Thiol-ene Modifications to alter CNF Film Properties

AUTHORS:
Kendra Fein
Douglas Bousfield
William Gramlich

PRESENTED BY:
Kendra Fein
PhD Candidate
University of Maine

Motivation

- The market is saturated with non-biodegradable packaging
- Bio-plastics and PLA are not always biodegradable
- Cellulose nanofibrils (CNFs) can potentially be an oxygen or grease barrier in a packaging system
  - oxygen barrier properties are sensitive to moisture
  - CNF layers also expected to be brittle
- Chemical modification of CNF may overcome these issues

Example- Chip Bags

- Multiple-layer construction
- Impossible to separate for recycling
- Aluminum processing requires high energy and creates toxic byproducts

Polypropylene: moisture barrier

Aluminum: oxygen barrier
grease/oil barrier

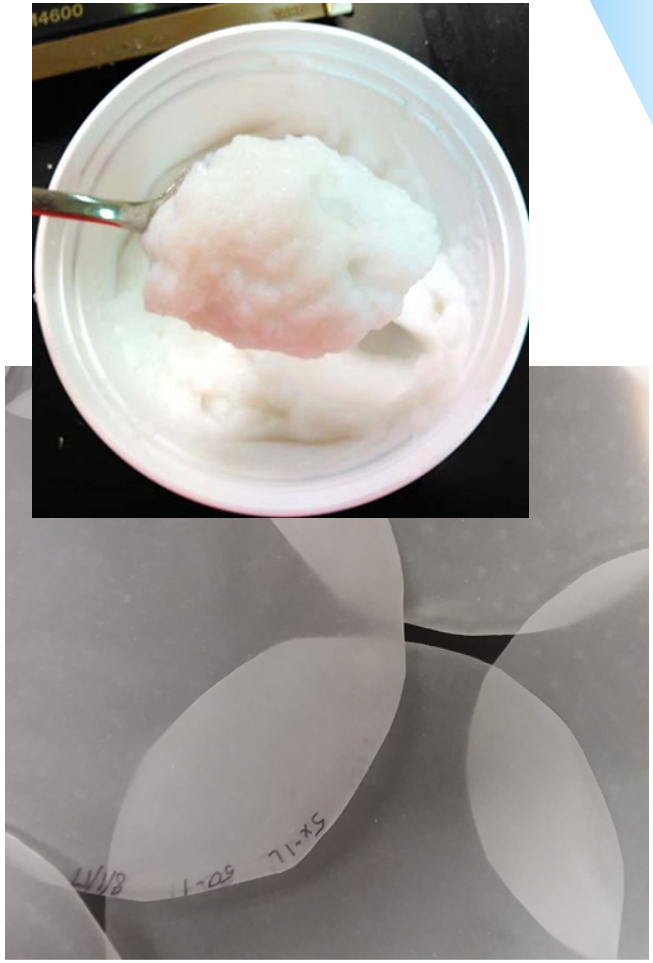
CNF layer could replace aluminum to provide needed properties

Objectives

- Create competitive and scalable bio-based packaging material
- Understand the potential to improve flexibility and sensitivity to moisture of CNF layers

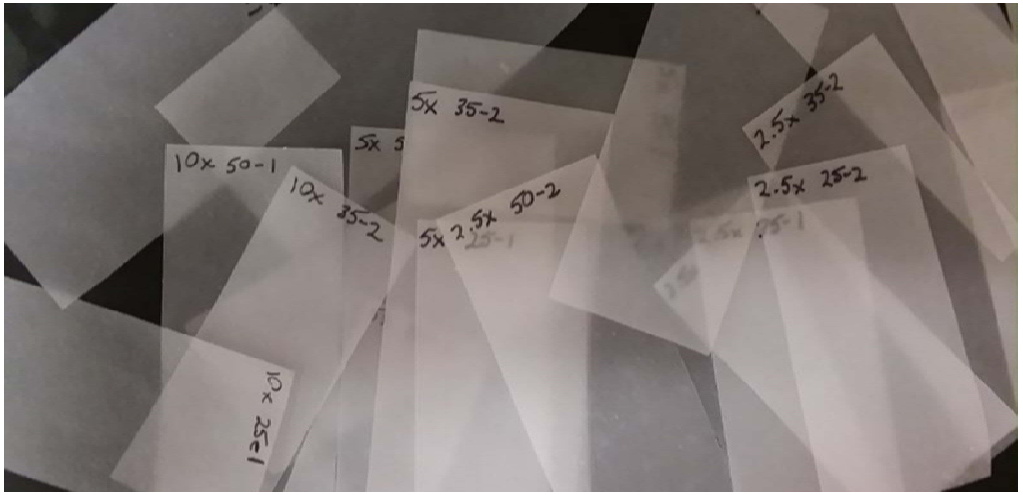
Approach

- Modify CNFs in water with various chemistries
- Generate free standing films
- Test mechanical and barrier properties



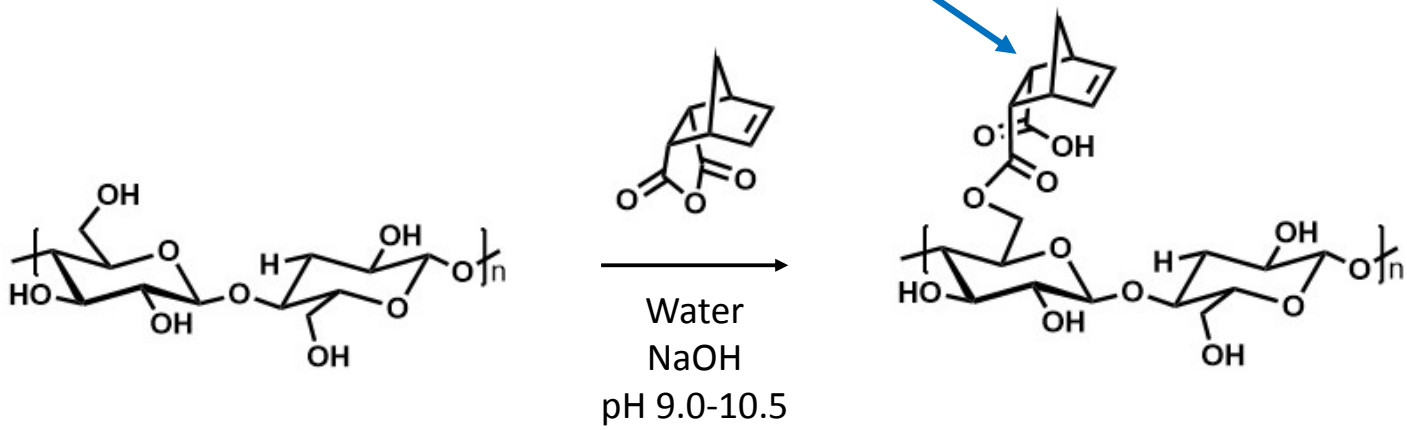
Hypotheses

- Hydrophilic group addition may alter fibril interactions to change flexibility and strain at break
- Hydrophobic group addition may help with water sensitivity and dimensional stability



Carbic-Functionalization of CNF

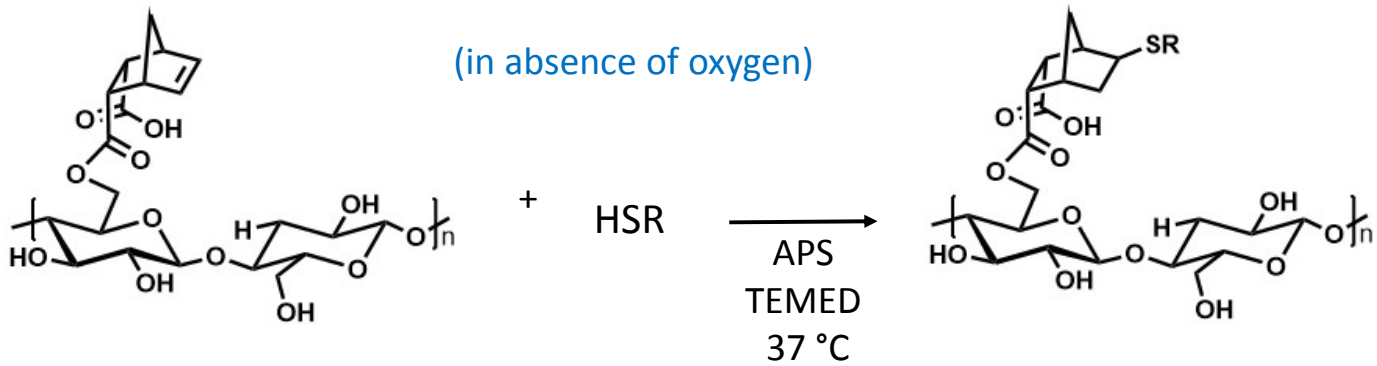
Highly reactive due to ring strain and bond angles



CNF surface

Carbic anhydride-functionalized CNF (cCNF)

Thiol-ene Reaction of cCNF



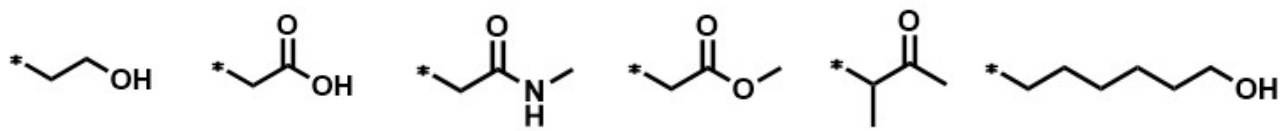
cCNF

thiol molecules

thiol-functionalized cCNF

(denoted by thiol molecules)

