# Reduce cement content in concrete by enhancing mechanical properties with chitin nanofibers and nanocrystals


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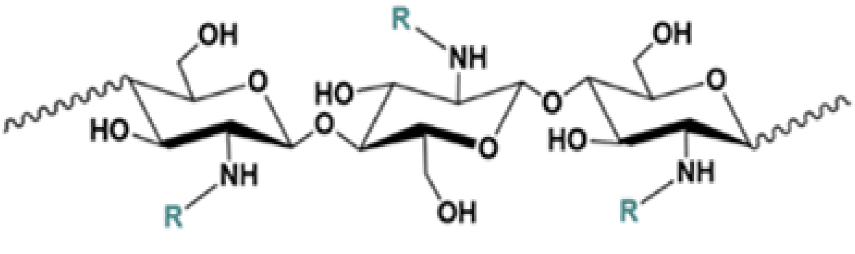
Funding agency:

# Chitin

- Second most abundant biopolymer after cellulose
- Glycosaminoglycan-repeating structure like cellulose but acetamide groups at C-2 positions




Sources of Chitin [2]

- ~100 B tons/yr in living organisms [1]
  - Crustaceans, fungi, yeast, insects, other plants/animals




[1] Kurita, K. (1998). Chemistry and application of chitin and chitosan. Polymer Degradation and stability, 59(1-3), 117-120

[2] Rinaudo, M. & Pérez S. (2019). From Chitin to Chitosan. Available online: http://www.glycopedia.eu/e-chapters/chitin-chitosan (accessed December 27, 2021)

# Seafood Waste as Source of Chitin

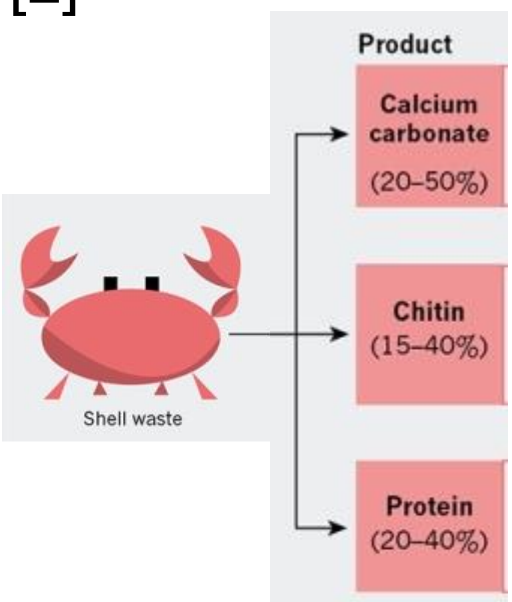
- Barks from seafood industry: 6-8 million ton/year [1]
- 200,000 tons of shrimps, 35,000 tons of lobsters, and 90,000 tons of crabs processed in the US [2]
  - Mostly composted, discarded in ocean or landfilled, expensive to treat before disposal

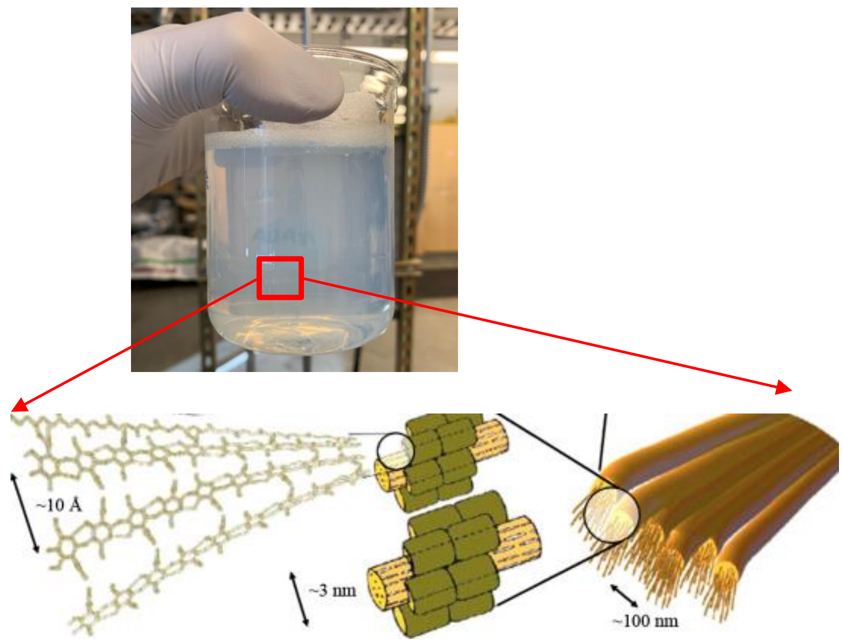
[1] Yan, N., & Chen, X. (2015). Sustainability: Don't waste seafood waste. Nature News, 524(7564), 155.
[2] Whistler, ROY L. "CHAPTER 22 - CHITIN." In *Industrial Gums (Third Edition)*

