A supercritical CO_2-based process to generate cellulose nanofiber/polylactic acid composites

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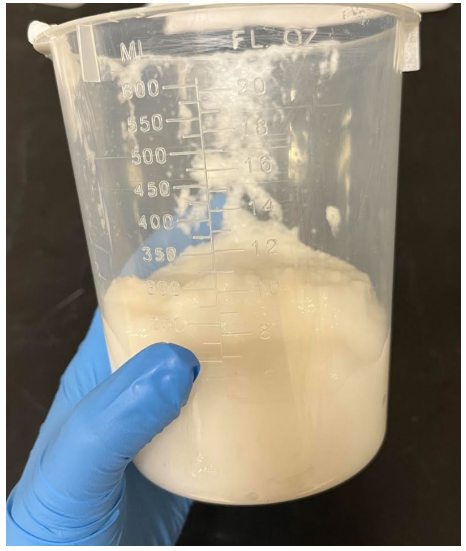
June 14th, 2023

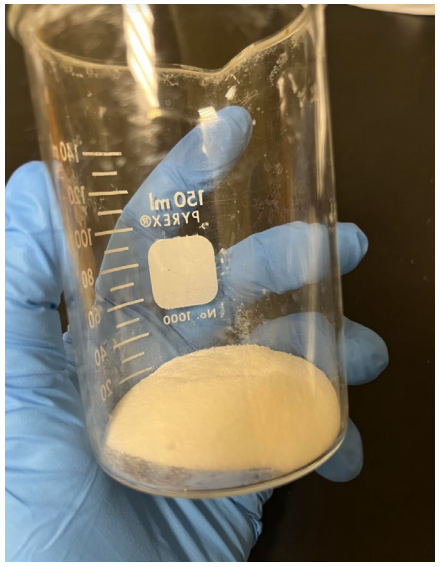
Goal: 3D print *bio-based* composites on the pilot scale



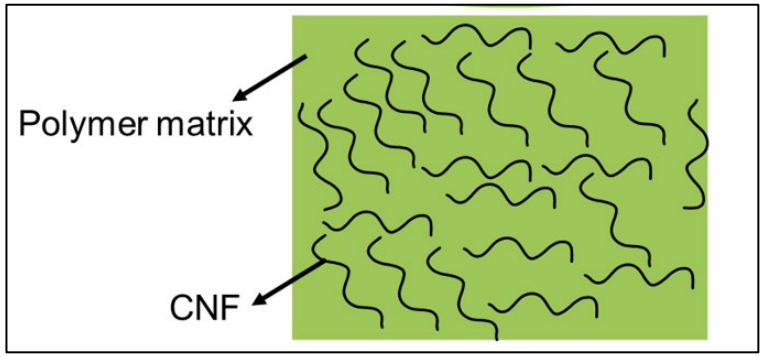
CNF
97% water!

Dry

Surface Modification



Poly Lactic Acid (PLA)



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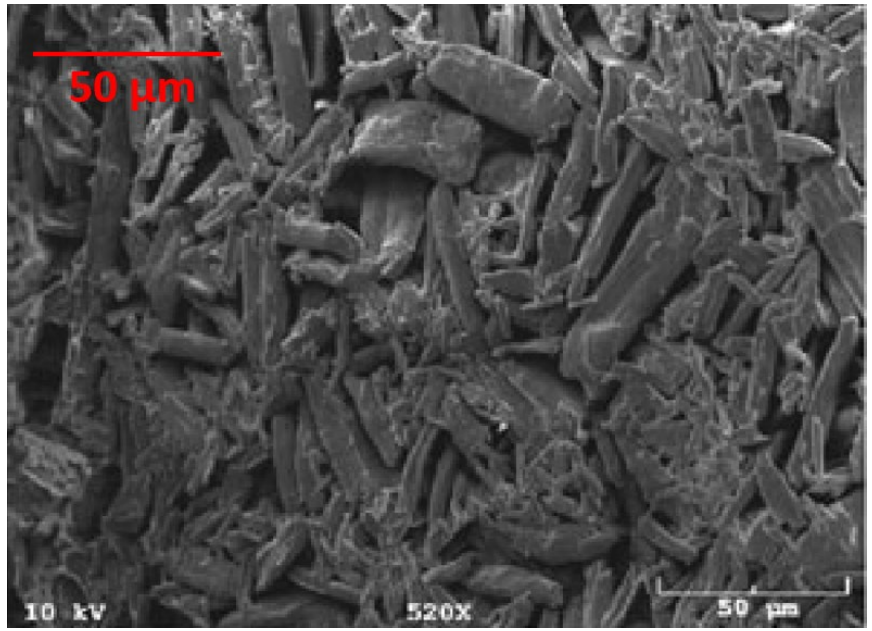
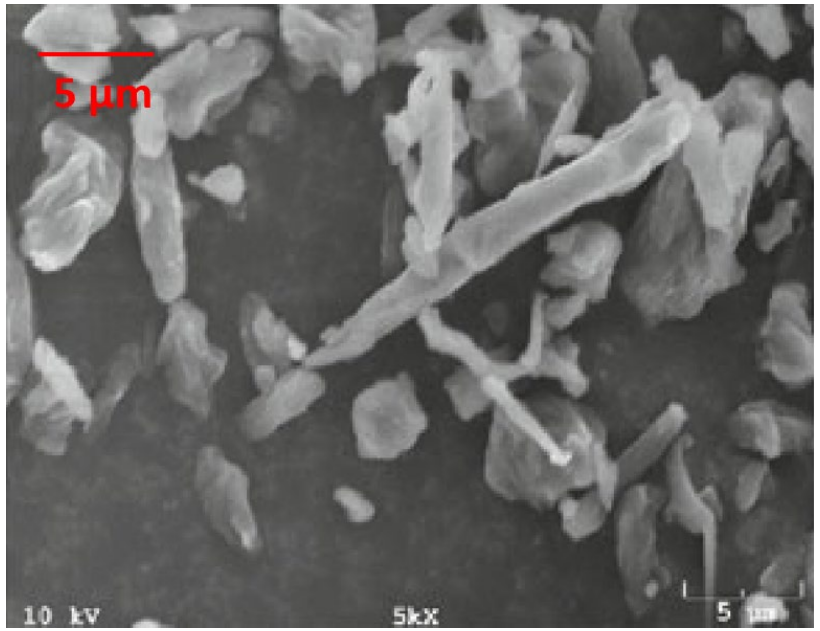
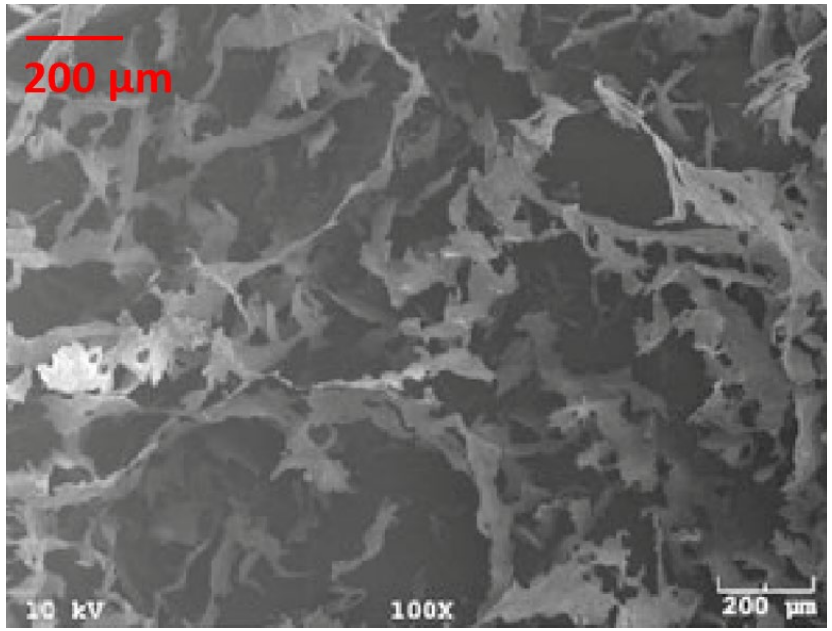
The Problem: CNF likes to aggregate during the drying process



Oven Dried CNF



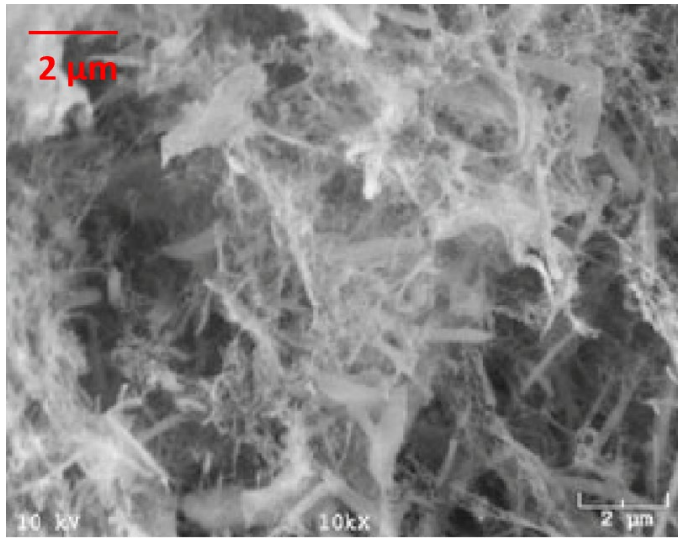
Spray-Dried CNF



Freeze Dried CNF

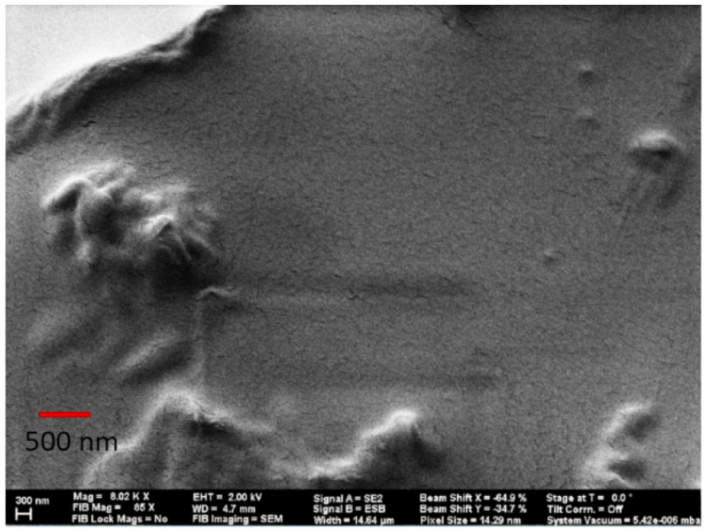
Yucheng Peng, Douglas J. Gardner, Yousoo Han. Drying cellulose nanofibrils: in search of a suitable method. *Cellulose.* **2011.**

Compounding of supercritical CO_2 "dried" CNF with PLA - Lu Wang

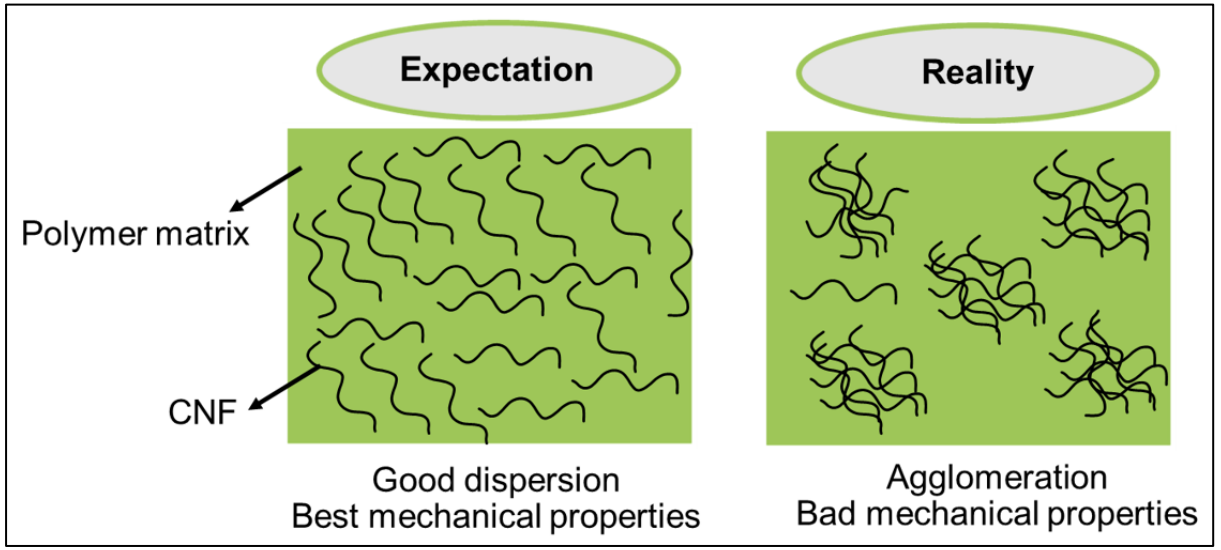


Melt mix with PLA
180 C

Native material or surface
Treated to be hydrophobic



Supercritical CO_2 dried CNF: "dust balls"

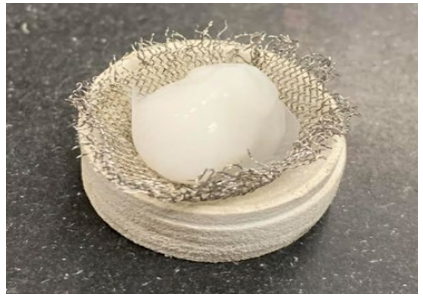


Challenges:

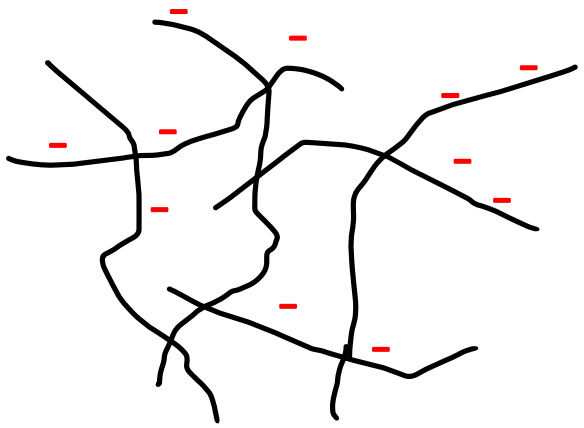
- Requires solvent exchange with ethanol
- CNF "dust ball's" do not disperse and distribute when compounded with PLA

Can we use contact dewatering and avoid ethanol?