R =

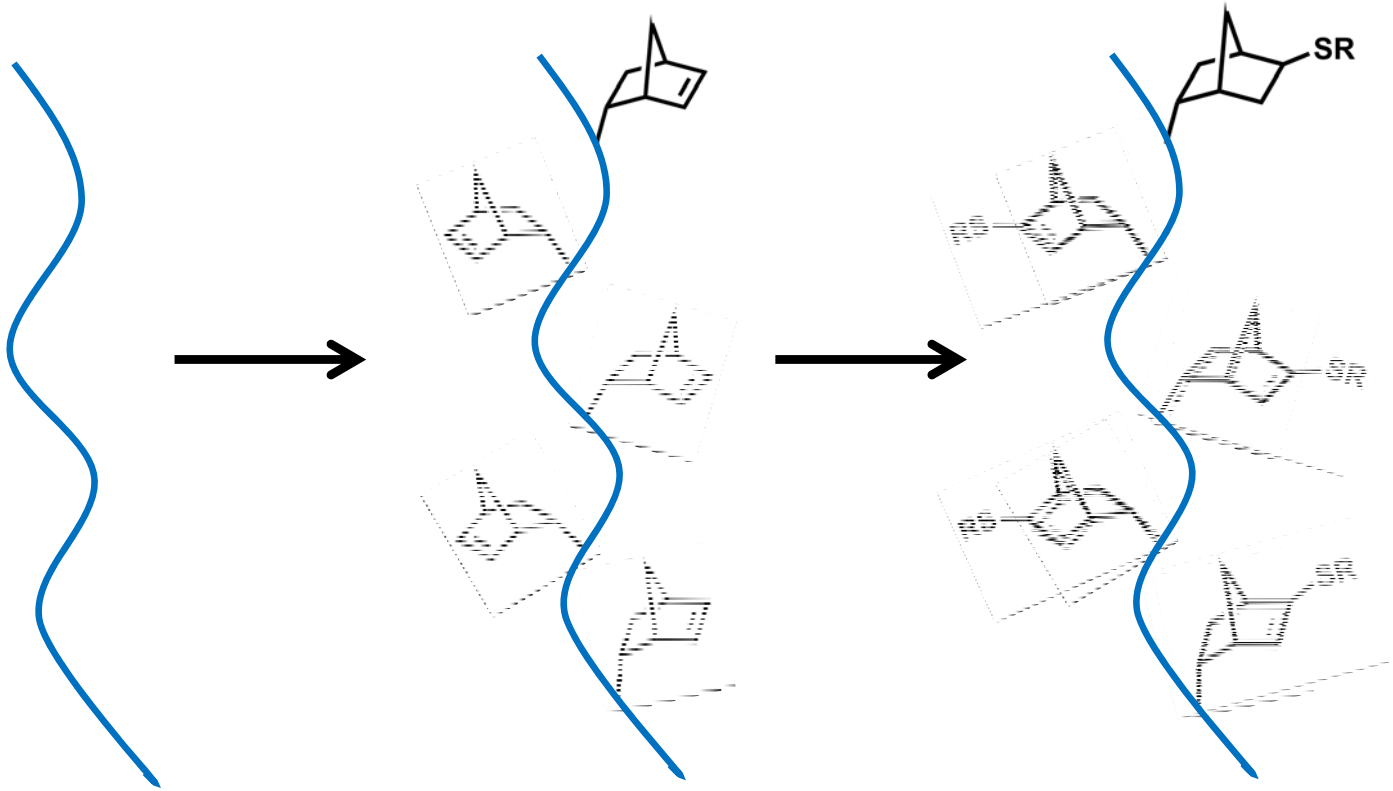


ME TA MMA MT MB MH

Cellulose fibrils

Carbic-Functionalized (cCNF)

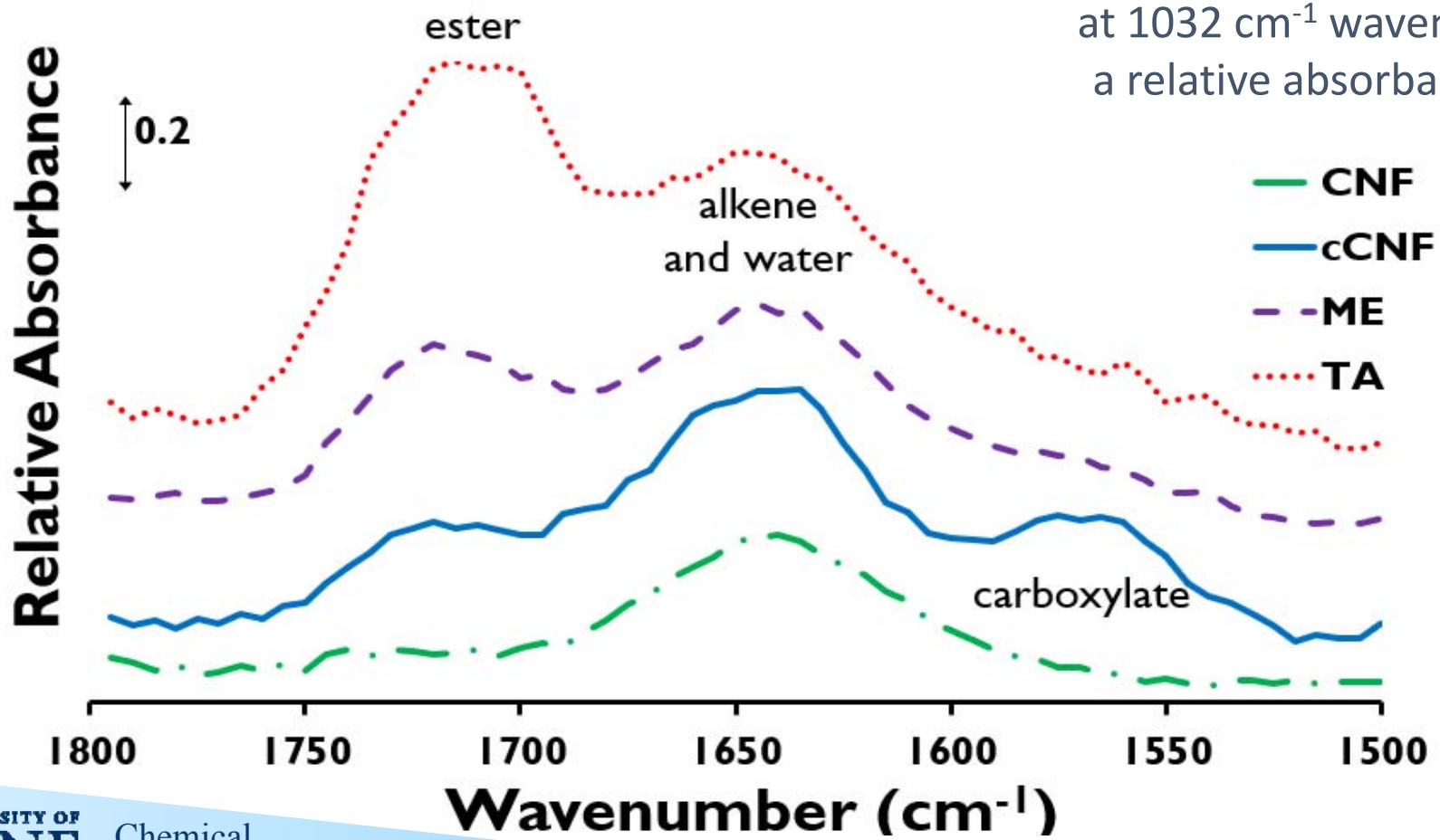
Thiol-Functionalized cCNF



Water-based and versatile chemistry

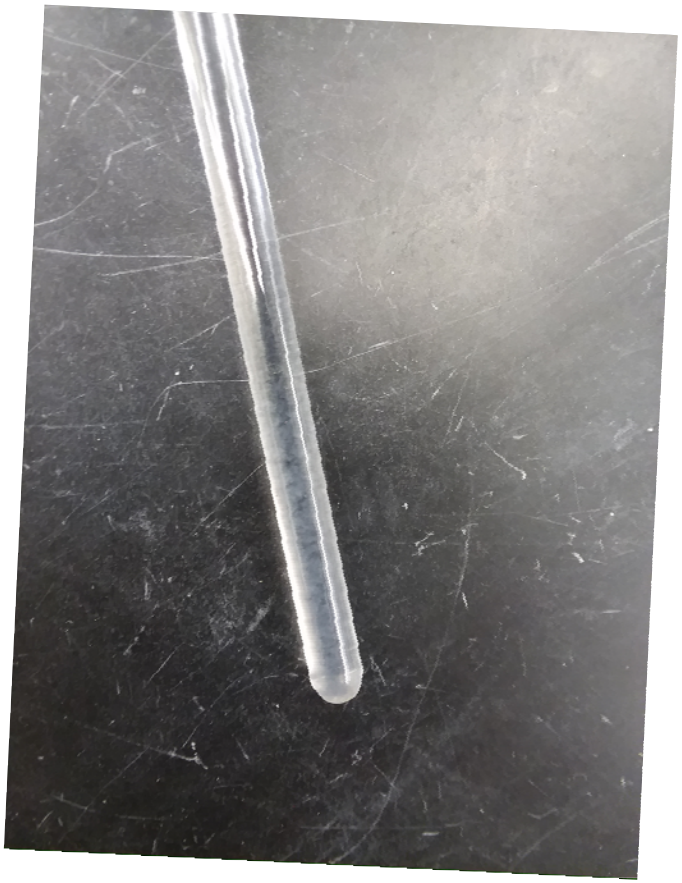
ATR-FTIR Spectra of Films

With respect to C-O stretch at 1032 cm^{-1} wavenumber at a relative absorbance of 10

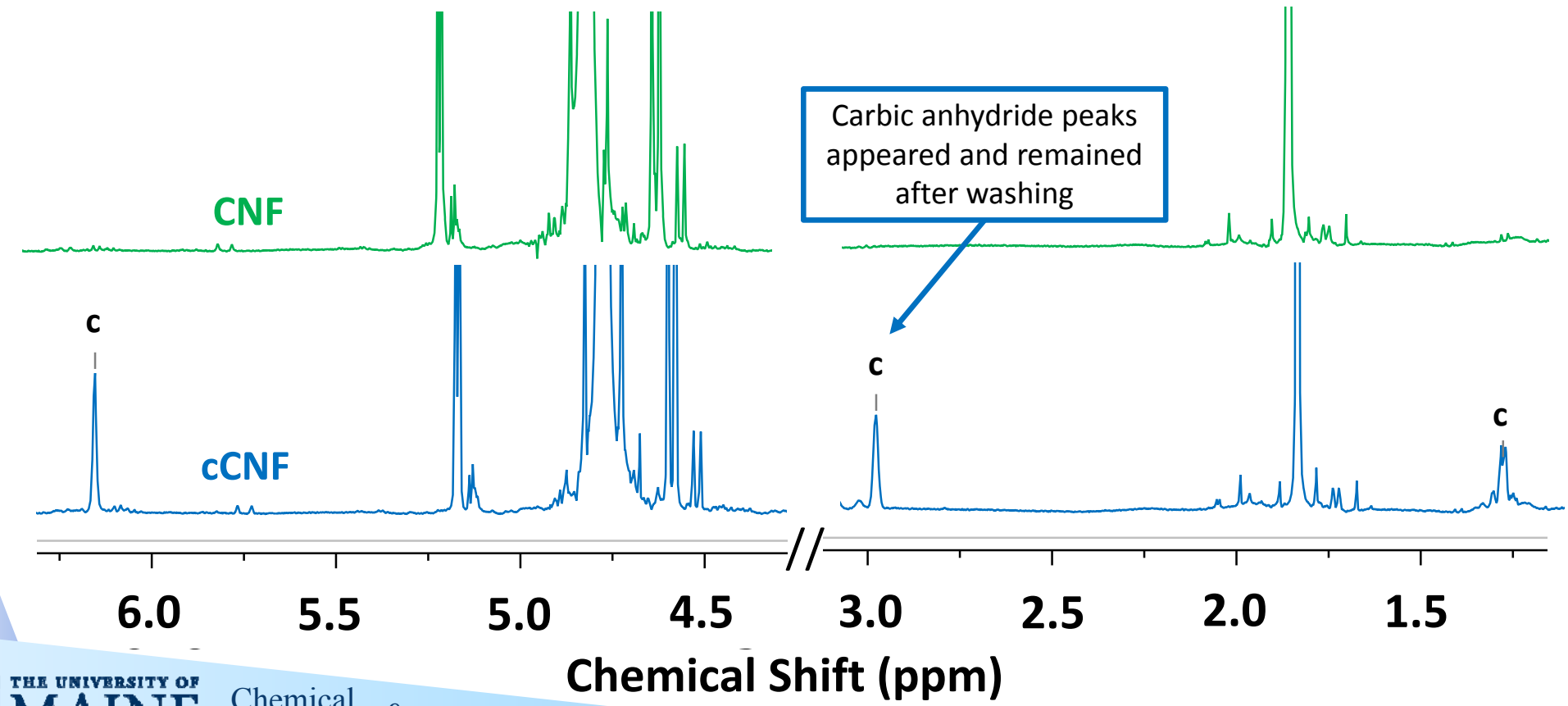


^{1}H-NMR Sample Prep

- Degrade CNF sample using cellulase enzyme
  - pH buffer solution (NaOAc)
  - heated
- Freeze dry sample
- Disperse in deuterium oxide (D_2O)