Workers pick meat from the lobster, which is rapidly frozen with nitrogen. The tail shells are composted nearby.
GRETA RYBUS FOR THE BOSTON GLOBE

# Chitin Nanofibers and Nanocrystals

- Seafood bark: ~15-40% Chitin [1]
- Found in combination with calcium carbonate to provide strong natural habitat
- Chitin nanofibers are wrapped in layers of protein from [2]



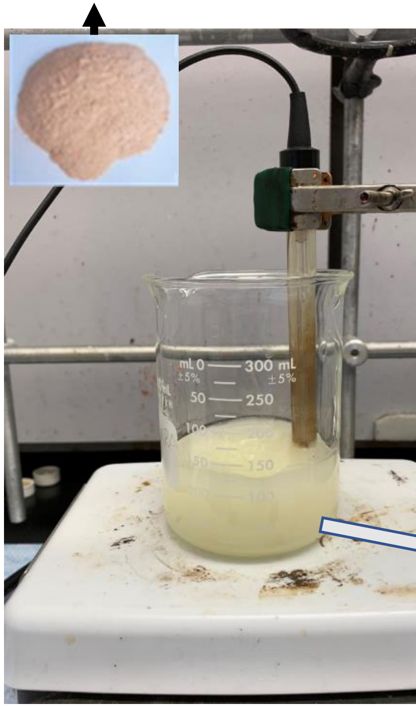




[1] Rinaudo, Marguerite. "Chitin and Chitosan: Properties and Applications." *Progress in Polymer Science* 31, no. 7: 603–32.
[2] Huang, W. (2018). Chitin Nanopapers. In *Nanopapers* (pp. 175-200). William Andrew Publishing.

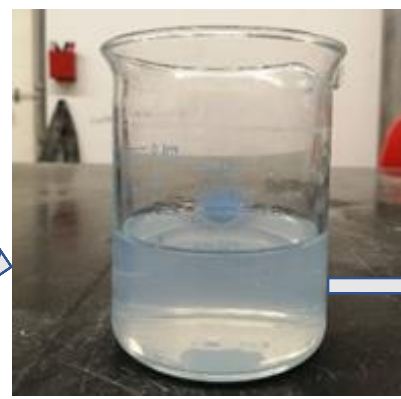
# Extraction of Chitin Nanomaterials (ChNM)

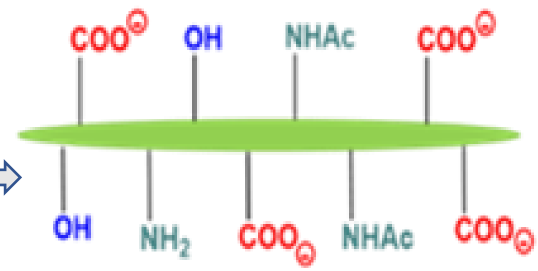
## Chitin-nanocrystals (Ch-NC): TEMPO-oxidation

Chitin Powder



- OH group in C-6 position selectively oxidized to COOH group.
- Suspension: ~1% solids weight concentration



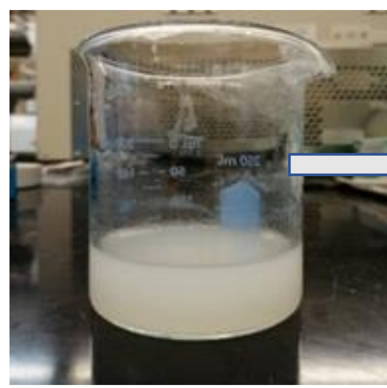


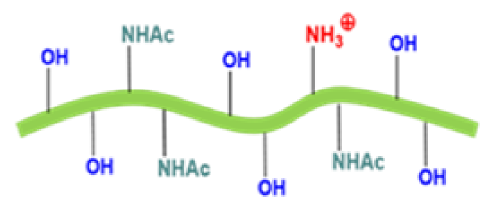
# Extraction of Chitin Nanomaterials (ChNM)