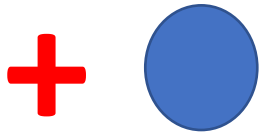
Mix PLA with
1% CNF slurry

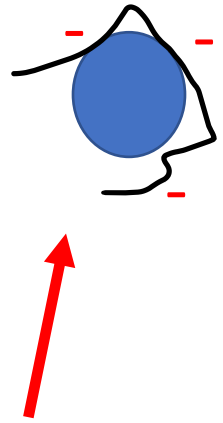


CNF



PLA particles

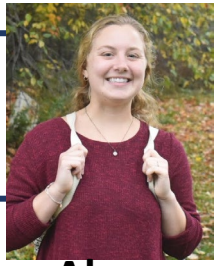




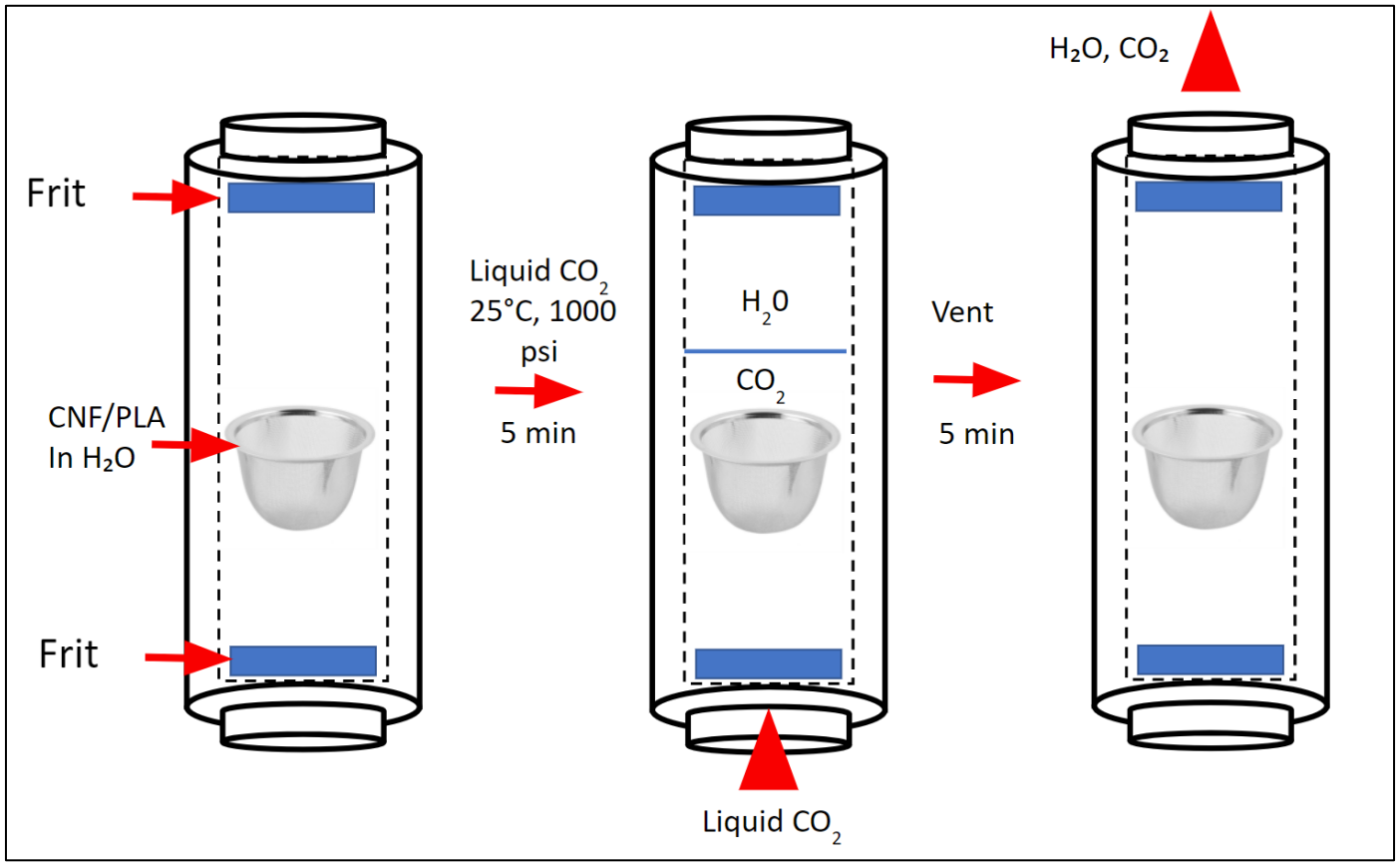
Water is retained inside the gel-like structure of CNF

Adsorption of the CNF on the PLA disrupts the gel-like structure allowing the release of water

Contact Dewatering/Liquid CO_2 Solvent Exchange

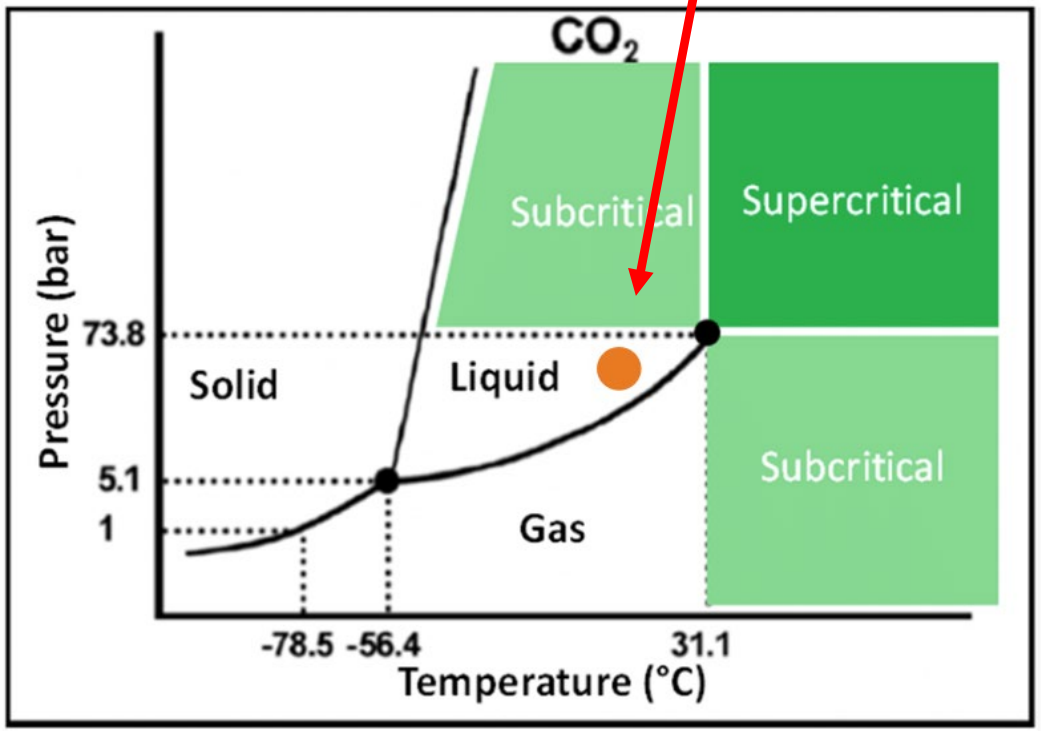


Alyson Manley



One Cycle

You are here



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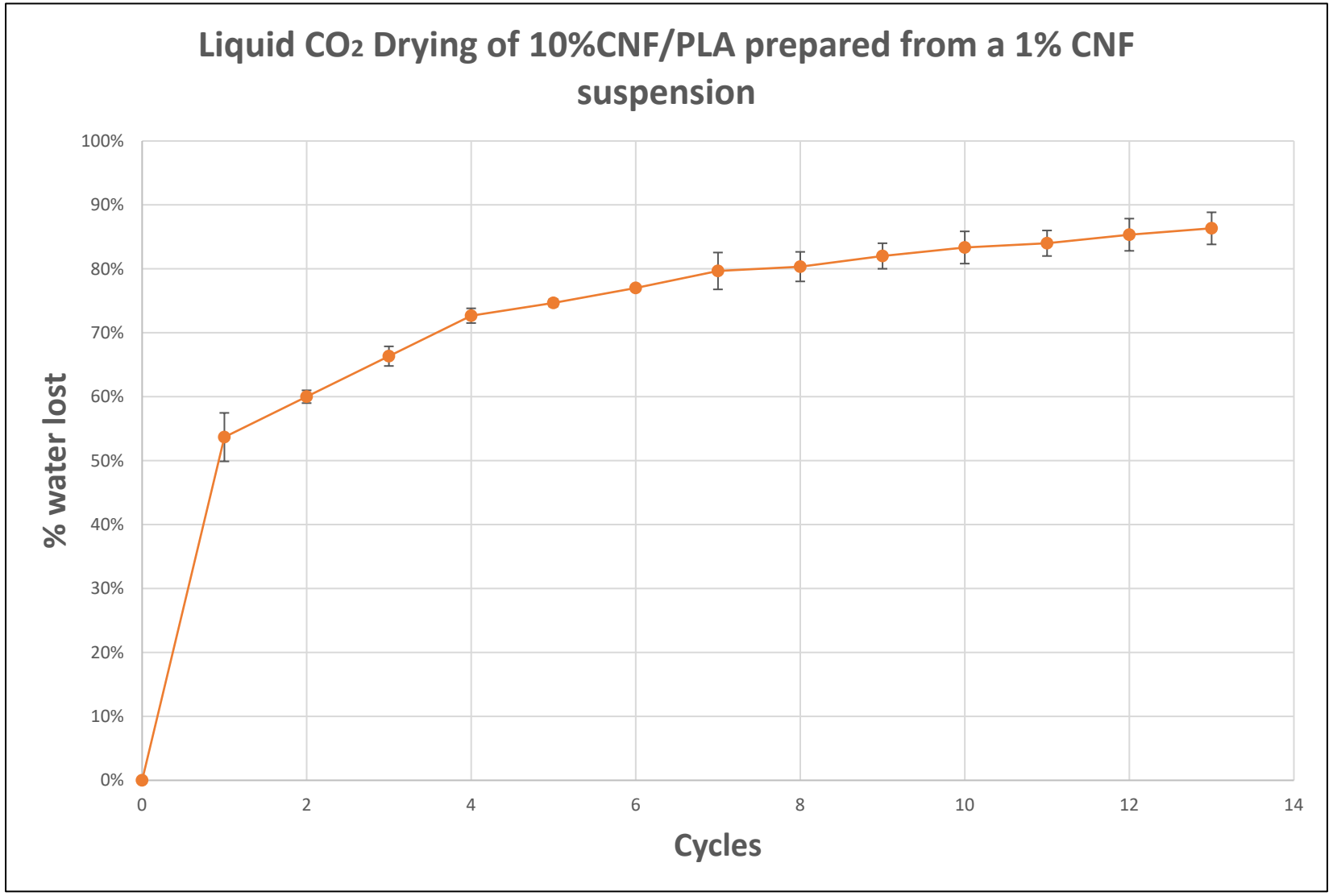
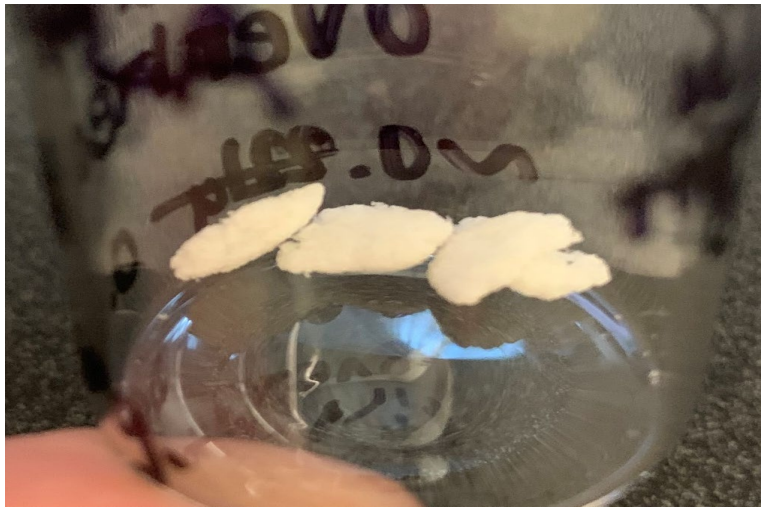
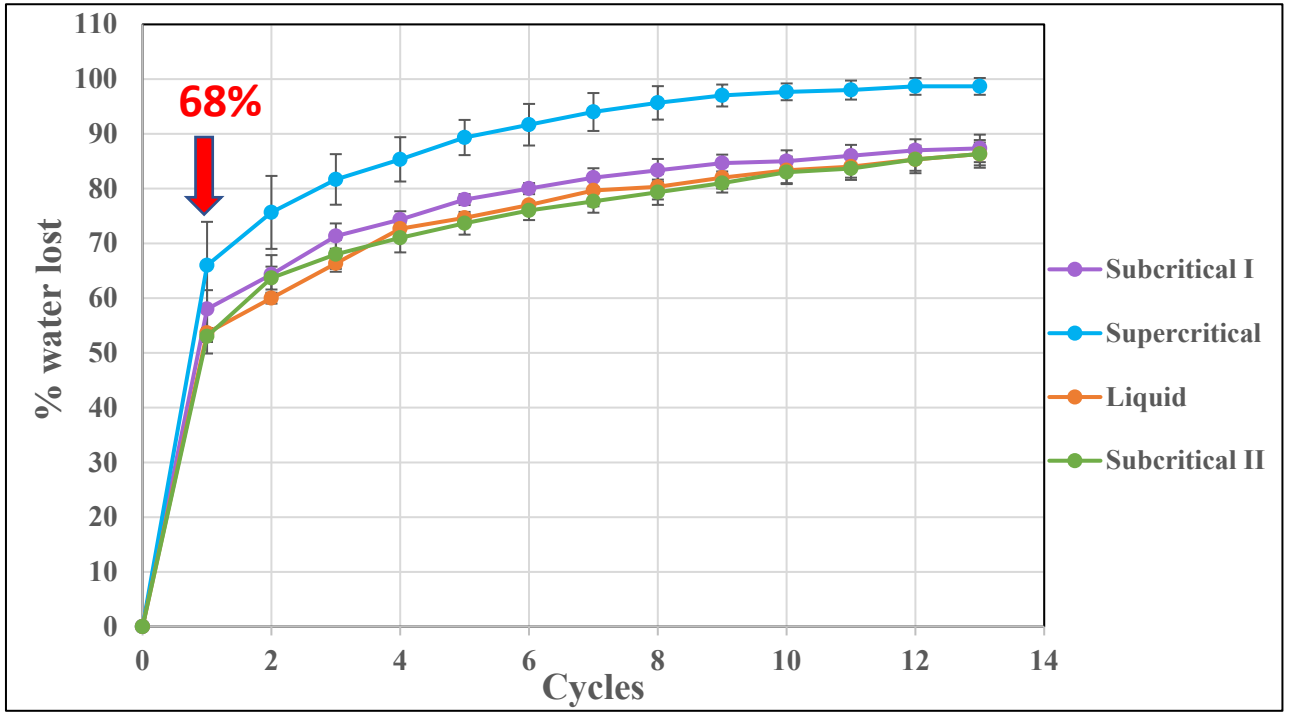
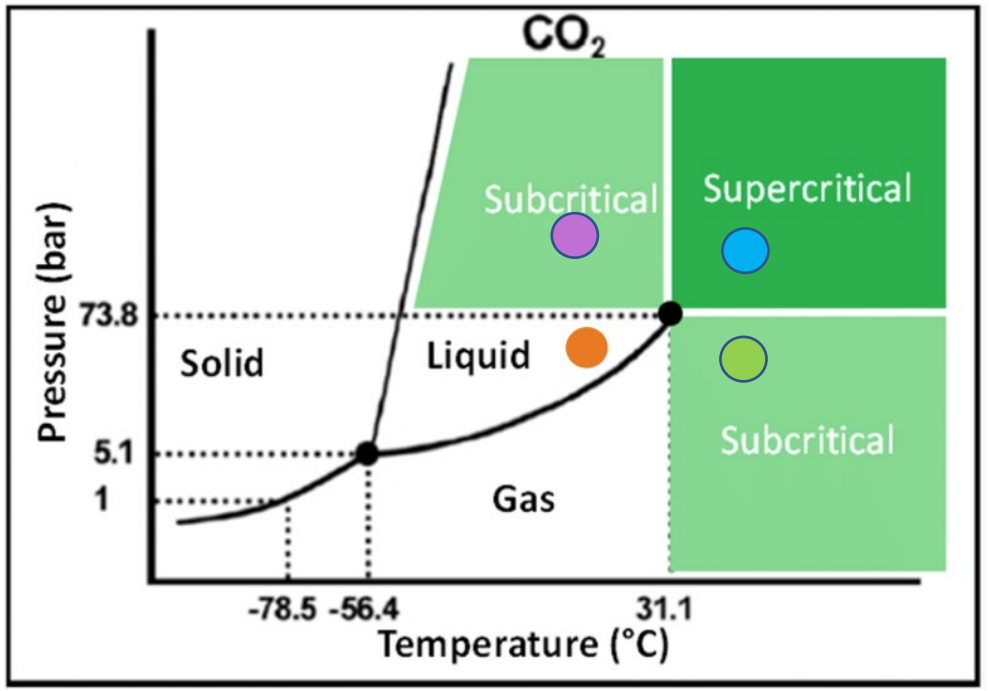
Contact Dewatering/Liquid CO_2 Solvent Exchange