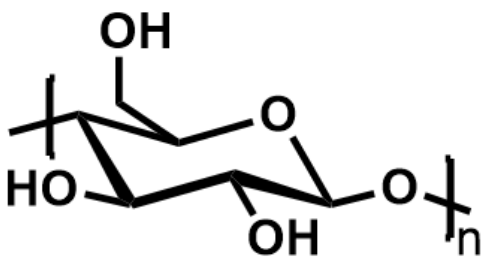
^{1}H-NMR Spectroscopy



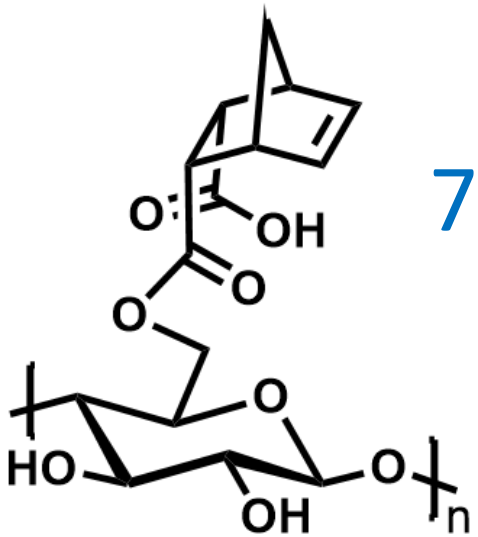
Percent Carbic-functionalization of CNF

100 repeat unit basis:

93/100



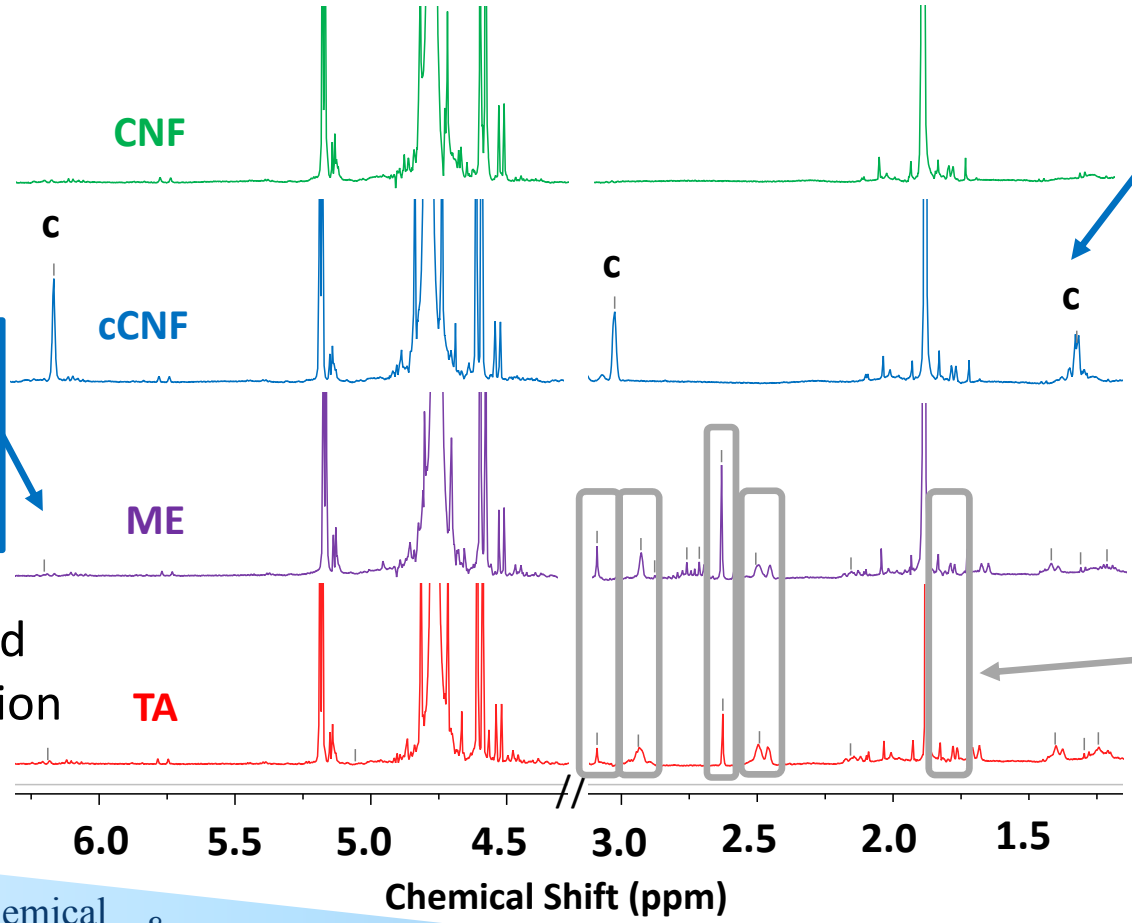
CNF repeat unit



carbic-functionalized

7/100 = 7%

^{1}H-NMR Spectroscopy



Carbic anhydride peaks appeared and remained after washing

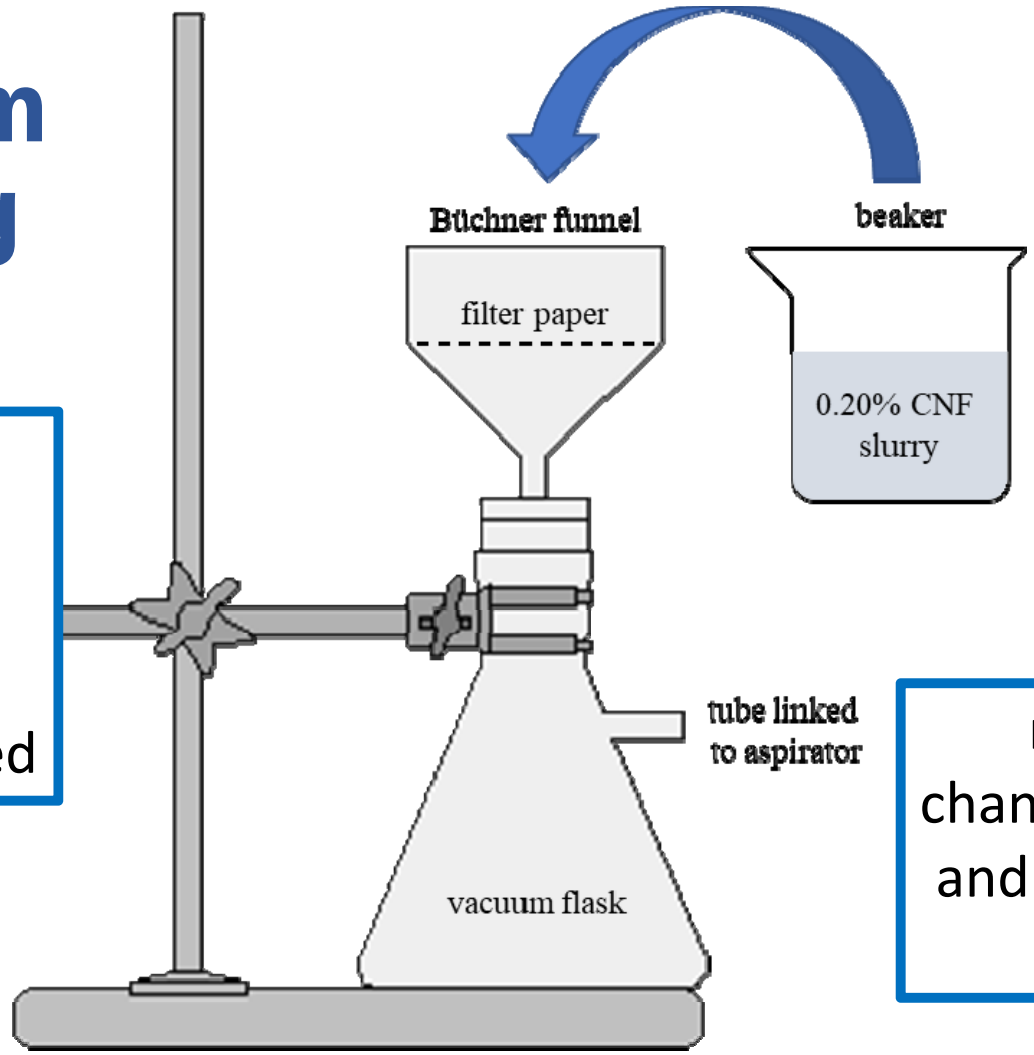
Carbic anhydride peaks disappeared validating thiol-ene reaction

