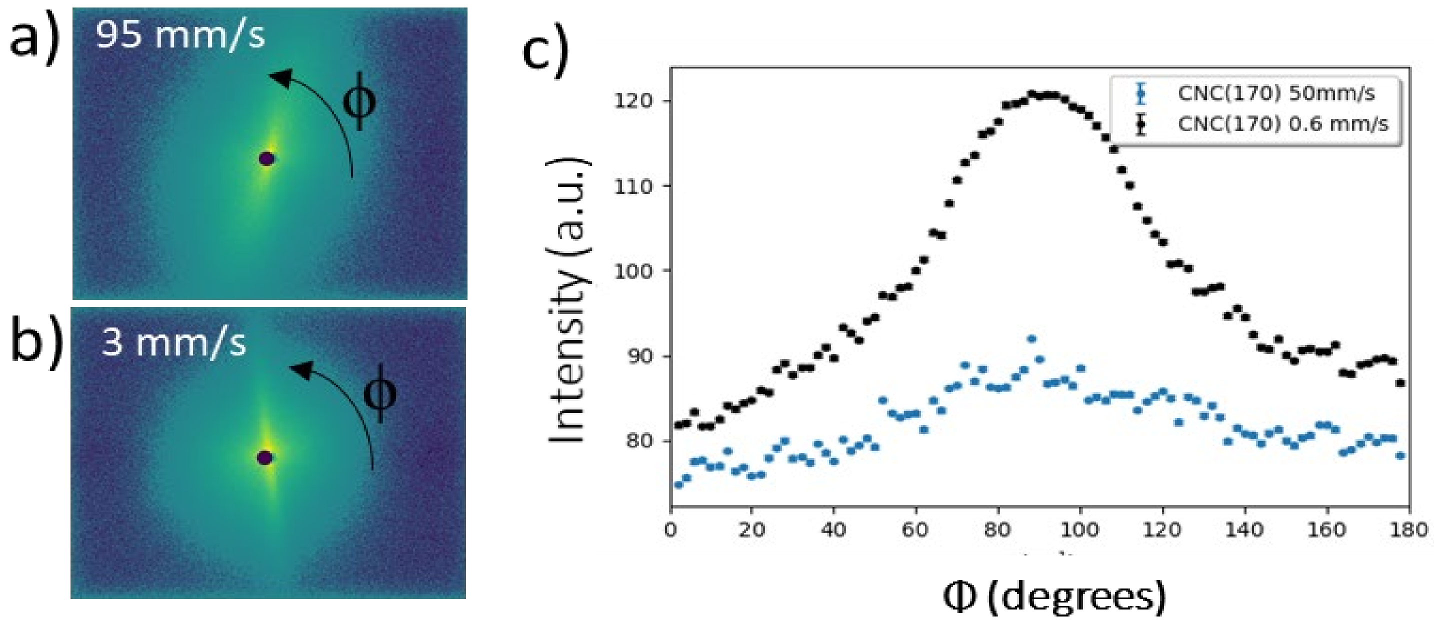


Figure 8: Scattering from blade coated CNC films. Light scattering patterns from CNC films produced with a blade coating speed (a) 95 mm/s and (b)0.6 mm/s. (c) Azimuthally integrated profiles showing the orientation distribution of the scattering from the CNCs showing the higher alignment at slower speeds.

Conclusions

- Cellulose nanomaterials have excellent oxygen and grease barriers
- Preliminary work showed without additives or additional layers CNFs outperformed CNCs in barrier performance
- Carboxymethyl cellulose is a durable barrier, but thick coatings are needed
- Dewatering/drying is a major challenge for these coatings
- CN morphology and structure appear to affect barrier performance but structure is not well understood

Acknowledgments

- Neil Gribbins, barrier testing
- Michael Landry, barrier testing
- Tim Ketelboeter, microscopy
- Peter Kitin, microscopy
- Rick Reiner, CN production
- Nayomi Plaza, light scattering
- Carl Houtman, light scattering
- Laurent Matuana
- Nicole Stark, Zhiyong Cai, and Biljana Bujanovic
- FPL Facilities
- PPS (Procurement and Property Services)
- US Endowment for Forestry and Communities

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