## Chitin-nanofibers (Ch-NF): Mechanical fibrillation

Super Mass Collider

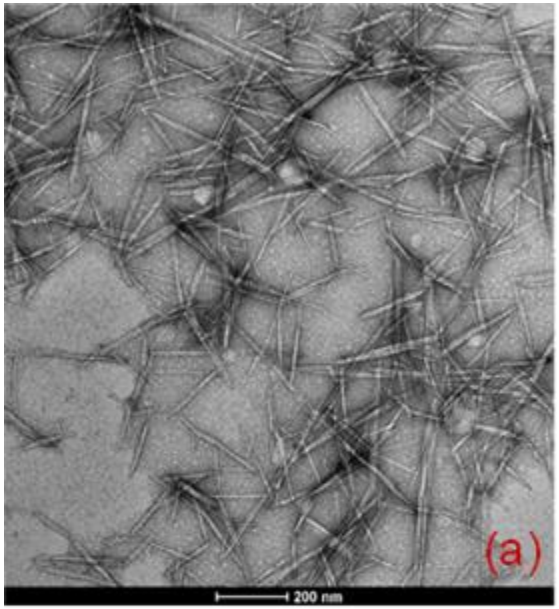
- Grinding disc applies compression, shearing and friction forces in a Super Mass Collider
- Combination of 20 µm disc gap, 4-hr griding: 0.82% solids





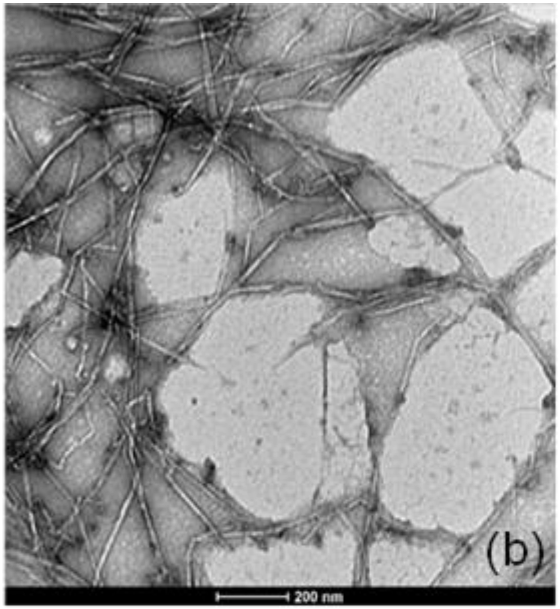
# Characterization of Chitin-Nanomaterials

## Size and Morphology




| Width | Length | Aspect Ratio |
|---|---|---|
| 8.7 ± 4 nm | 211 ± 80 nm | 24 |

**(a) Chitin-nanocrystals (Ch-NC)**




| Width | Length | Aspect Ratio |
|---|---|---|
| 16 ± 10 nm | 1068 ± 765 nm | 7-290 |