Product peaks similar in all thiol-modified CNFs

Most showed ≥91% conversion

CNF Film Forming

CNF films restrained and dried on filter paper then peeled after dried

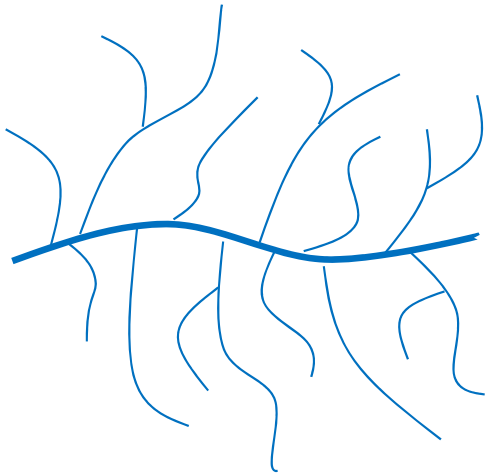


modifications changed drainage rate and cCNF adhered to filter paper

CNF Structure and Fibril Mobility

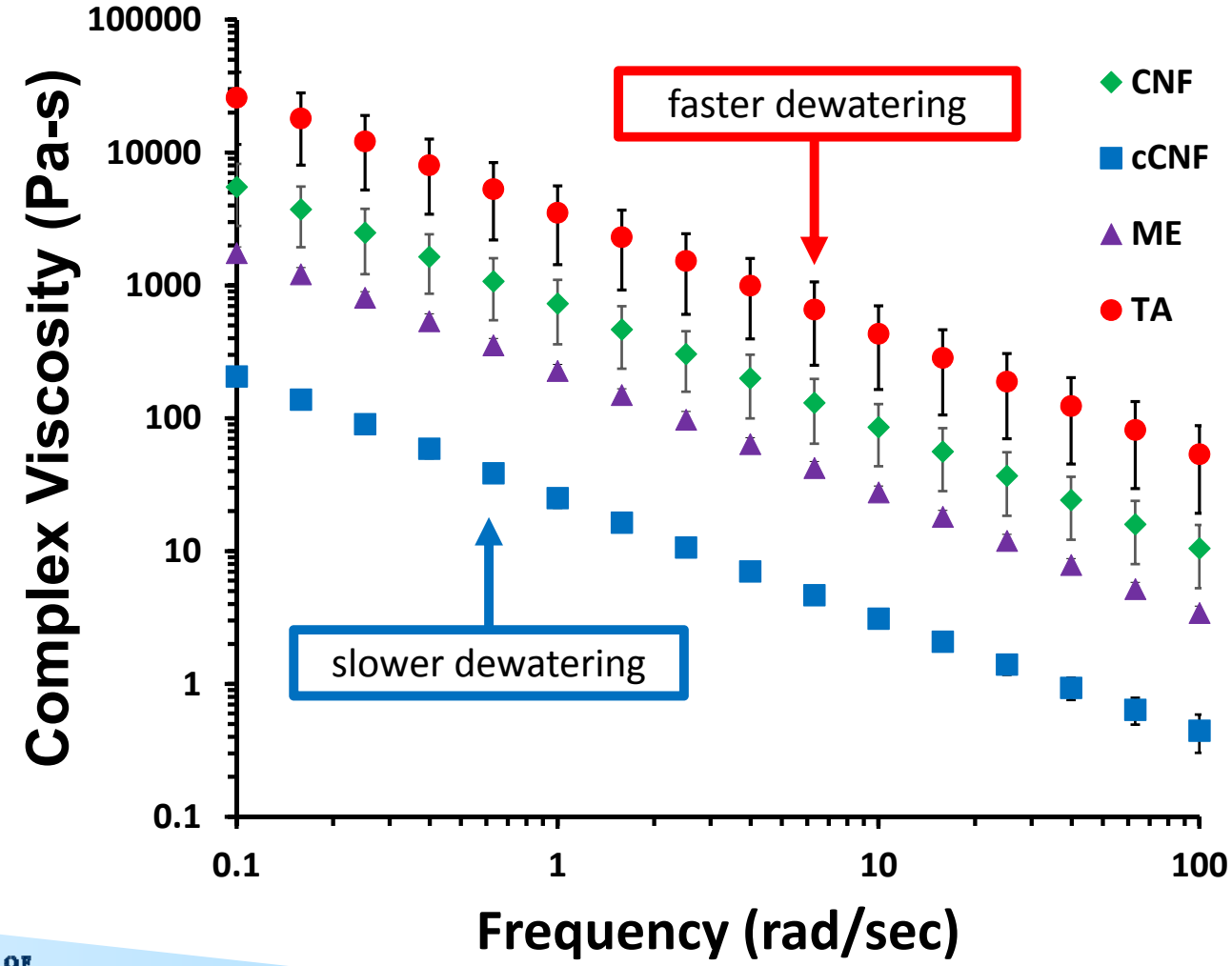
Increased viscosity likely due to entanglement

Expected fibril mobility associated with viscosity



Surface modification in this work alters these interactions

In this work, fibril mobility refers to colloidal particles sliding past one another


Complex Viscosity (Pa-s)
100000
10000
1000
100
10
1
0.1
0.1
1
10
100
Frequency (rad/sec)
faster dewatering
slower dewatering
CNF
cCNF
ME
TA

Changes in Drainage, Viscosity and Filter Paper Adhesion

CNF (separates from filter paper)

- Fiber-fiber interactions create self-sustaining network
  - entanglement could create surface above filter paper
  - passages do not plug

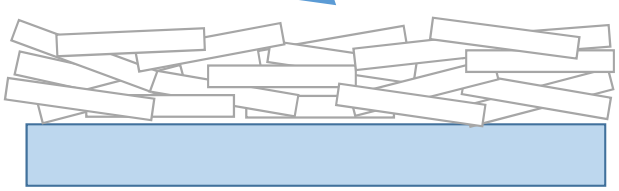
cCNF (adheres to filter paper)

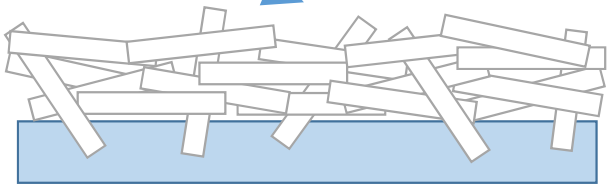
- Increased fibril mobility
  - Fibrils slip through network to plug pores and enter filter paper

Dewaters ~ 3 mins

fiber layer causes filtration resistance

Dewaters ~ 19 mins





dispersed fibers/sealed pores harder to dewater

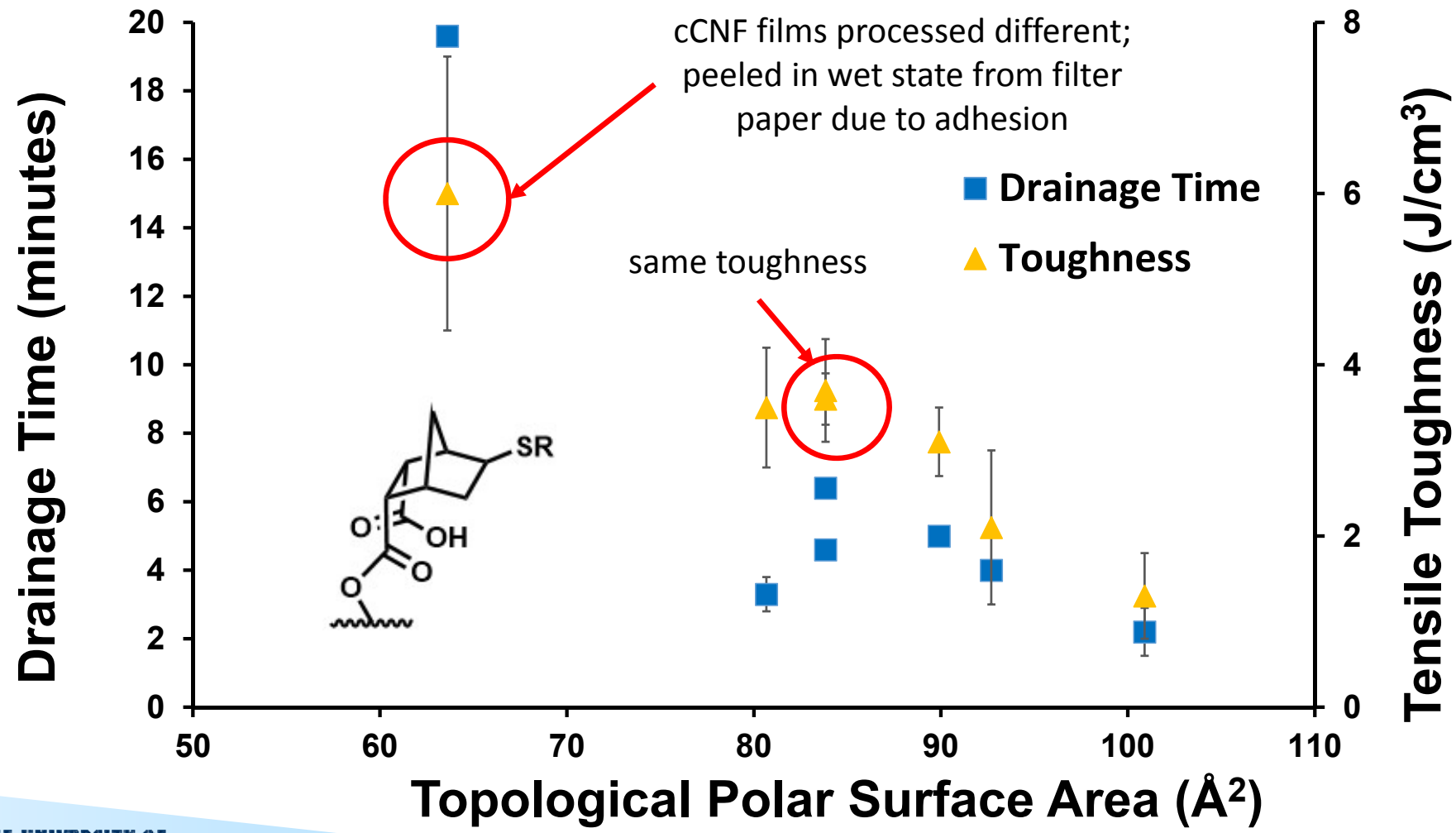
Topological Polar Surface Area (tPSA)

- Widely used to predict transport properties of drugs
- Calculates tPSA by summing surface contributions of polar fragments
  - new method showed accurate correlations when neglecting geometry
- Could have applications for modified CNF interactions