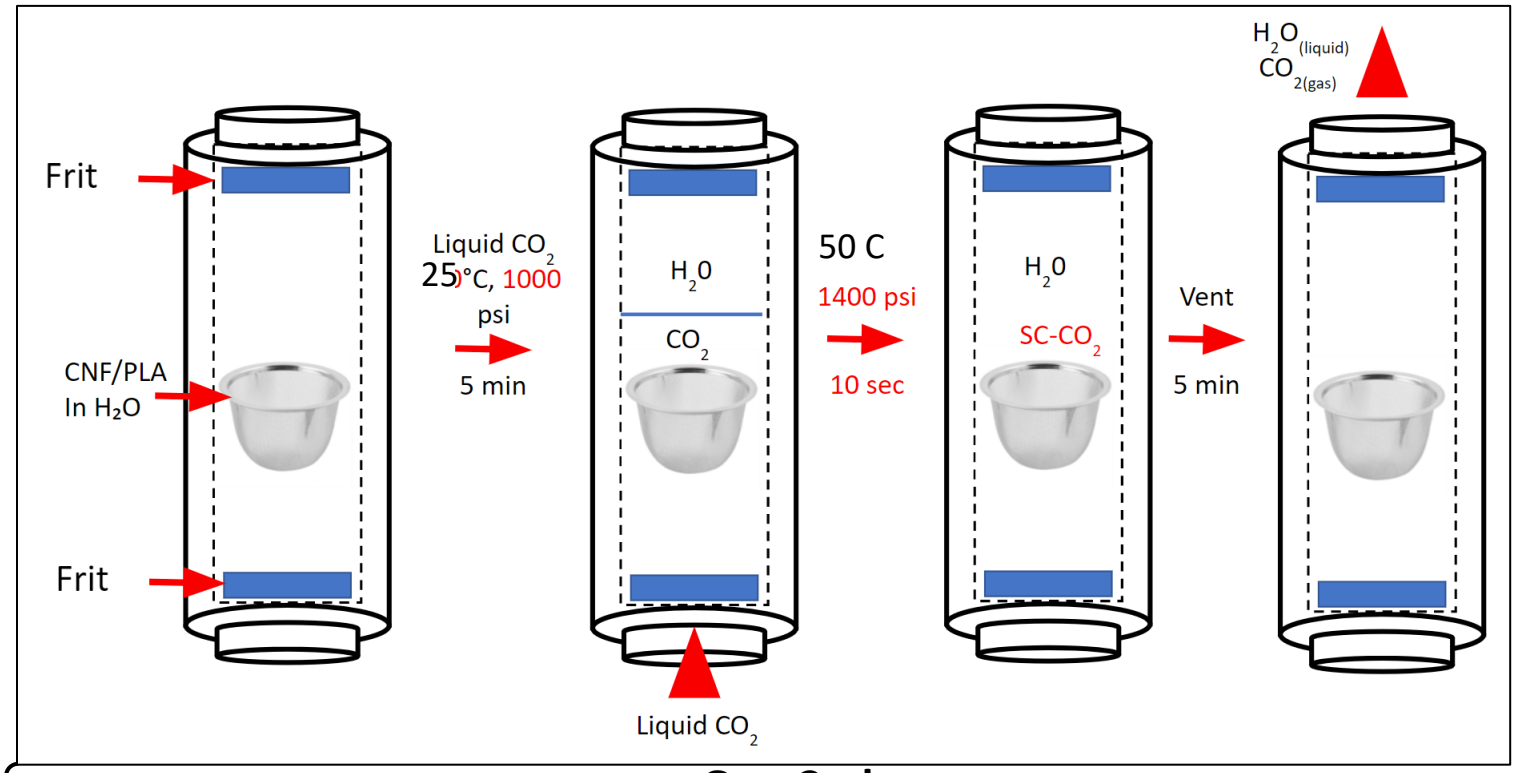


4 Quadrants: Why is supercritical CO_2 better at drying CNF?



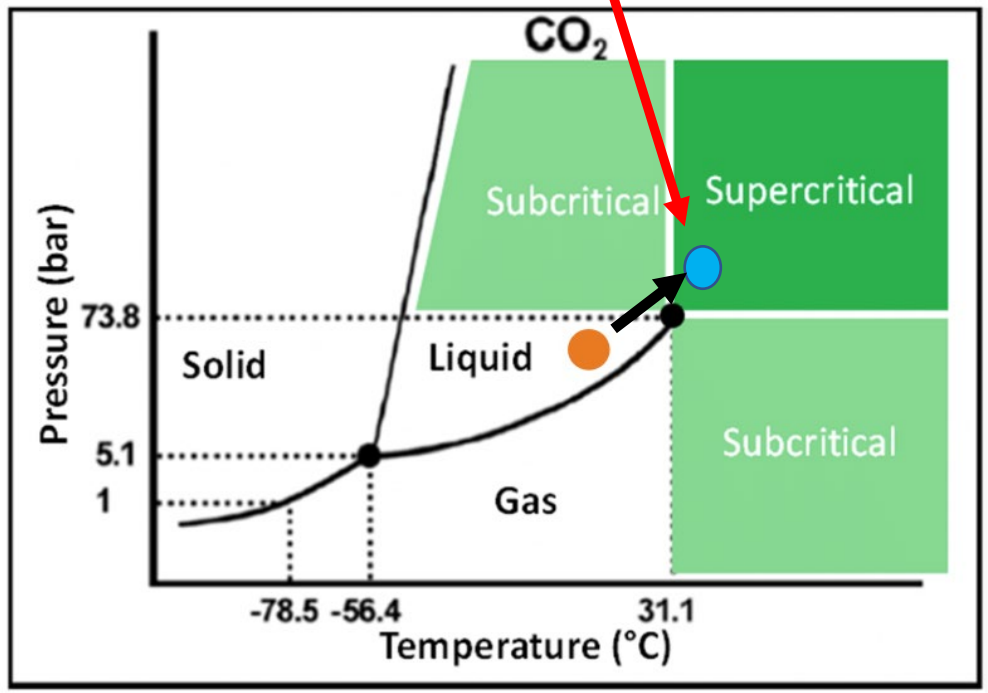


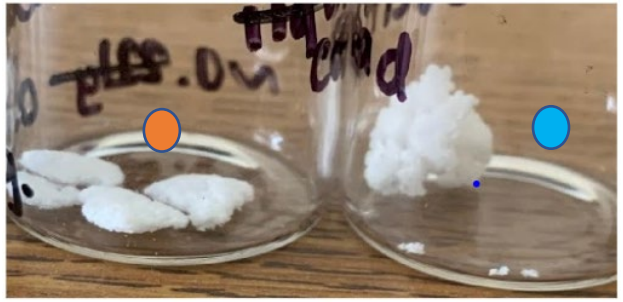
Liquid CO_2 Solvent Exchange + scCO_2 Drying – The Set Up