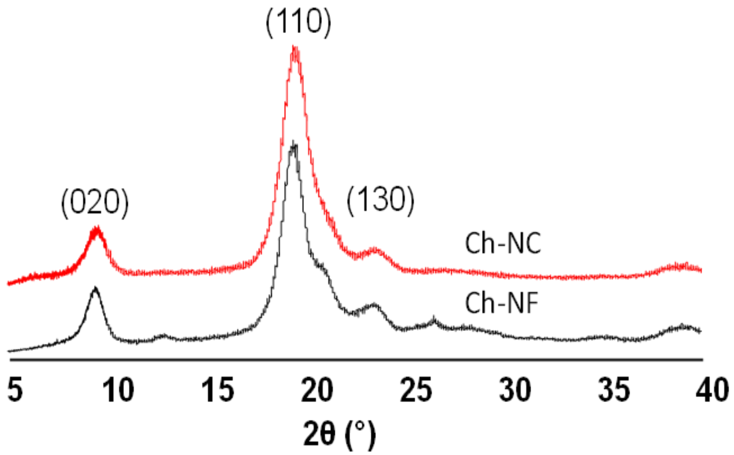
**(b) Chitin-nanofibers (Ch-NF)**

# Characterization of Chitin-Nanomaterials

## XRD and Zeta Potential

| Zeta Potential (mV): | ChNC | ChNF |
|---|---|---|
| DI water | -56.1± 4.5 (pH=7.6) | +3.9 ± 0.7 (pH=6.9) |
| Pore solution | -28.04 ± 2.6 (pH=12.71) | -24.02 ± 9.1 (pH=12.71) |

- Zeta potential: Large negative surface charges in pores solution



XRD of ChNMs

$$CrI = \frac{(I_{110} - I_{AM})}{I_{110}} \times 100\%$$

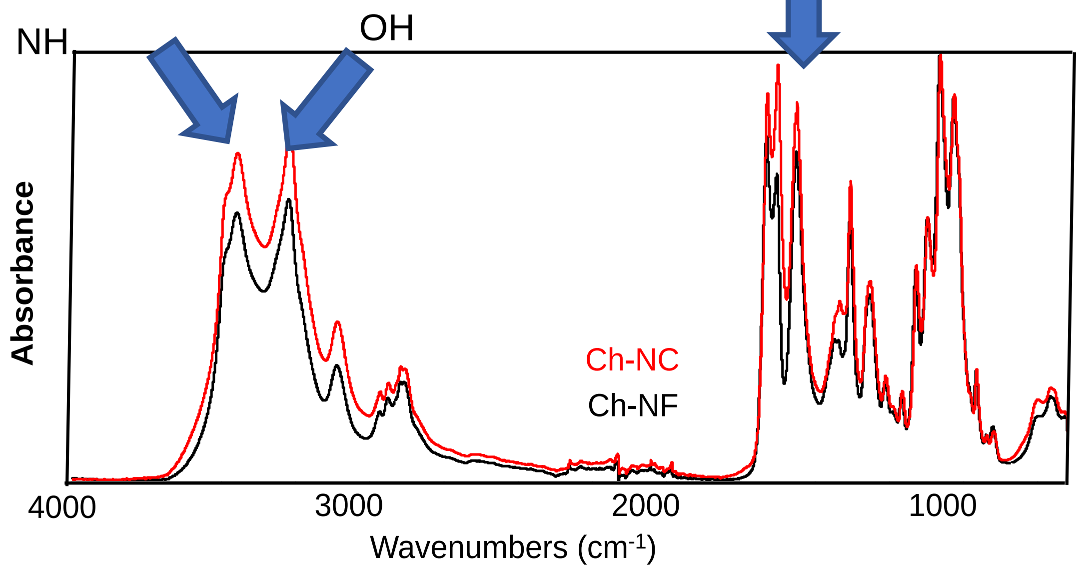
- Crystalline index (CrI) based on XRD: 92%

# Characterization of Chitin-Nanomaterials

## Surface Groups by FTIR & titration methods

**Ch-NC higher intensity of OH and NH**
Due to more surface area of Ch-NC with smaller size

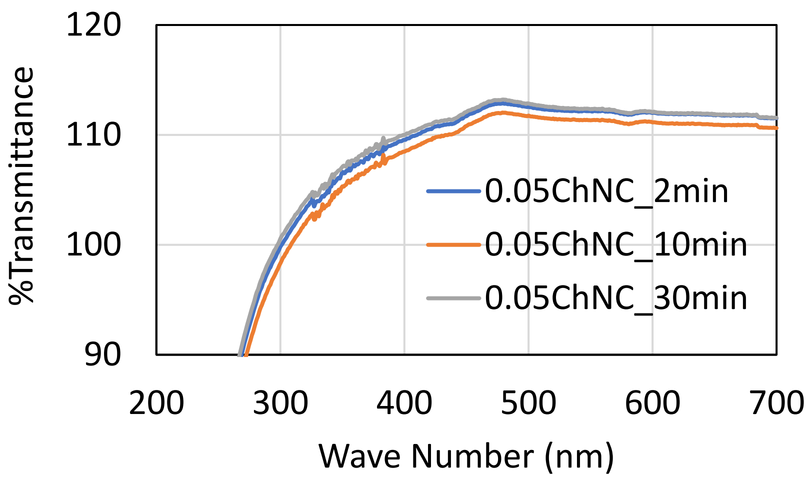
**Ch-NC higher intensity COOH**
Conversion of OH to COOH by TEMPO