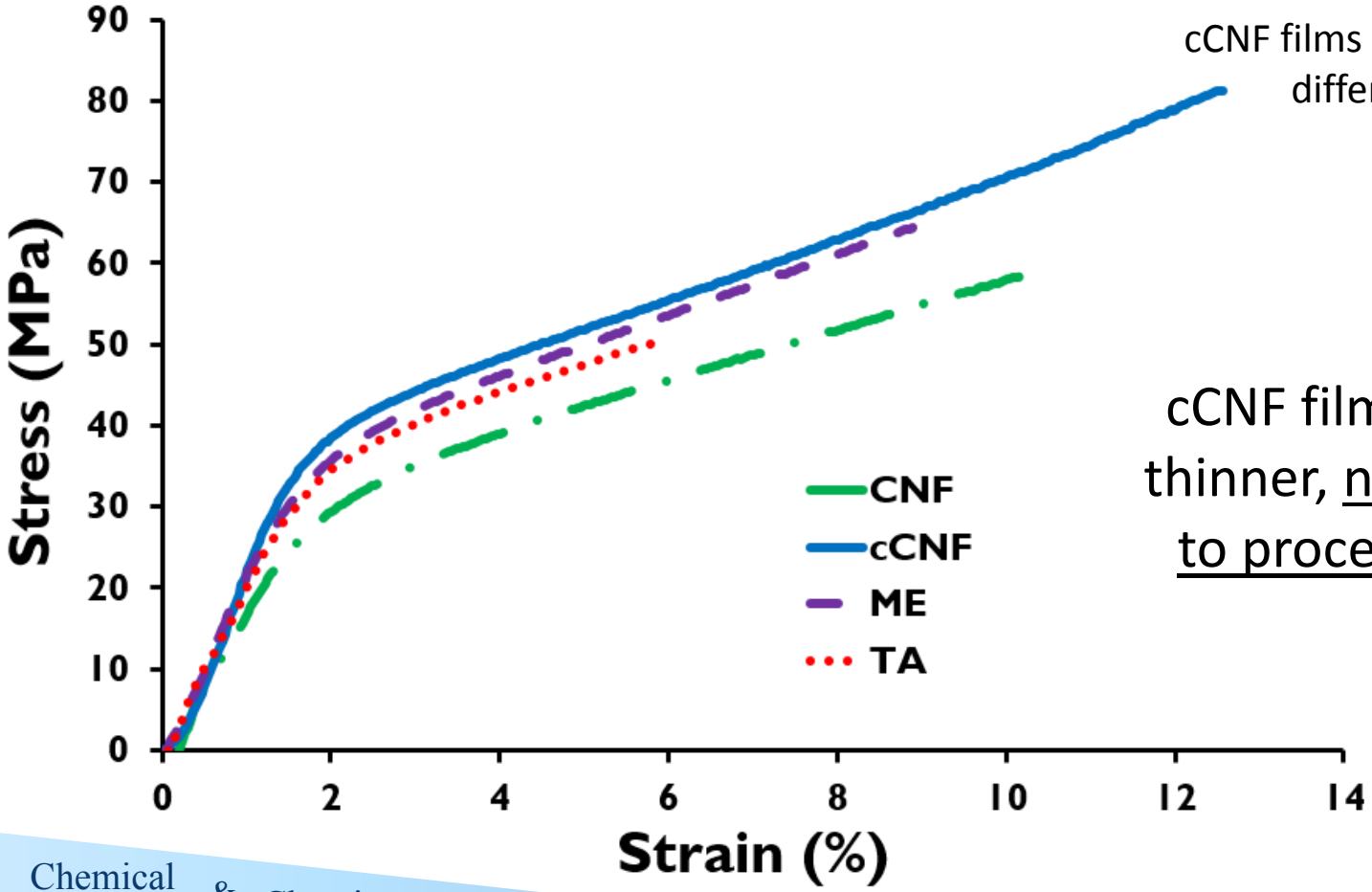
Table 1. Atomic Contributions (Å^2) to PSA

atom type[a]	PSA contrib	atom type[a]	PSA contrib
[N](−*)(−*)−*	3.24	[nH](:*):*	15.79
[N](−*)=*	12.36	[n+](:*)(:*):*	4.10
[N]#*	23.79	[n+](−*)(:*):*	3.88
[N](−*)(=*)=* [b]	11.68	[nH+](:*):*	14.14
[N](=*)#* [c]	13.60	[O](−*)−*	9.23
[N]1(−*)−*−*−1[d]	3.01	[O]1−*−*−1[d]	12.53
[NH](−*)−*	12.03	[O]=*	17.07
[NH]1−*−*−1[d]	21.94	[OH]−*	20.23
[NH]=*	23.85	[O−]−*	23.06
[NH2]−*	26.02	[o](:*):*	13.14
[N+](−*)(−*)(−*)−*	0.00	[S](−*)−*	25.30
[N+](−*)(−*)=*	3.01	[S]=*	32.09
[N+](−*)#* [e]	4.36	[S](−*)(−*)=*	19.21
[NH+](−*)(−*)−*	4.44	[S](−*)(−*)(=*)=*	8.38
[NH+](−*)=*	13.97	[SH]−*	38.80
[NH2+](−*)−*	16.61	[s](:*):*	28.24
[NH2+]=*	25.59	[s](=*)(:*):*	21.70
[NH3+]−*	27.64	[P](−*)(−*)−*	13.59
[n](:*):*	12.89	[P](−*)=*	34.14
[n](:*)(:*):*	4.41	[P](−*)(−*)(−*)=*	9.81
[n](−*)(:*):*	4.93	[PH](−*)(−*)=*	23.47
[n](=*)(:*):* [f]	8.39		

Ertl, Peter, Bernhard Rohde, and Paul Selzer. 2000. "Fast Calculation of Molecular Polar Surface Area as a Sum of Fragment-Based Contributions and Its Application to the Prediction of Drug Transport Properties." Journal of Medicinal Chemistry 43 (20): 3714–17. https://doi.org/10.1021/jm000942e.


cCNF films processed different; peeled in wet state from filter paper due to adhesion
same toughness
Drainage Time
Toughness
SR
OH
O
O
O
Drainage Time (minutes)
Tensile Toughness (J/cm³)
Topological Polar Surface Area (Å²)
0
2
4
6
8
10
12
14
16
18
20
50
60
70
80
90
100
110