One Cycle

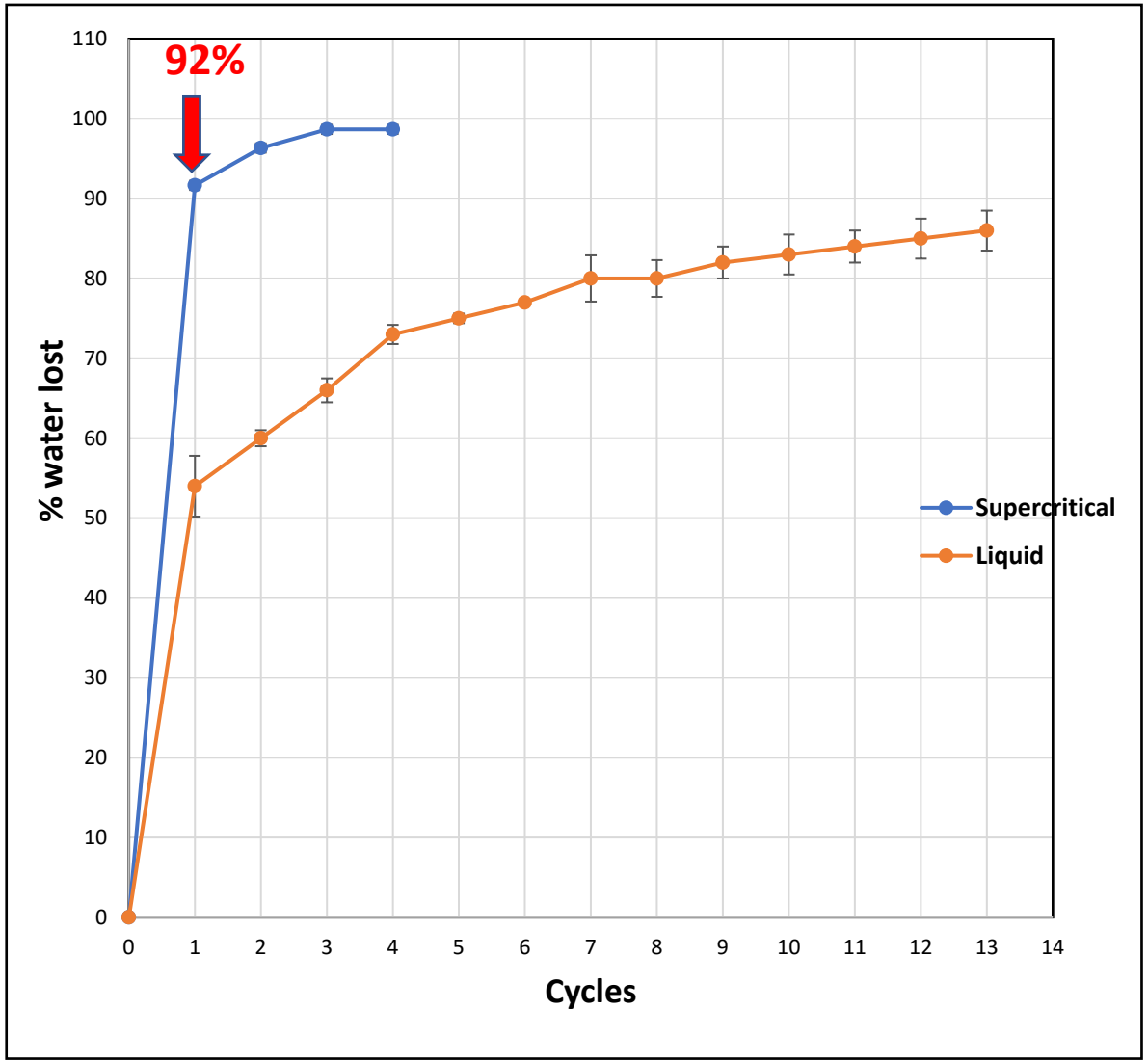
You are here

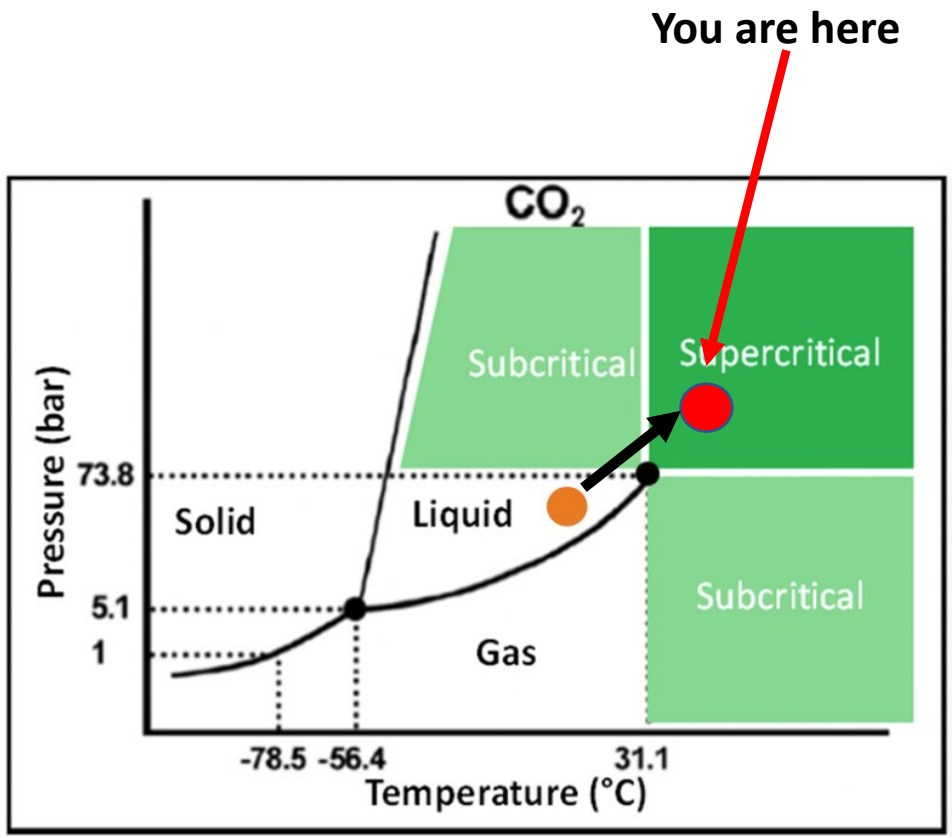




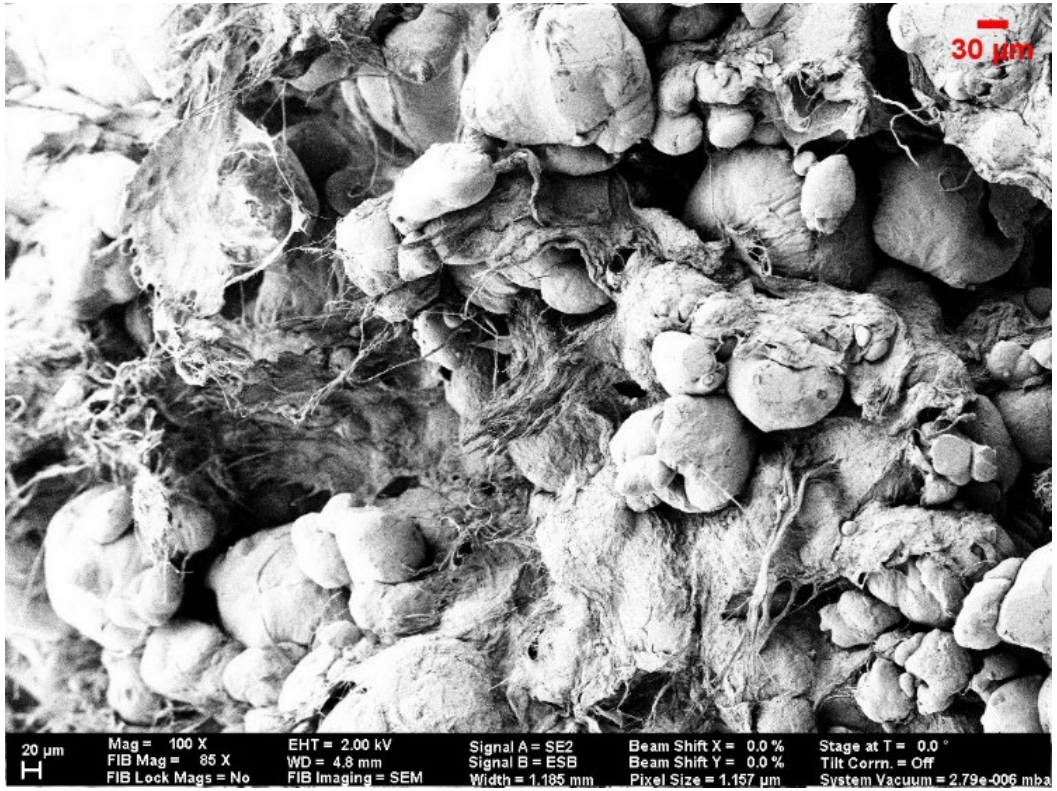
Liquid CO_2 Solvent Exchange + $scCO_2$ Drying

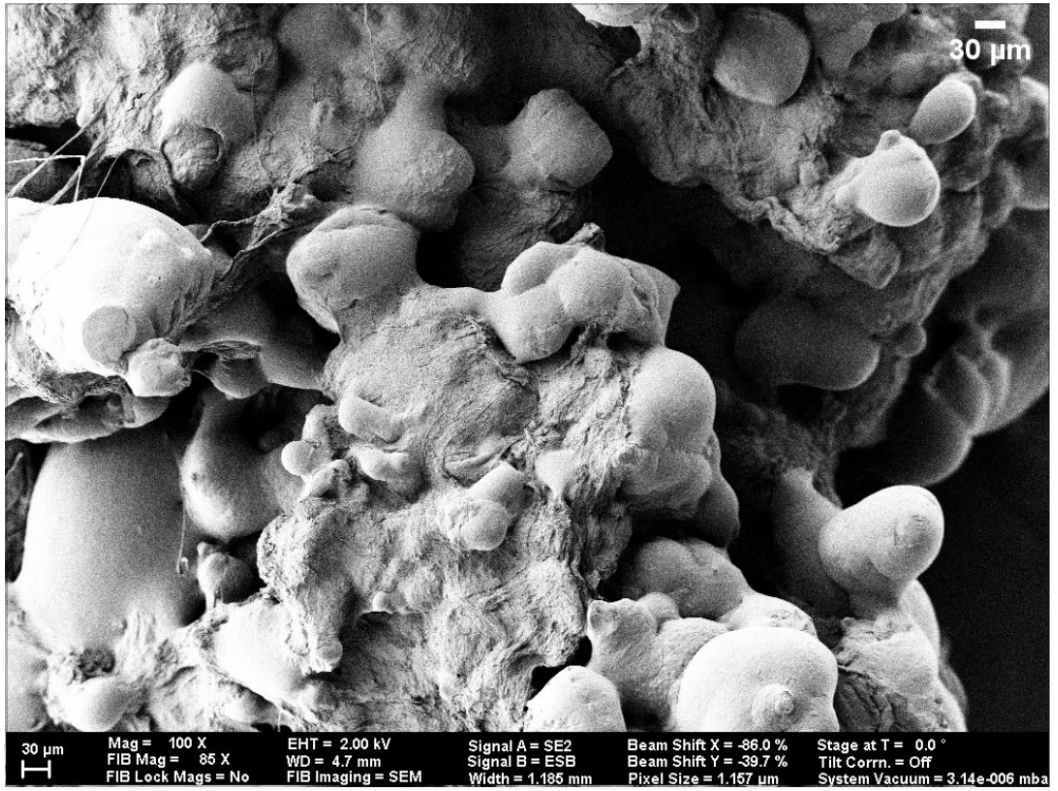
Drying of 10%CNF/PLA prepared from a 1% CNF suspension



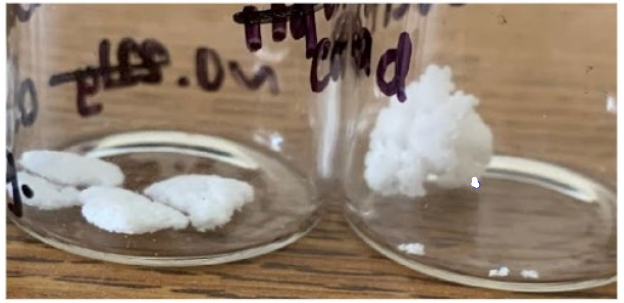


SEM (micron-scale)