- Titration results: ChNC more COOH groups than CHNF

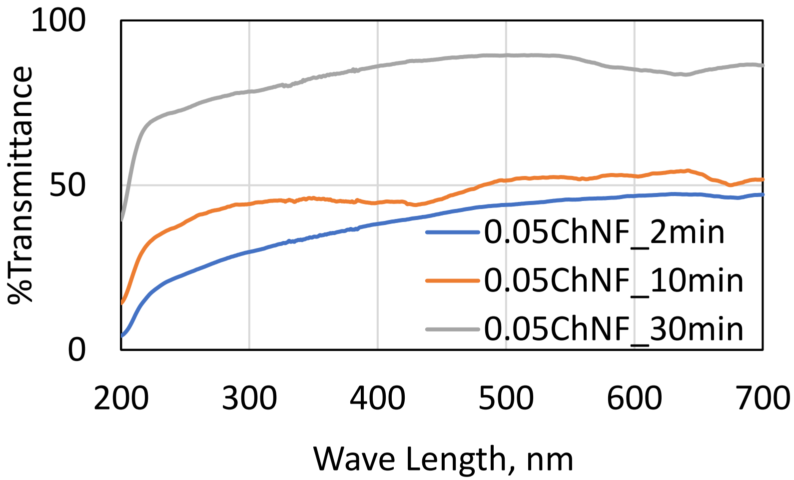
| **ChNM Type** | **ChNC** | **ChNF** |
|---|---|---|
| **Surface Groups (COOH)** | 0.36 mmol | 0.01 mmol |

# Dispersion by Ultrasonication

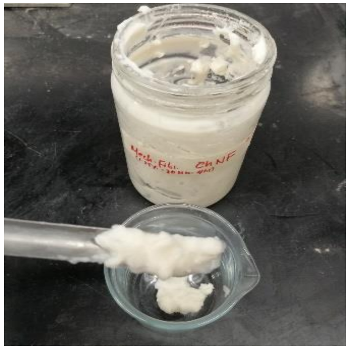



**Chitin Nanocrystals**

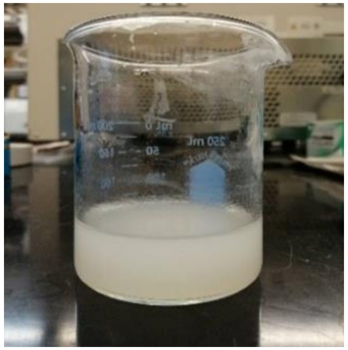
10 mins Sonication




**Chitin Nanofibers**



10 mins Sonication



- 10 min sonication based on UV-i Spectroscopy
- 30 mins sonication alter the size as seen on TEM after sonication of CNF

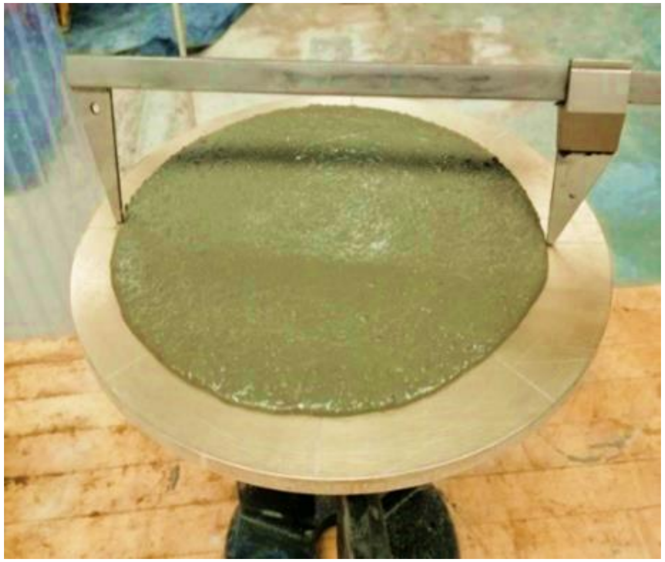
# Preparation of Cement-Mortar

- Sand:Cement:Water = 2.5:1:0.52
- ChNC: 0.02%, 0.035%, 0.045%, 0.05% & 0.10% (%dry cement by mass)
- ChNF: 0.035%, 0.045%, 0.05%, 0.065% & 0.10%
- Two mixes with superplasticizer (0.10% Ch-NC & 0.10%Ch-NF + 0.10% SP)
- One combination of Ch-NC & Ch-NF (0.05% of each)