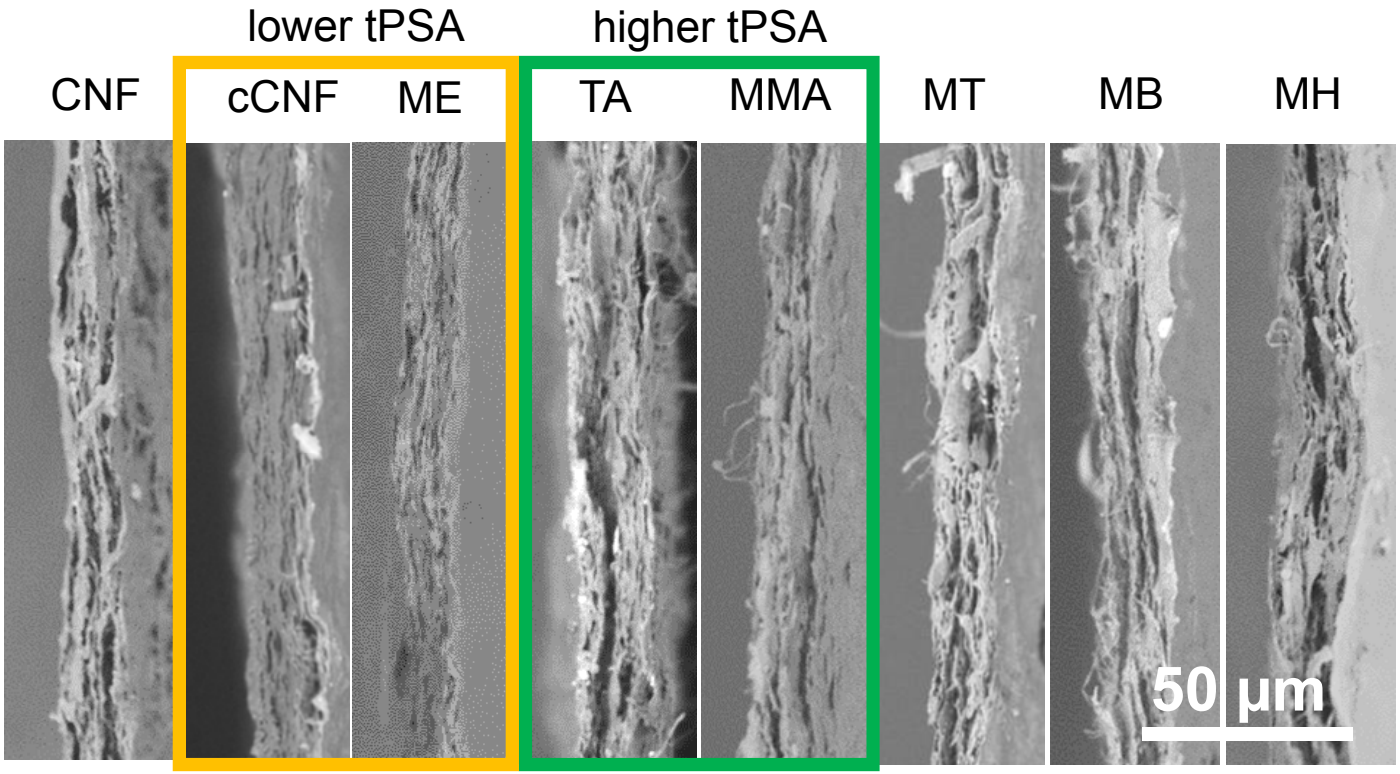
Representative Stress-Strain Curves



cCNF films processed different

cCNF film 25% thinner, <u>not due to processing</u>

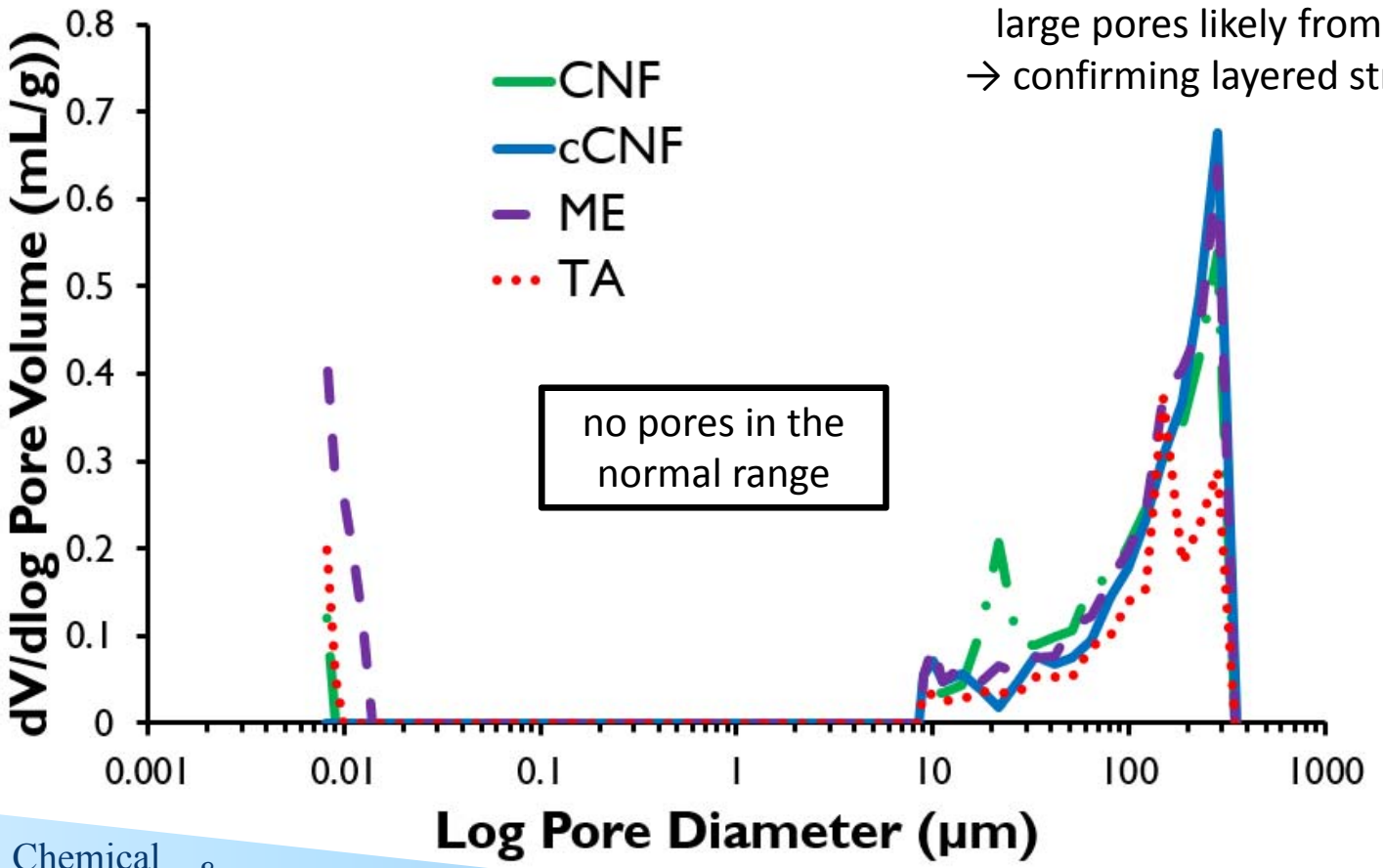
Cross Sections of Films

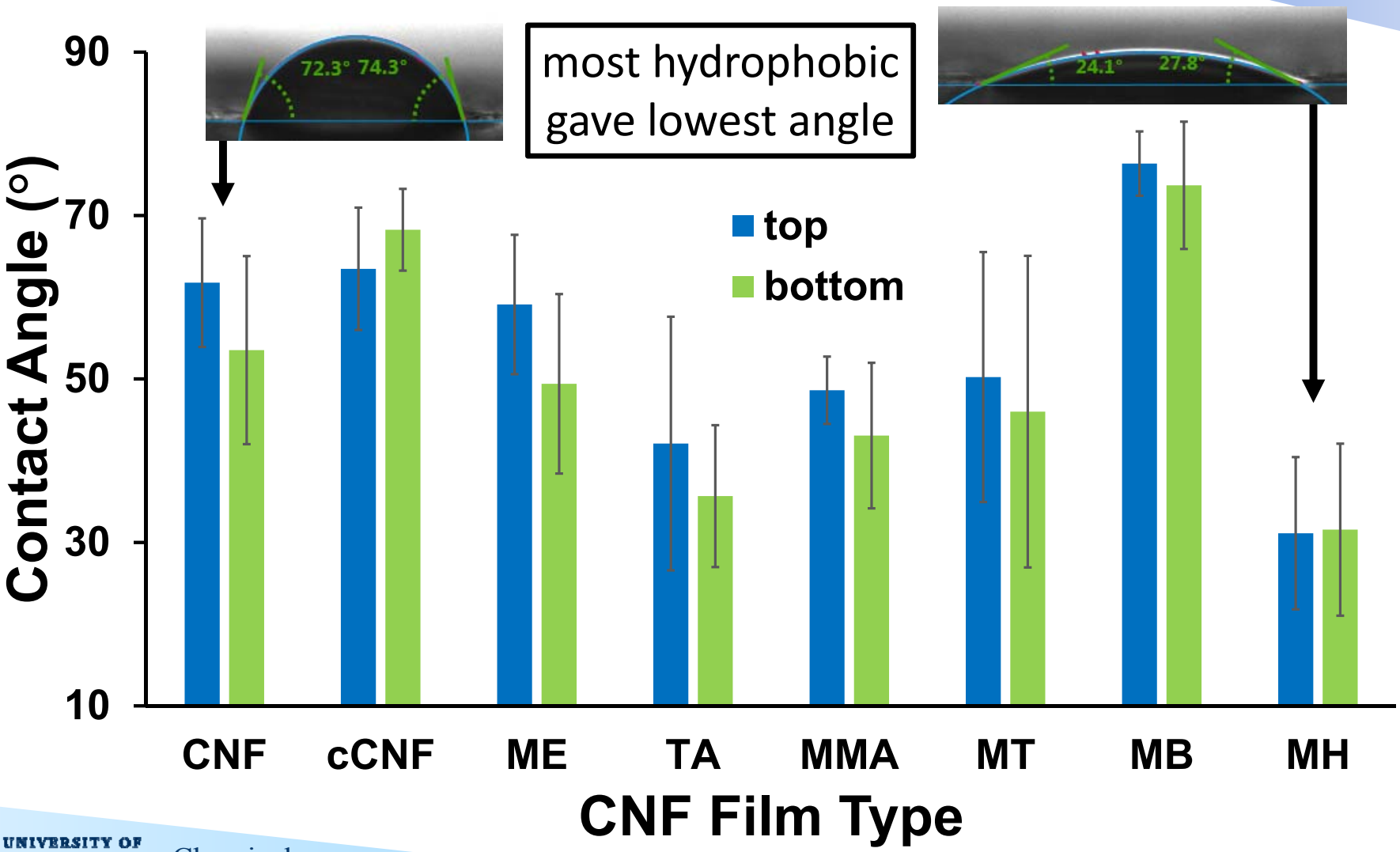


tighter packing

'layered' structure shown by linear voids

Log Differential Volume of Pore Size




most hydrophobic gave lowest angle
72.3° 74.3°
24.1° 27.8°
top
bottom
Contact Angle (°)
90
70
50
30
10
CNF
cCNF
ME
TA
MMA
MT
MB
MH
CNF Film Type

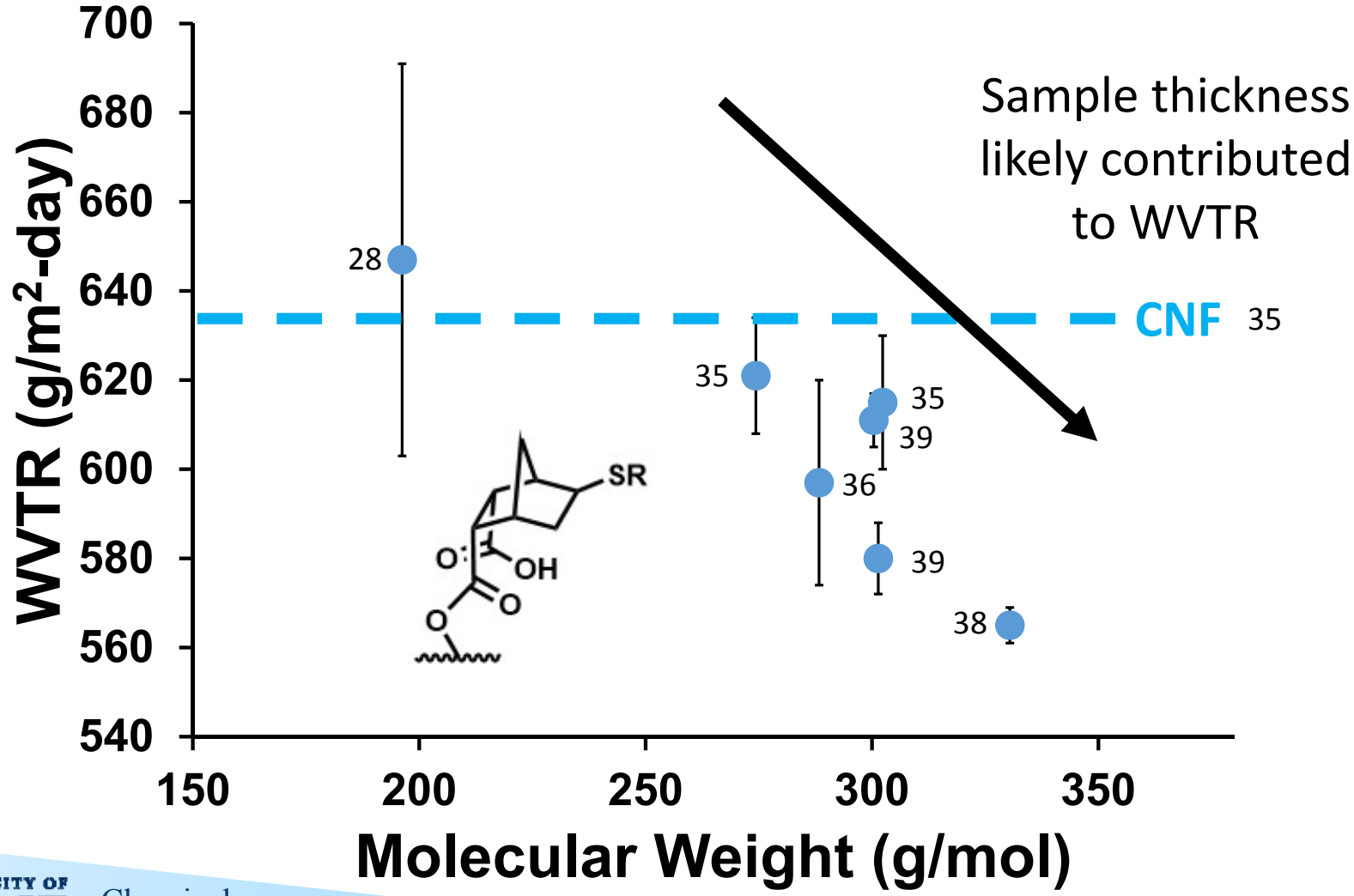
Water Vapor Transmission Rate (WVTR)

Assuming outside 50% RH

← substrate (CNF film)
← silicone gasket and metal ring

Assuming inside 100% RH

← deionized water


WVTR (g/m2-day)
700
680
660
640
620
600
580
560
540
150
200
250
300
350
Molecular Weight (g/mol)
28
35
35
39
36
39
38
CNF 35
Sample thickness likely contributed to WVTR
SR
OH
O
O
O

Conclusions

- CNFs can be modified in water-phase
  - simplifies processing
  - versatile chemistry
- Reactions altered slurry and film forming properties of CNFs
  - Improved fibril mobility for decreased viscosity could aid in coating applications with limited speeds and shear rates
  - Increased tPSA on surface could improve drainage and retention for wet end applications
- Mechanical properties not changed by large extent

Conclusions

- Contact angles changed but not expected trend
- CNF films have layered structure and quite porous
- Water vapor barrier showed some changes
  - Could be contributed by size of molecules added
  - 11% reduction in WVTR
  - 20% reduction in WVP
- Unmodified films folded
  - No loss of WVTR
  - No loss of grease barrier