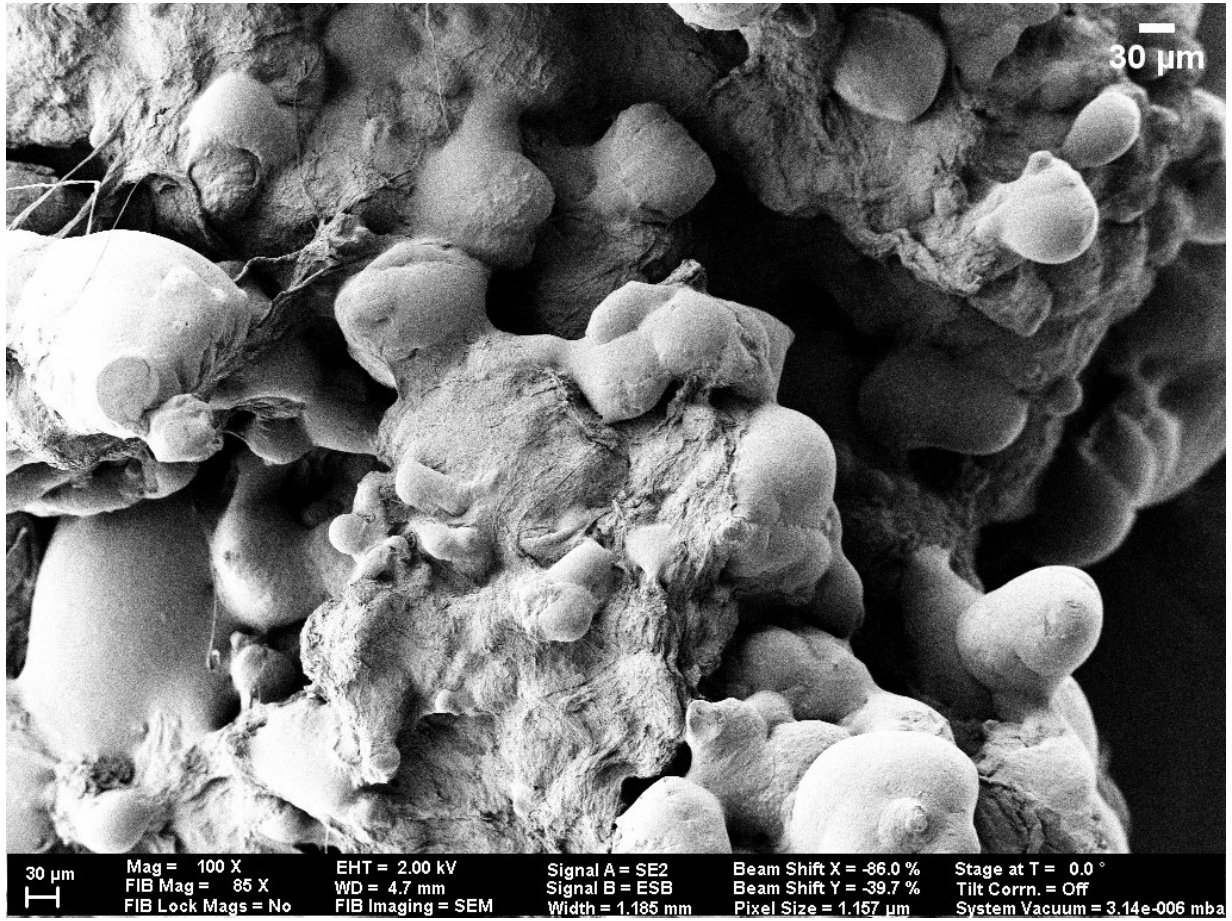
Liquid CO_2



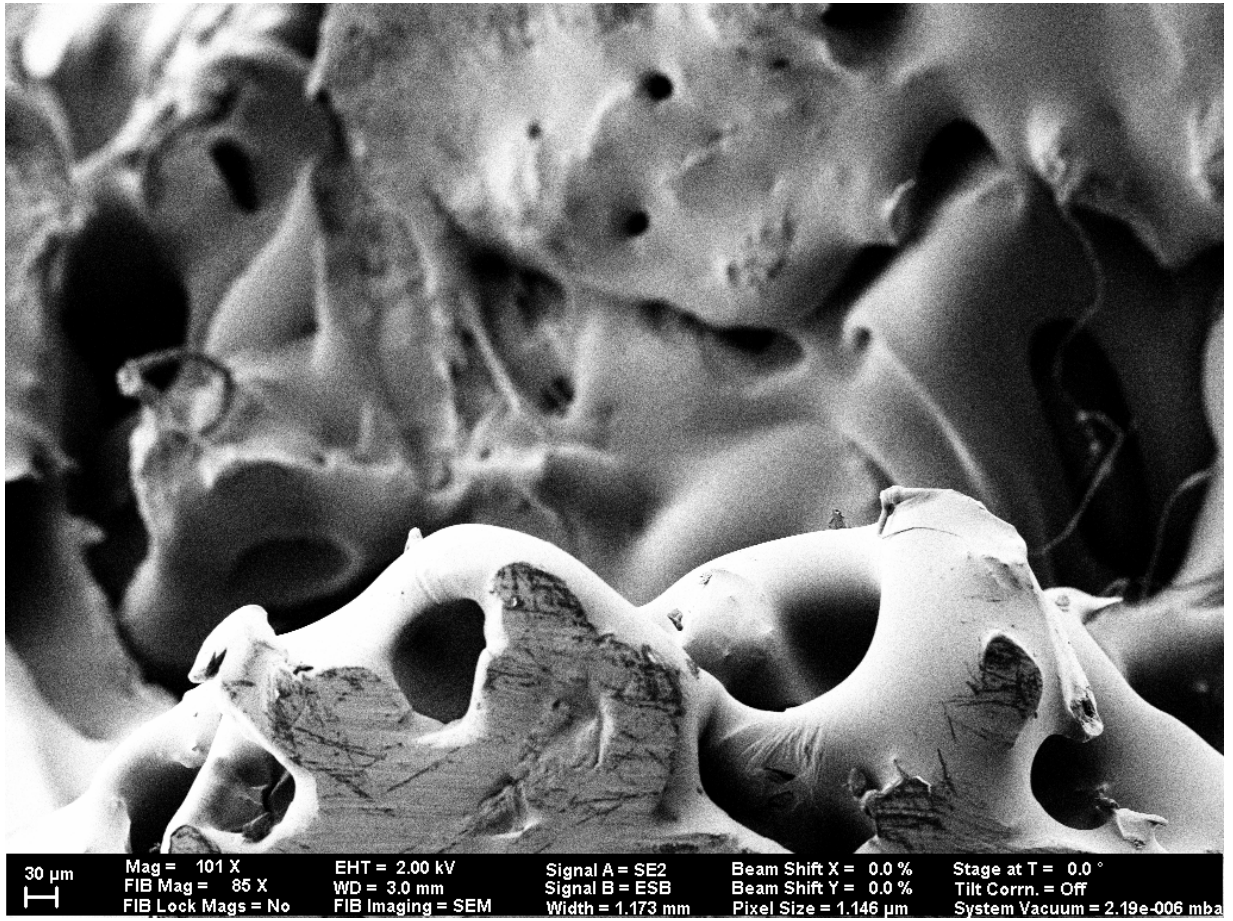
Supercritical CO_2

Melt Mixing- Supercritical Dried 10% CNF/PLA

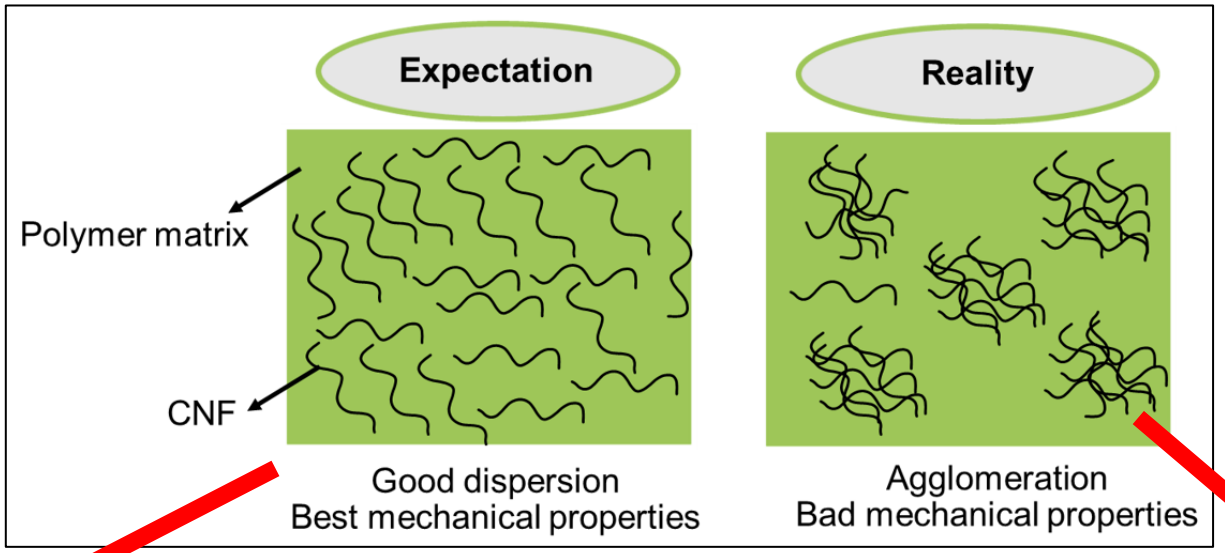
Before Melting



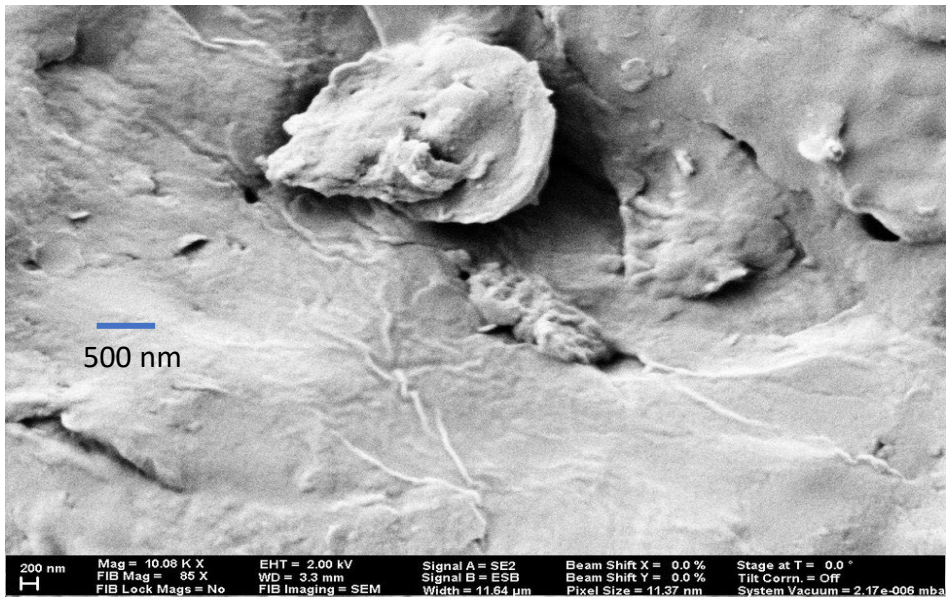
After Melting



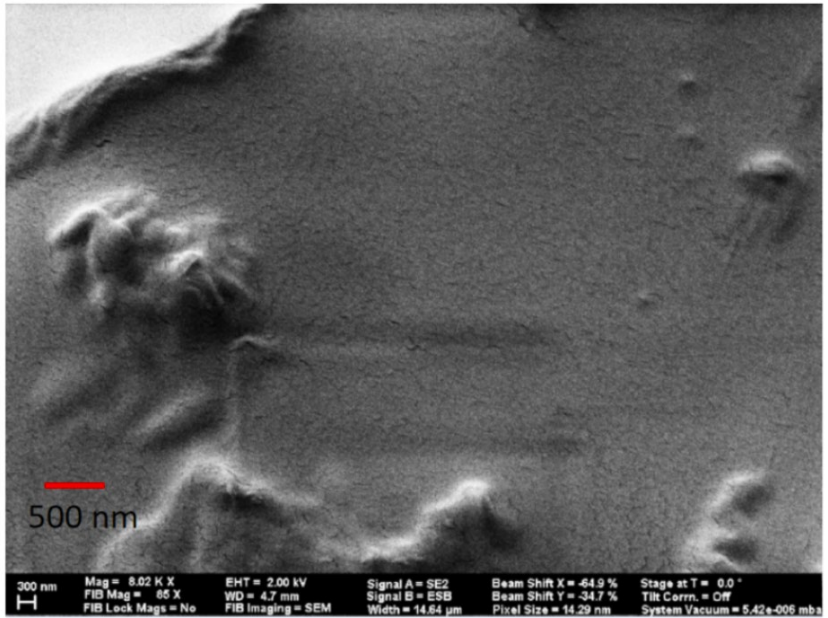
Melt Mix



Melt Mix CNF/PLA



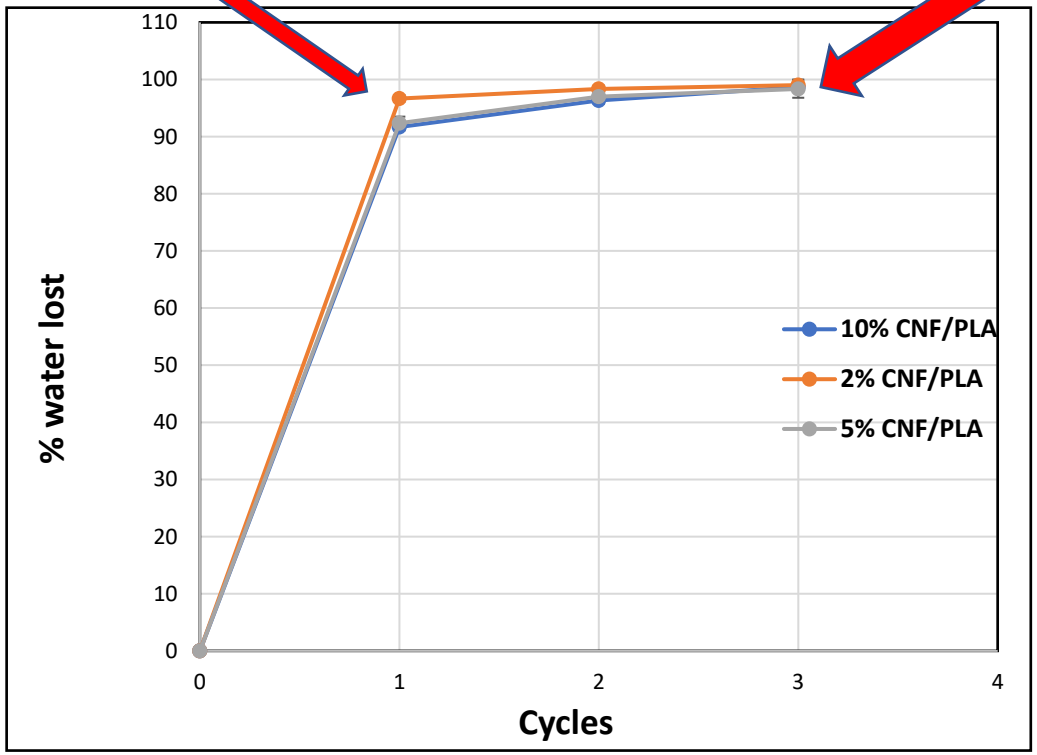
Melt Mix
Dust Balls with
PLA pellets



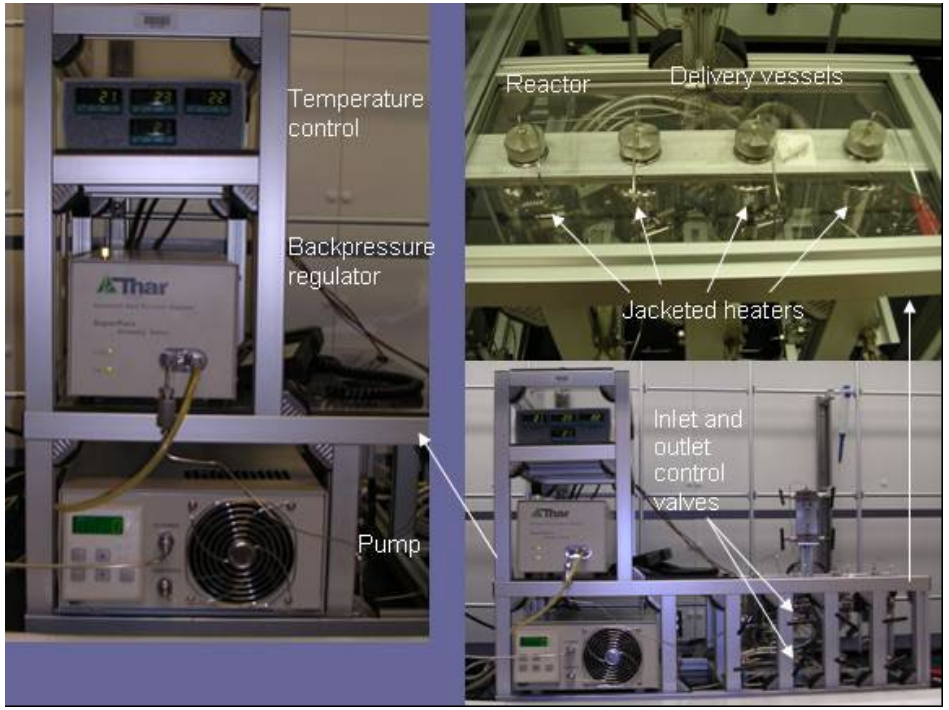
Supercritical CO_2 Drying of CNF

97% dried after 1 cycle

<99% after 3 cycles



Scale- up



Supercritical Fluid Deposition System
0.2 g CNF/PLA

Scale up

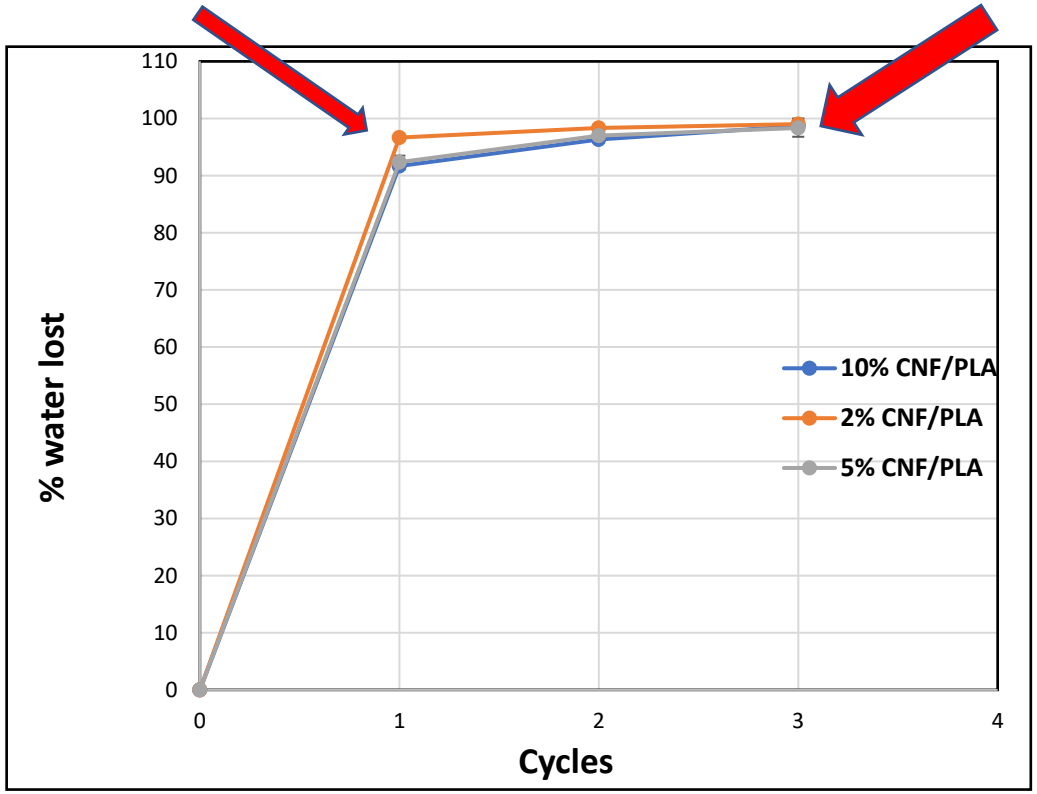
Measure mechanical properties

New Supercritical Fluid Deposition System