Thank you

PRESENTED BY

Kendra Fein

PhD Candidate

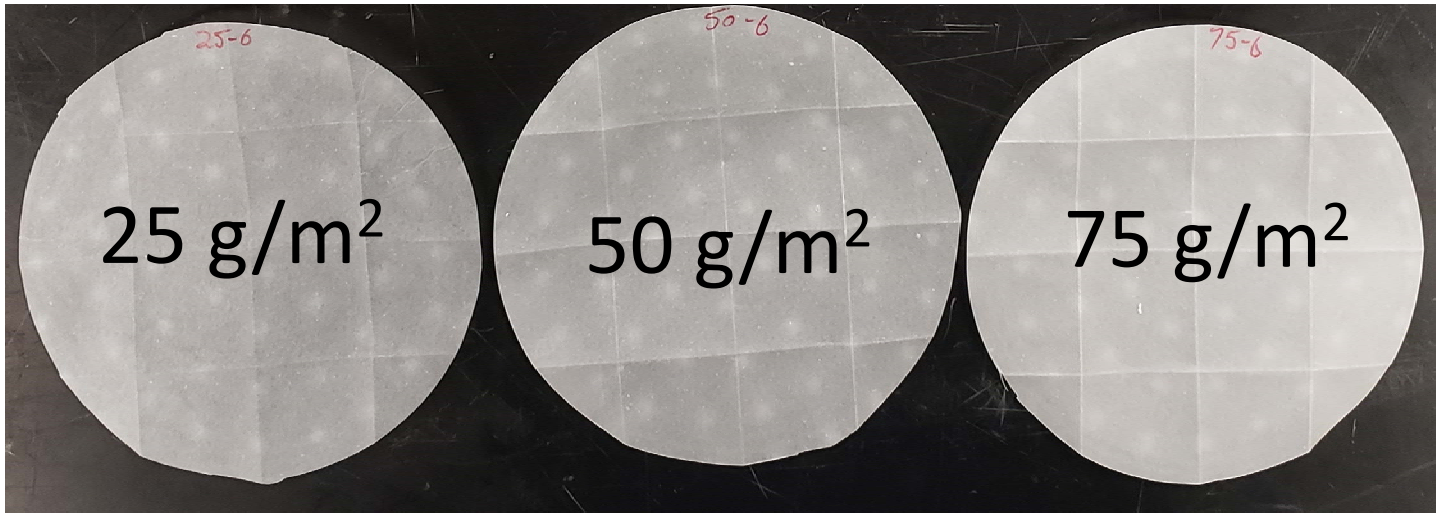
University of Maine

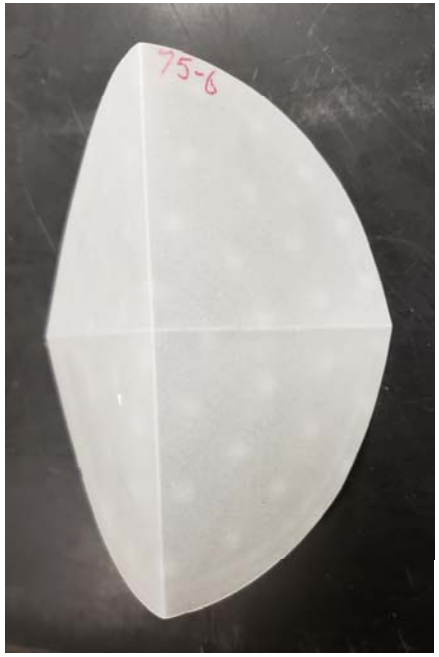
kendra.fein@maine.edu

1865 THE UNIVERSITY OF MAINE

TAPPI

Folding Unmodified CNF Films





Passed 12-rating TAPPI kit test
for all films before and after folding

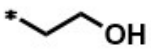
More whitening on
folds of heavier films

CNF Films Properties from Processing Changes

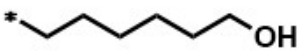
Film Type	Drainage Time (mins)	Basis Weight (g/m^2)	Thickness (μm)	Max Stress (MPa)	Strain at Break (%)	Young's Modulus (GPa)	Toughness (J/cm^3)
CNF	3.2 ± 0.1	29.9 ± 0.3	37.2 ± 2.0	60.4 ± 3.6	9.7 ± 1.2	2.17 ± 0.13	4.1 ± 0.7
cCNF	19.6 ± 1.1	27.5 ± 0.5	27.9 ± 2.9	82.6 ± 11.4	11.1 ± 1.7	2.31 ± 0.59	6.0 ± 1.6
carbic mixed	4.0 ± 0.2	28.2 ± 0.2	36.7 ± 2.1	49.1 ± 6.2	7.4 ± 1.4	2.01 ± 0.40	2.6 ± 0.8
slow drained CNF	10.3 ± 2.5	30.1 ± 0.8	37.1 ± 2.1	71.5 ± 8.8	10.6 ± 1.7	2.19 ± 0.29	5.2 ± 1.3
wet peeled CNF	3.6 ± 0.1	32.7 ± 2.5	38.0 ± 8.1	62.6 ± 8.9	14.7 ± 2.3	2.40 ± 0.43	6.3 ± 1.2
Petri dish CNF	-	30.3 ± 0.7	35.2 ± 1.6	61.0 ± 7.3	10.8 ± 2.1	3.05 ± 0.46	4.4 ± 1.2

- Higher fiber mobility may reduce drainage and create thinner films
- Slower vacuum filtration may create higher stress films
- Rate and direction of drying may affect strain

Physical Properties of CNF Films



Same tPSA



CNF Film Type	Density (g/cm^3)	Max Stress (MPa)	Strain at Break (%)	Toughness (J/cm^3)
CNF	0.78 ± 0.03	60 ± 4	9.7 ± 1.2	4.1 ± 0.7
cCNF	0.82 ± 0.11	83 ± 11	11.1 ± 1.7	6.0 ± 1.6
ME	0.79 ± 0.01	64 ± 4	8.3 ± 0.5	3.6 ± 0.3
TA	0.85 ± 0.02	44 ± 6	4.2 ± 1.2	1.3 ± 0.5
MMA	0.76 ± 0.02	49 ± 6	5.8 ± 1.9	2.1 ± 0.9
MT	0.77 ± 0.03	58 ± 3	7.6 ± 0.6	3.1 ± 0.4
MB	0.73 ± 0.03	56 ± 4	8.5 ± 1.7	3.5 ± 0.7
MH	0.74 ± 0.04	60 ± 8	8.7 ± 0.6	3.7 ± 0.6

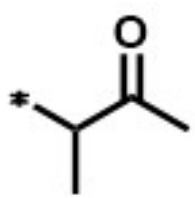
varied processing

highest tPSA

^{1}H-NMR Quantifying Thiol-ene Reaction

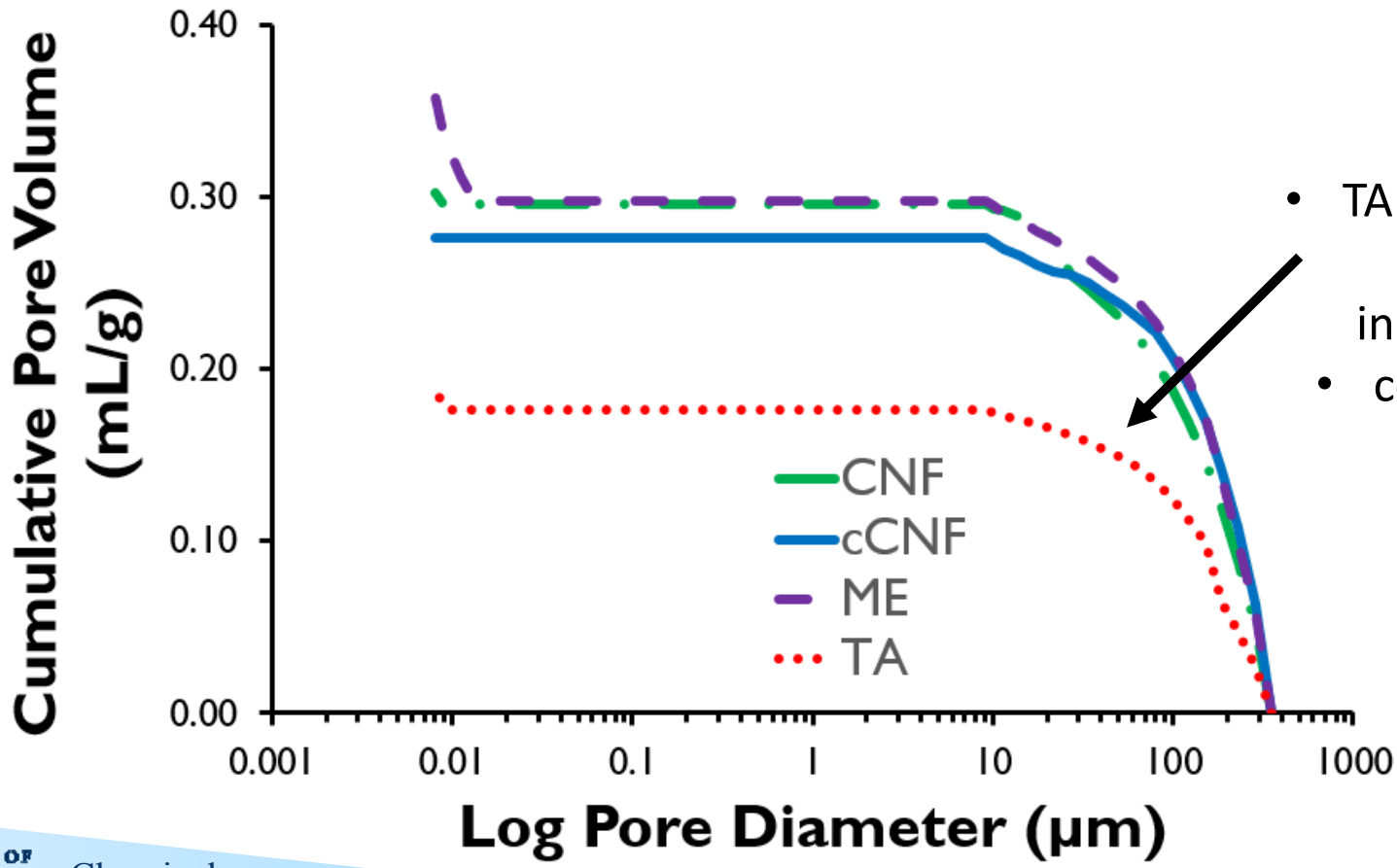
Calculations verified thiol-ene modifications

- MB sample had lower conversion
  - this one had a methyl group off of the thiol