40 g CNF/PLA

Supercritical CO_2 Drying of CNF-

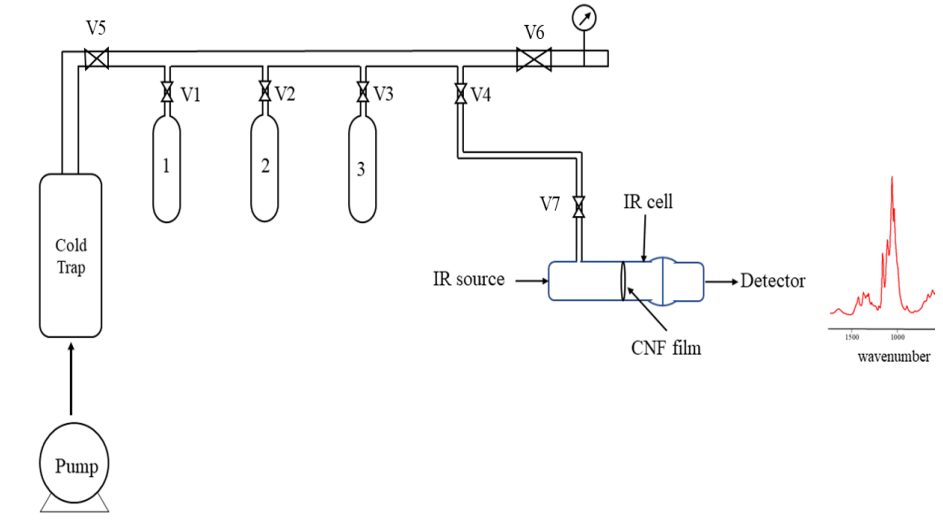
97% dried after 1 cycle

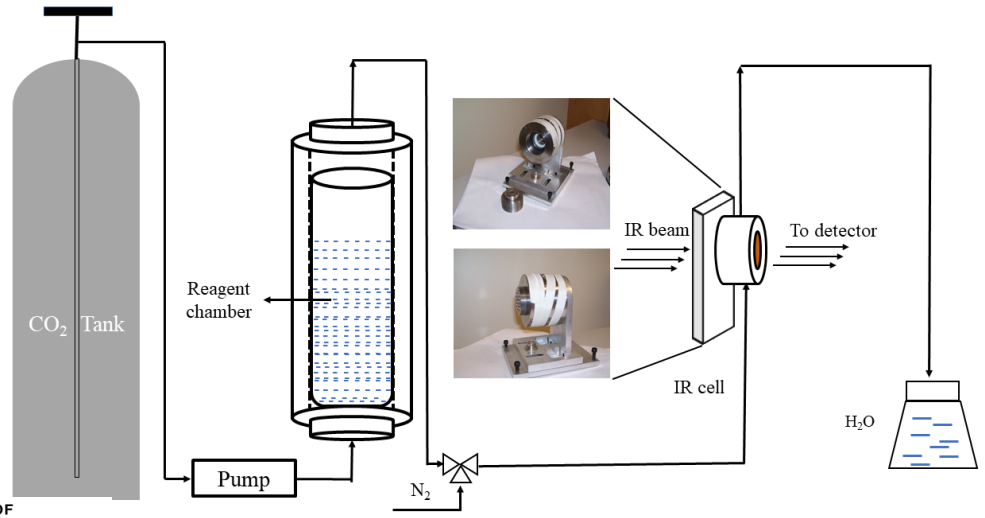
<99% still a lot of water!



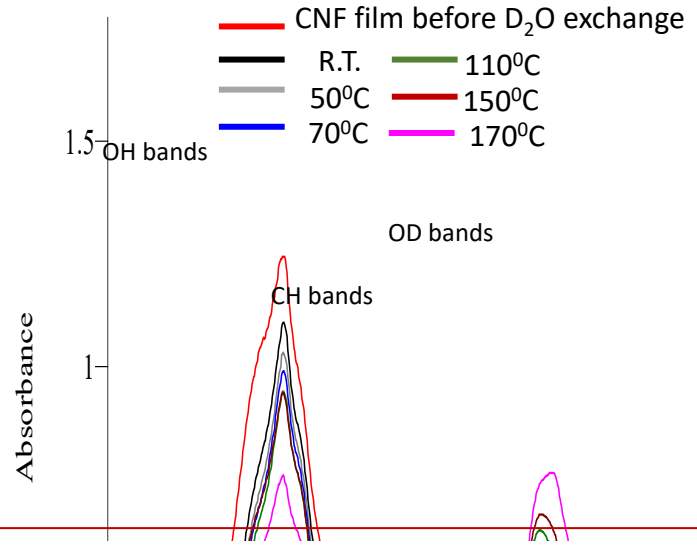
IR spectroscopy: D_2O exchange in the gas phase vs supercritical CO_2

Dr. Sabrina Sultana



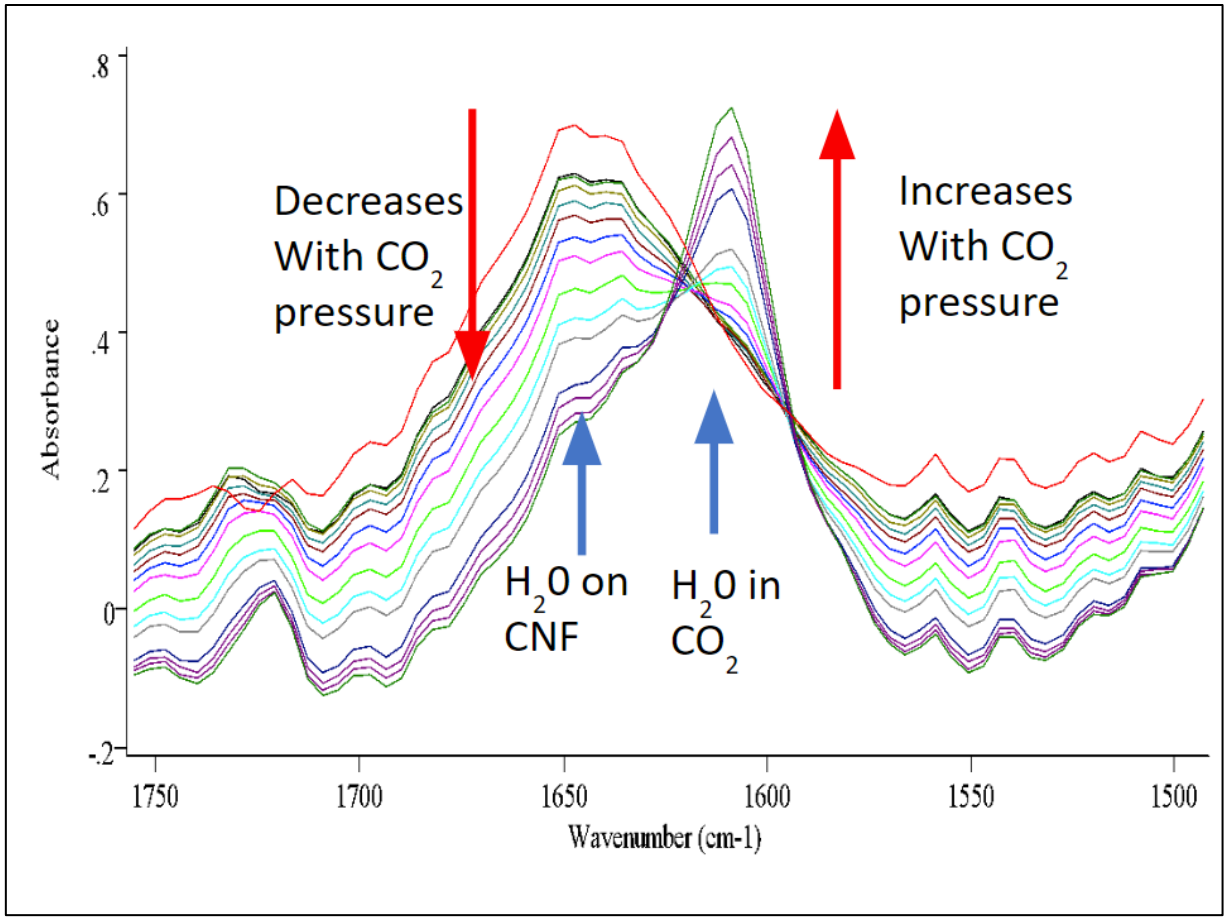


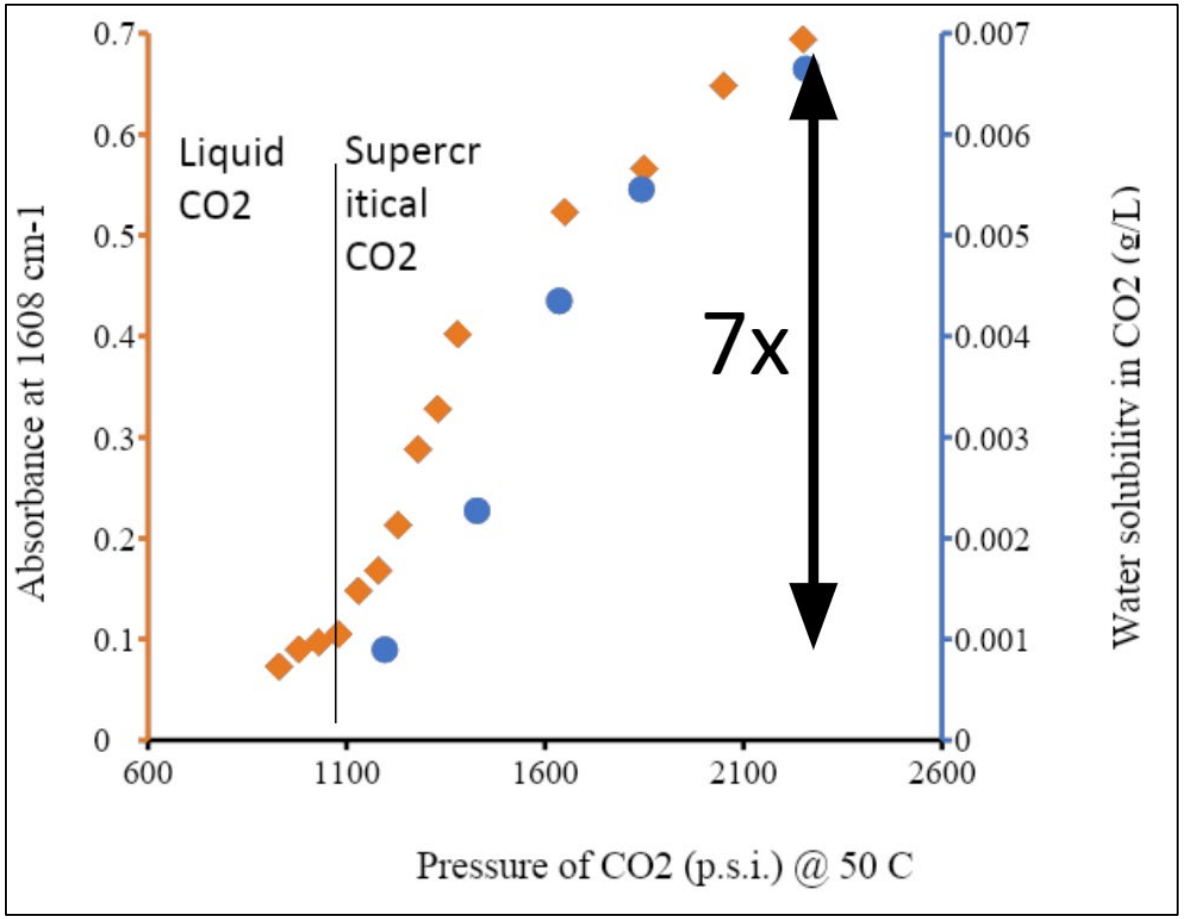
Gas-phase

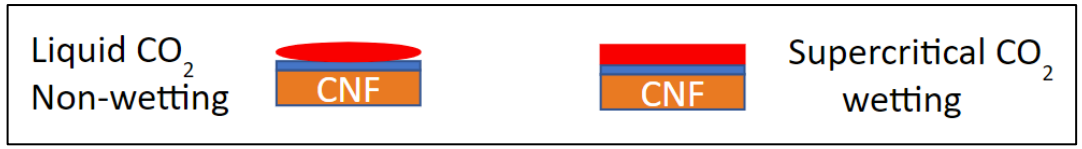


- 35% more D_2O exchanged with OH groups using $scCO_2$ at 50°C
- Same level of D_2O exchanged using $scCO_2$ at 50°C required heating at 150°C in the gas phase

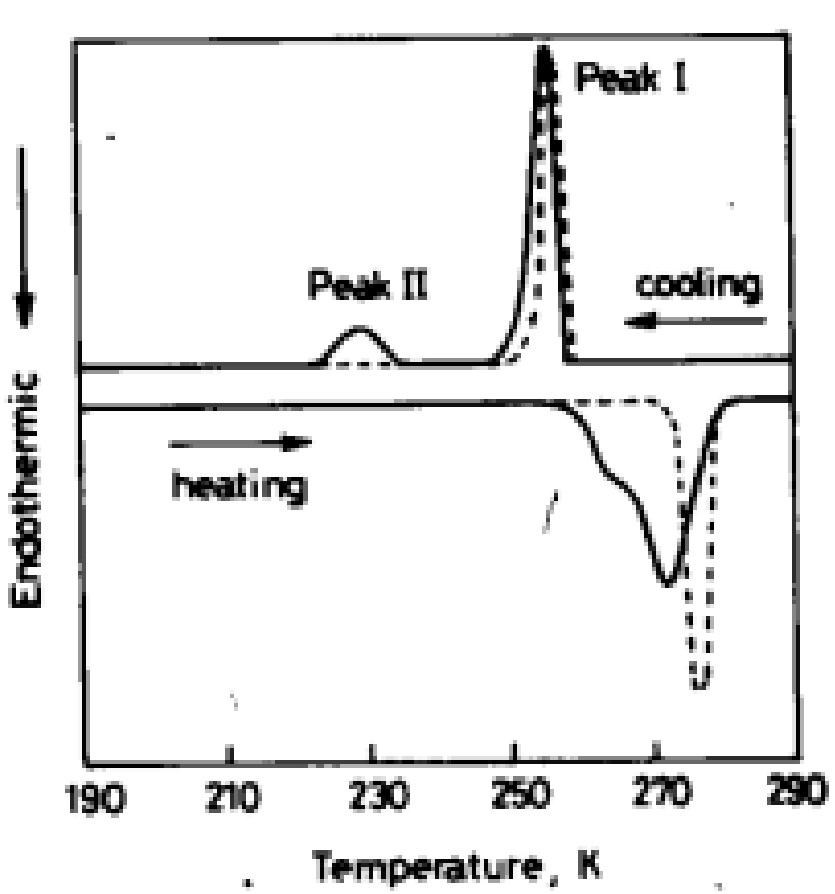
Supercritical CO_2 is better at removing the strongly adsorbed water

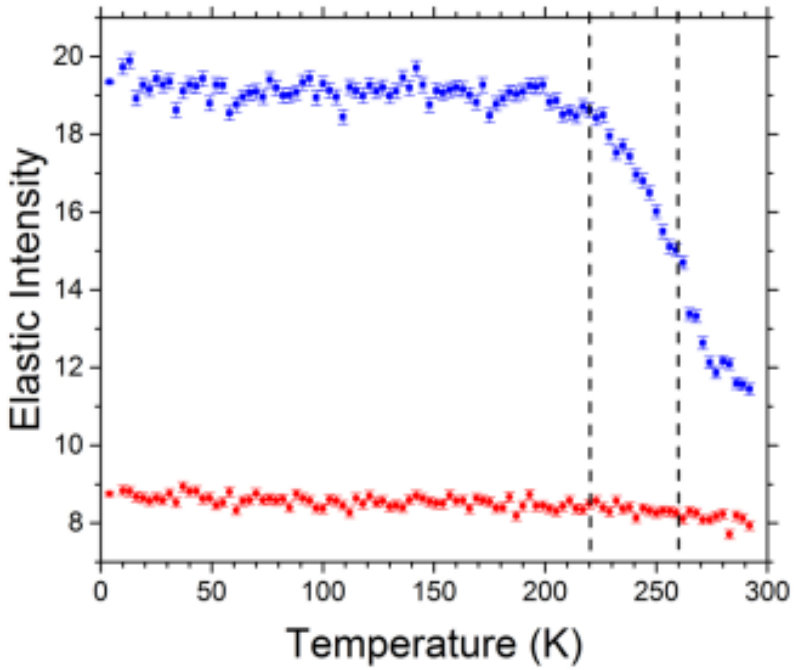






Adsorbed water on CNF

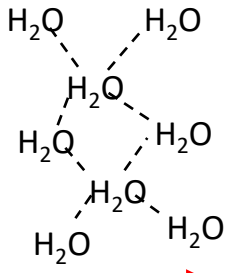




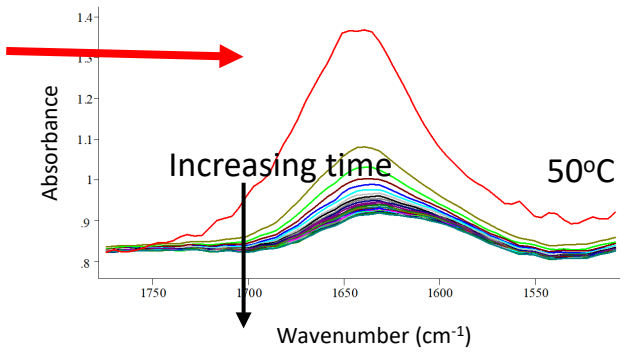
Nakamura et al. Textile Research Journal, pp. 607, 1981

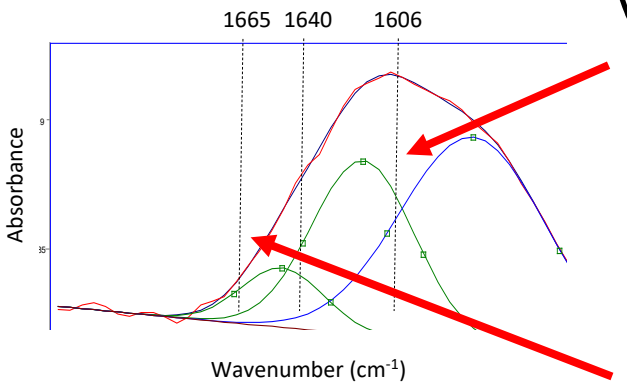
O'Neill et al. Scientific Reports 7:11840, 2017

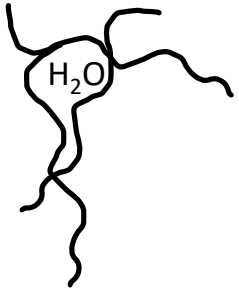
Drying CNF in air vs supercritical CO_2

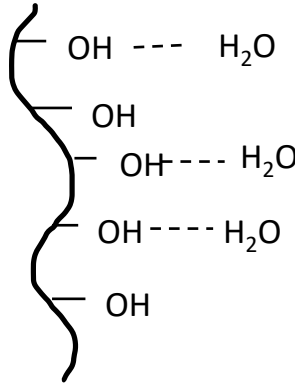


Dried CNF (7% water) dried in air

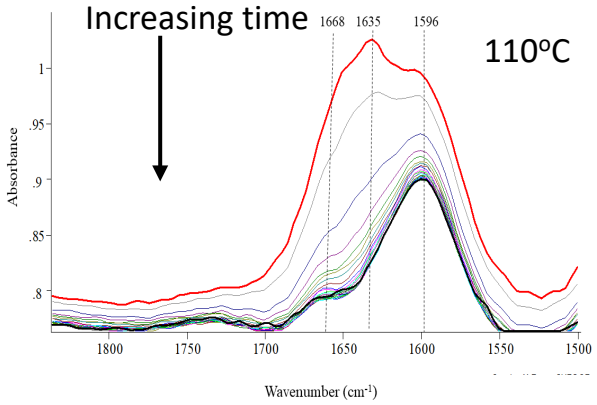


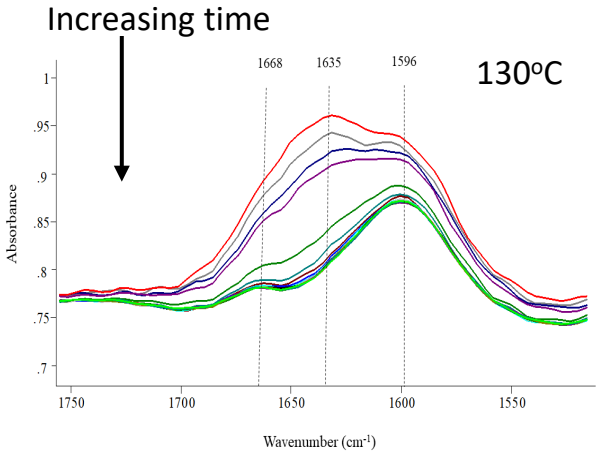




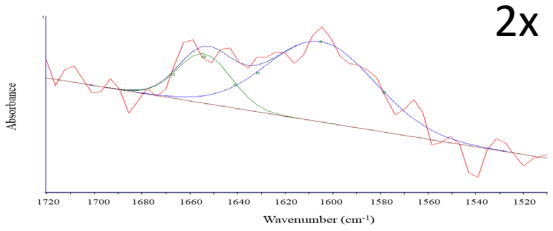


CNF wet film with 35-40wt% water dried in air



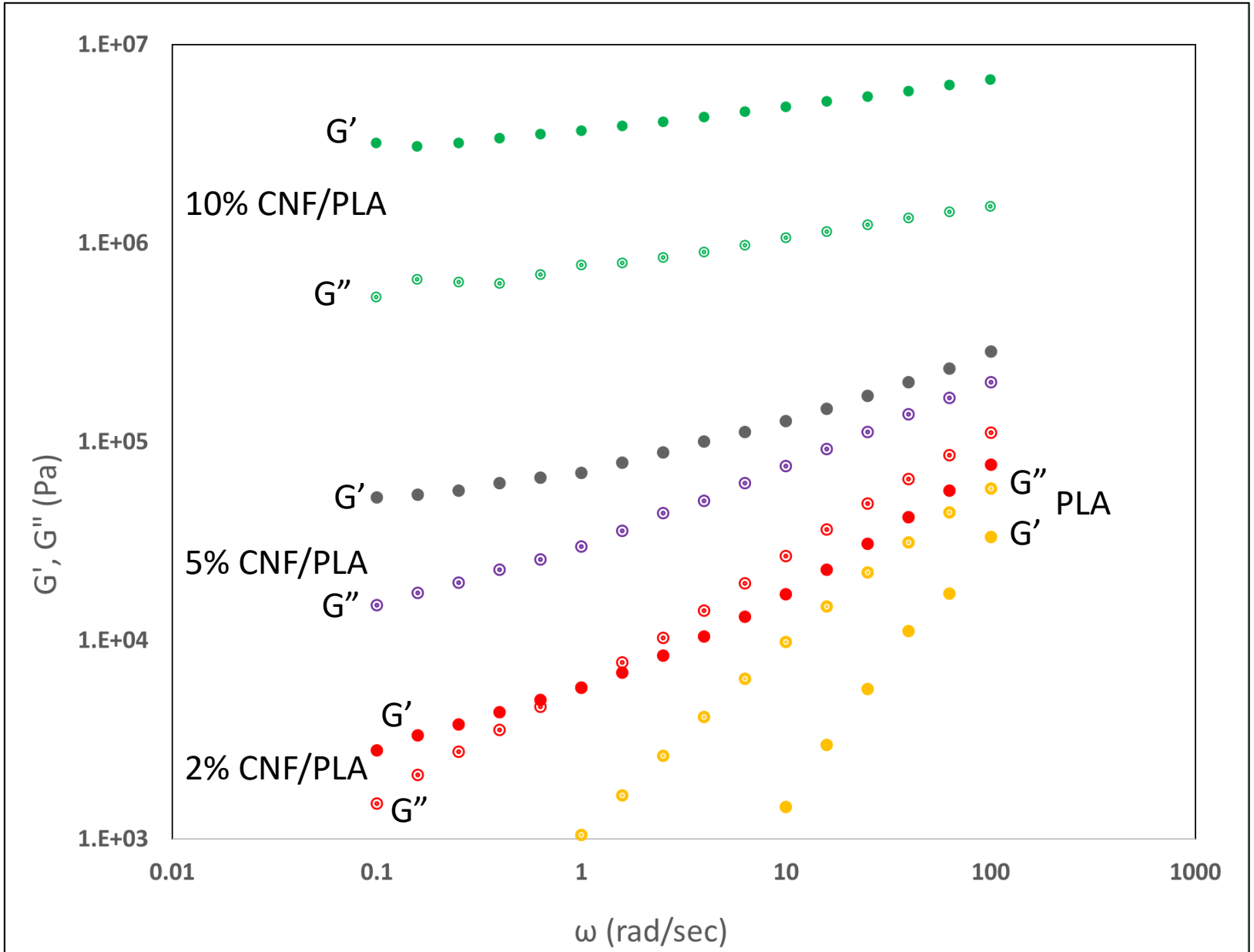


CNF wet film dried with $ScCO_2$ at 50°C

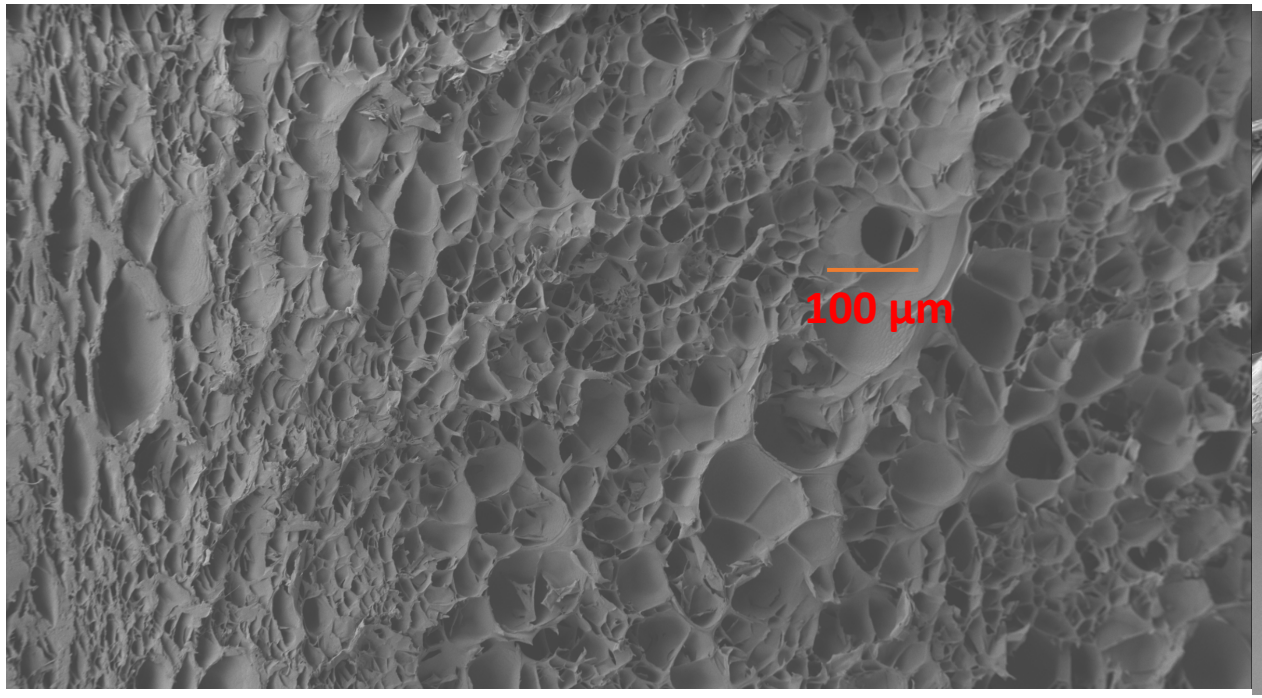


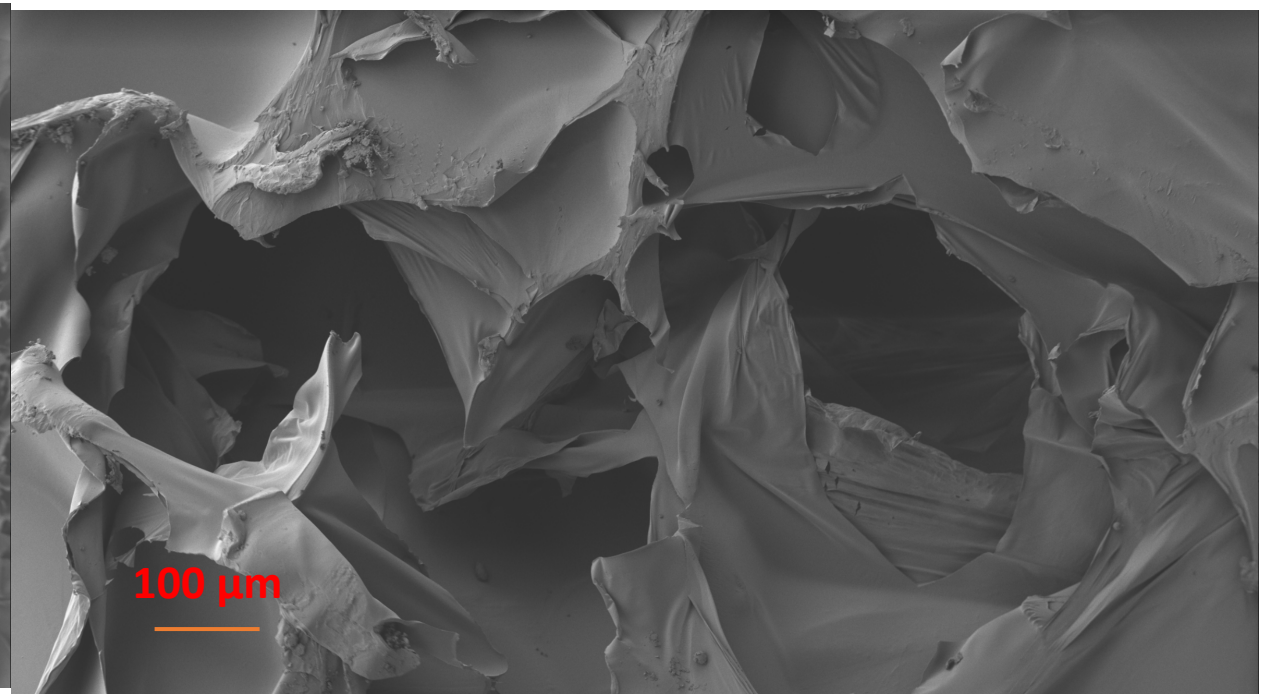
50% less trapped water compared to air-dried film at 130°C