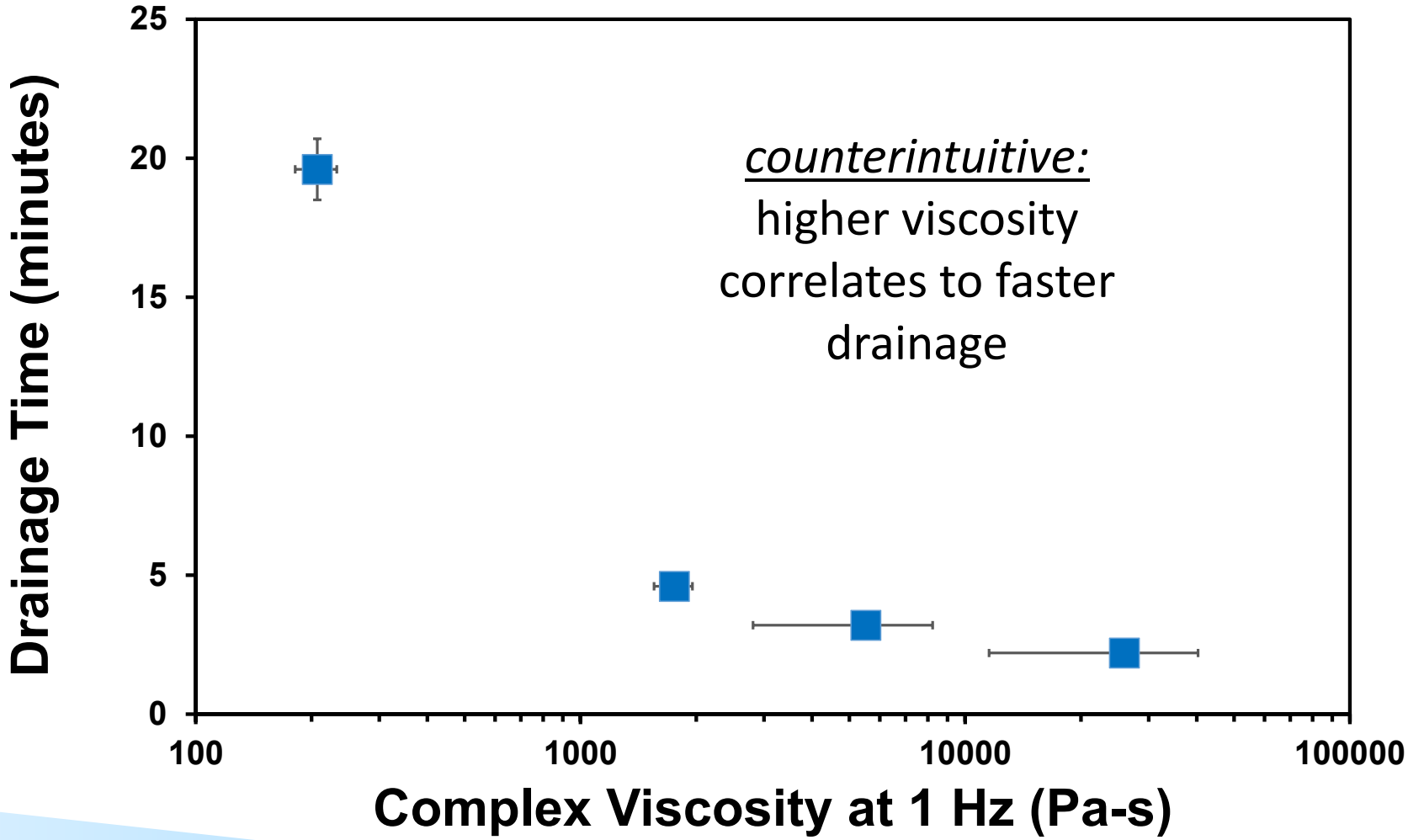


Thiol Molecule	% Thiol-ene Conversion
ME	97 ± 5
TA	92 ± 6
MMA	88 ± 9
MT	96 ± 1
MB	42 ± 4
MH	94 ± 3

Cumulative Volume of Pores



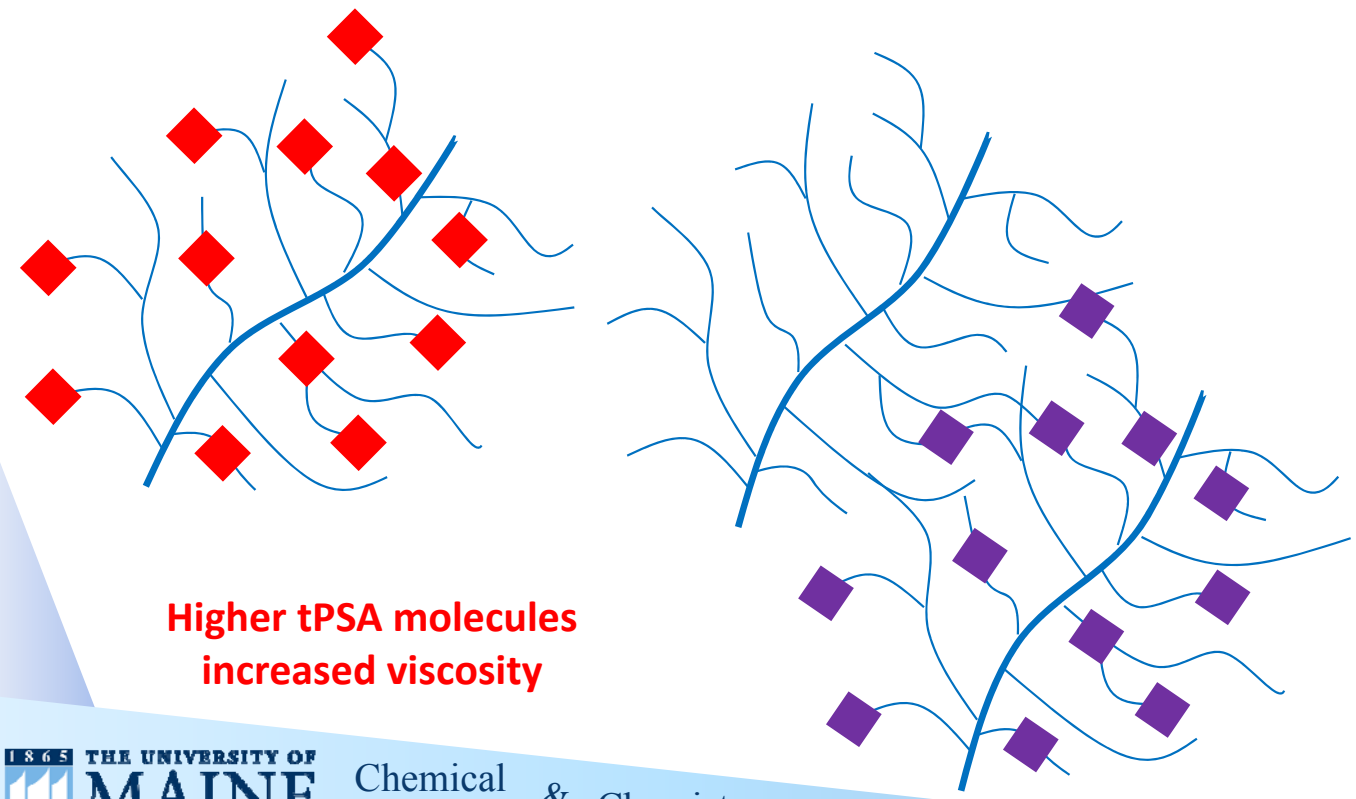
- TA highest density, but did not increase strength
- could be due to interactions


Drainage Time (minutes)
25
20
15
10
5
0
100
1000
10000
100000
Complex Viscosity at 1 Hz (Pa-s)
counterintuitive:
higher viscosity
correlates to faster
drainage

Fibril Mobility

Fibers interact through attractive forces

- Surface chemistry affects interactions



Higher tPSA molecules increased viscosity

lower tPSA molecules decreased viscosity

Formation Effects on Strength

<u>higher fibril mobility</u>

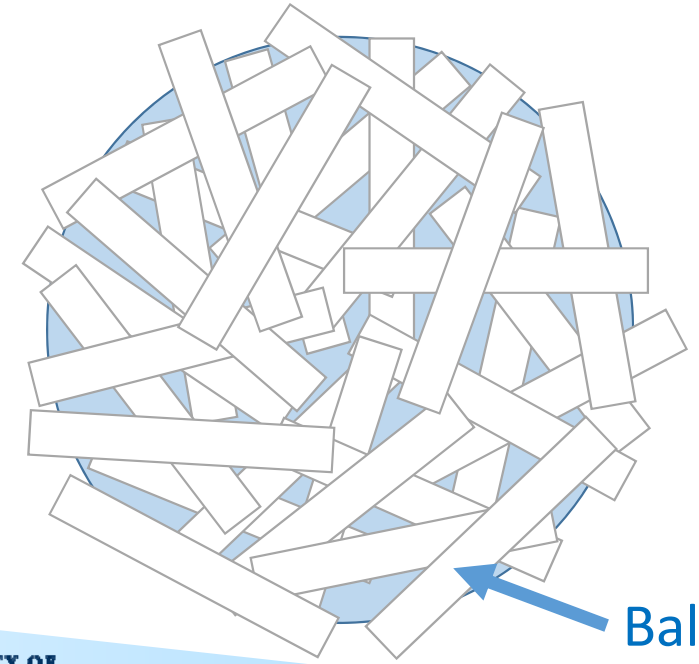
- slows drainage
- well-dispersed fibers → increases strength

<u>higher fibril attraction/lower mobility</u>

- create flocs
- improves drainage
- over flocculation → strength loss

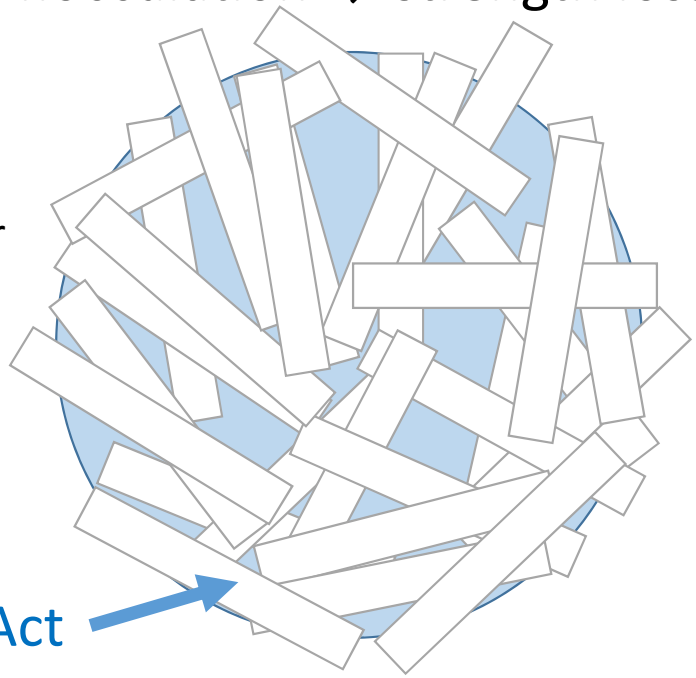
cCNF

Lower tPSA



TA

Higher tPSA



Balancing Act