Rheology


1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
G', G" (Pa)
0.01
0.1
1
10
100
1000
ω (rad/sec)
G'
10% CNF/PLA
G"
G'
5% CNF/PLA
G"
G'
2% CNF/PLA
G"
G"
PLA
G'

CNF reinforced PLA foams





Summary

- Created CNF-reinforced PLA composites by pre-mixing the CNF suspension with powdered PLA
- Utilized contact dewatering with liquid and supercritical CO_2 to dry the CNF/PLA suspension

ADVANTAGES

- Drying process does not require an ethanol exchange
- Aggregation of CNF fibers with drying is minimized

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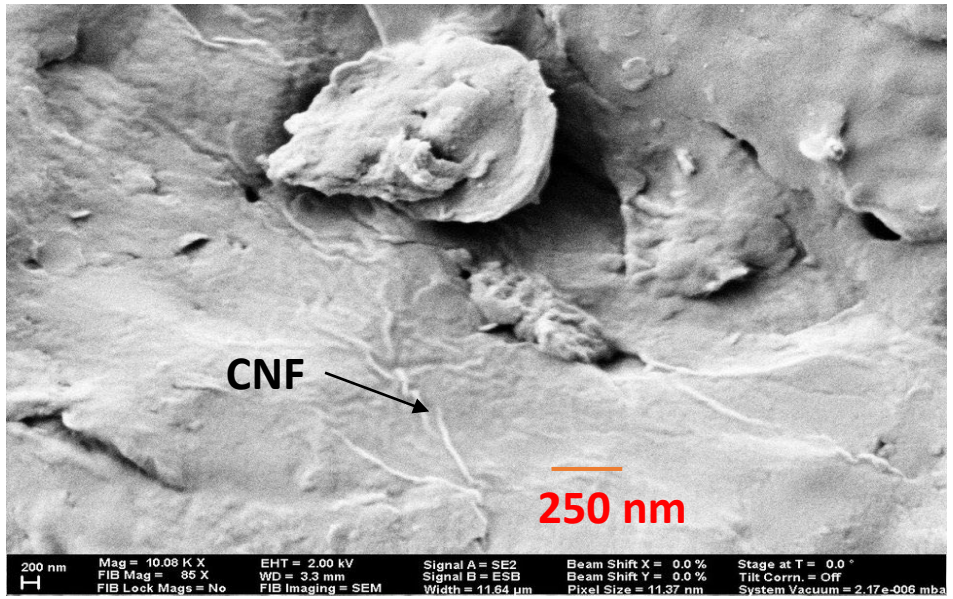
Thank You

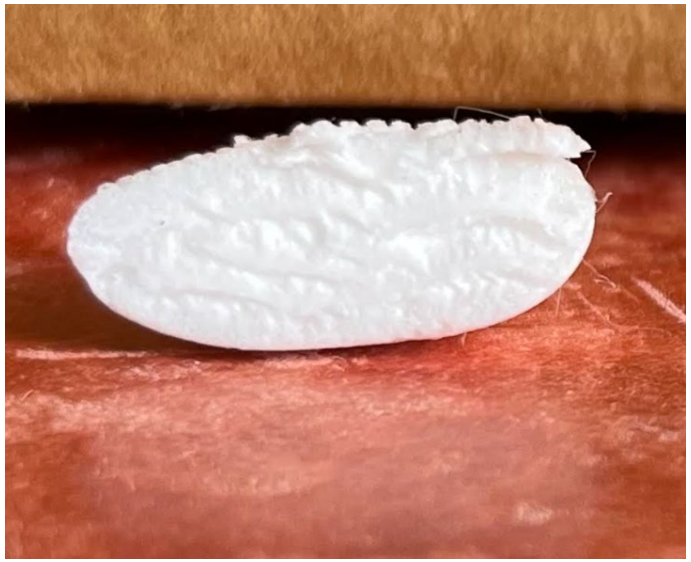
TAPPI NANO DIVISION

a)

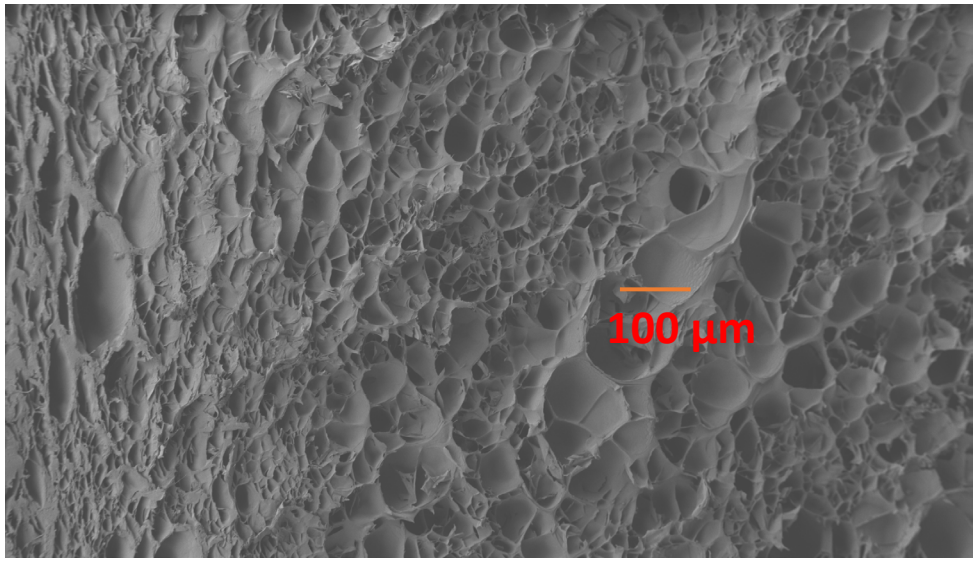
b)


CNF
250 nm
200 nm
Mag = 10.08 K X
FIB Mag = 85 X
FIB Lock Mags = No
EHT = 2.00 kV
WD = 3.3 mm
FIB Imaging = SEM
Signal A = SE2
Signal B = ESB
Width = 11.64 µm
Beam Shift X = 0.0 %
Beam Shift Y = 0.0 %
Pixel Size = 11.37 nm
Stage at T = 0.0 °
Tilt Corrn. = Off
System Vacuum = 2.17e-006 mba

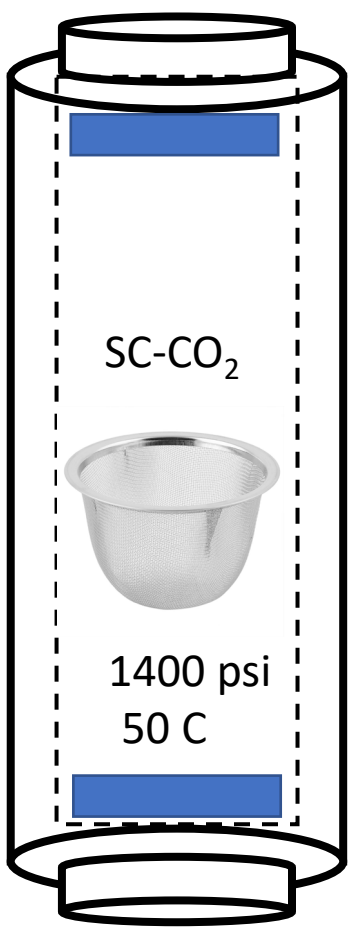
c)



d)

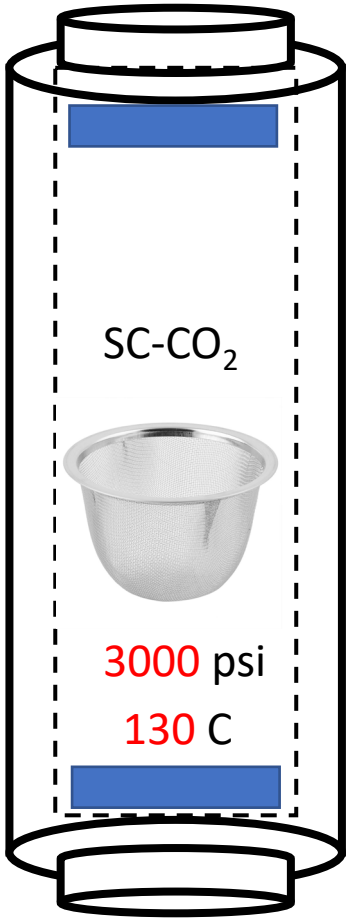

100 µm

Isostatic Melt Mixing: Vent Temperature?



Heat to 130 C

5 min



Vent at 130 C

No Change- Still a "fluffy ball"

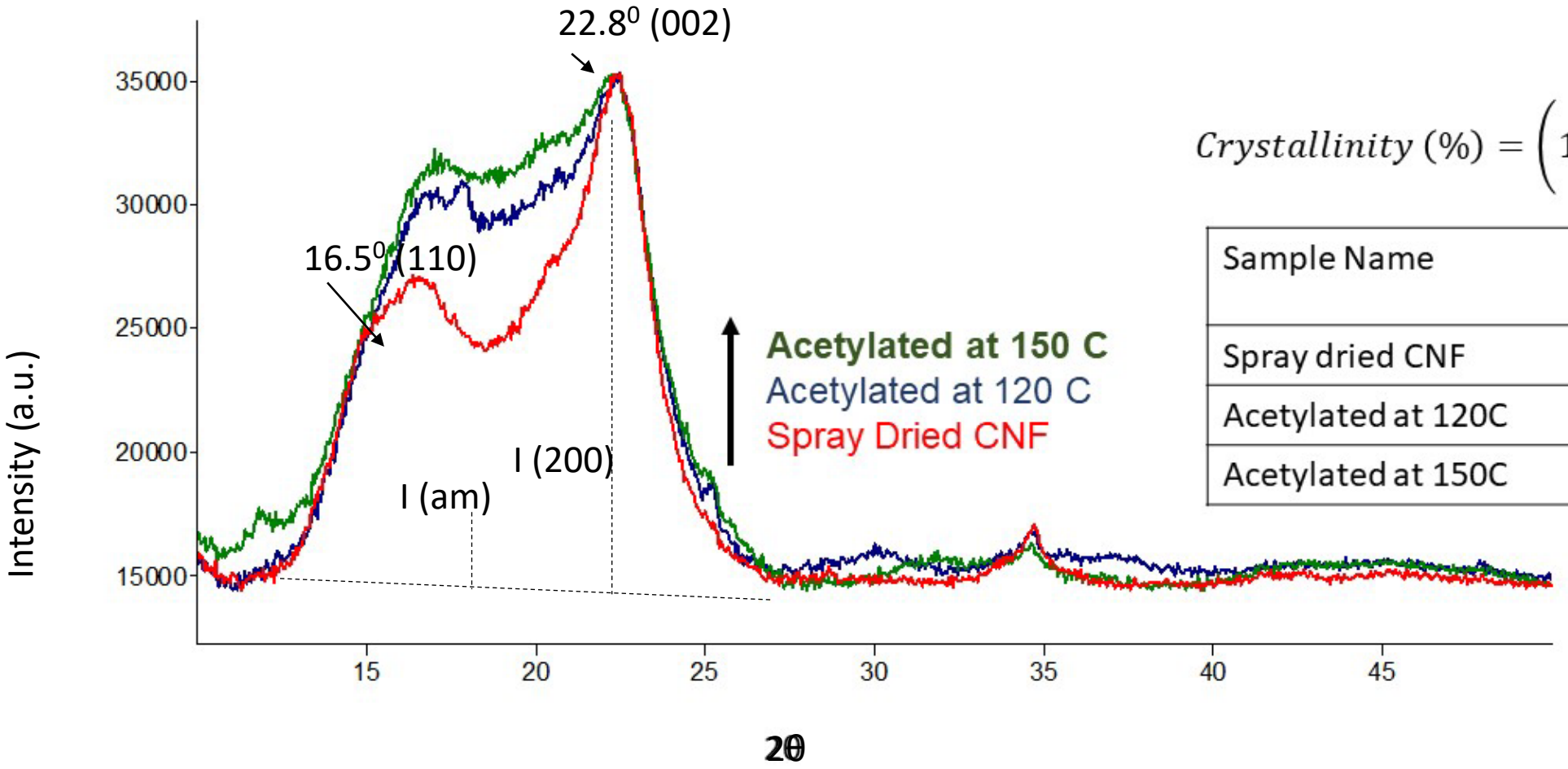
Cool to 23 C

Vent at 23 C

?

Lowers melting temperature of PLA from 180 C to 130 C.

XRD of acetylated CNF in $ScCO_2$



$$Crystallinity\ (\%) = \left(1 - \frac{I(200)}{I(am)}\right) \text{x } 100\%$$

Sample Name	% Crystallinity
Spray dried CNF	53.5
Acetylated at 120C	27
Acetylated at 150C	21

The solution: Mix 1% wt CNF slurry with PLA

Alyson Manley

➢ The Concept

Mix PLA with 1% CNFs → Exchange with ethanol → Exchange with Liquid CO_2 → Dry with Supercritical CO_2

10% wt/wt CNF/PLA

Dry with Supercritical CO_2 → Surface reaction Supercritical CO_2 → Melt Mix → Mechanical Properties

3 wt% CNF suspension → Dilute to 1 wt% → Add in PLA powder → Stir for 30 minutes