Preparation of mortar using a benchtop mixer

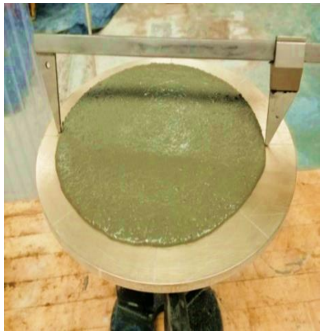
# Tests of Fresh Properties of Mortar

**Flow Table Test for workability**

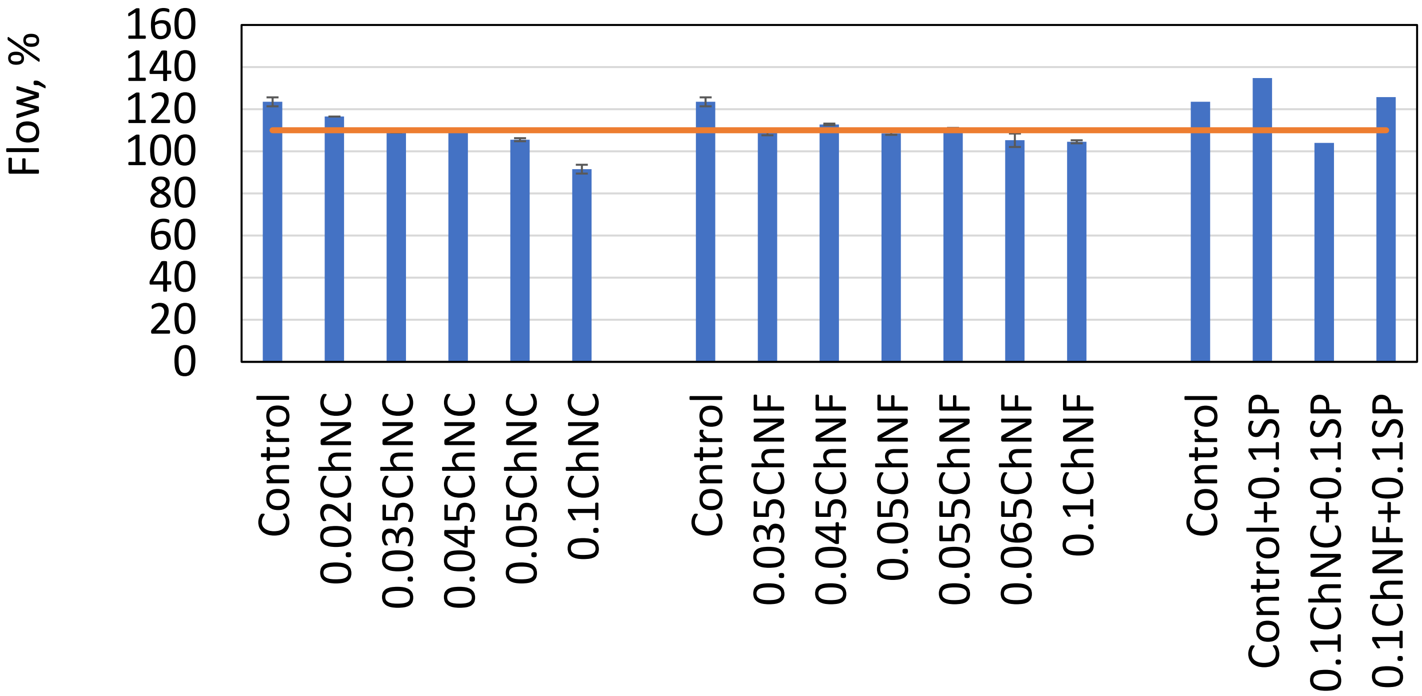


**Setting time test by penetration resistance**


# Flow Table Test Results



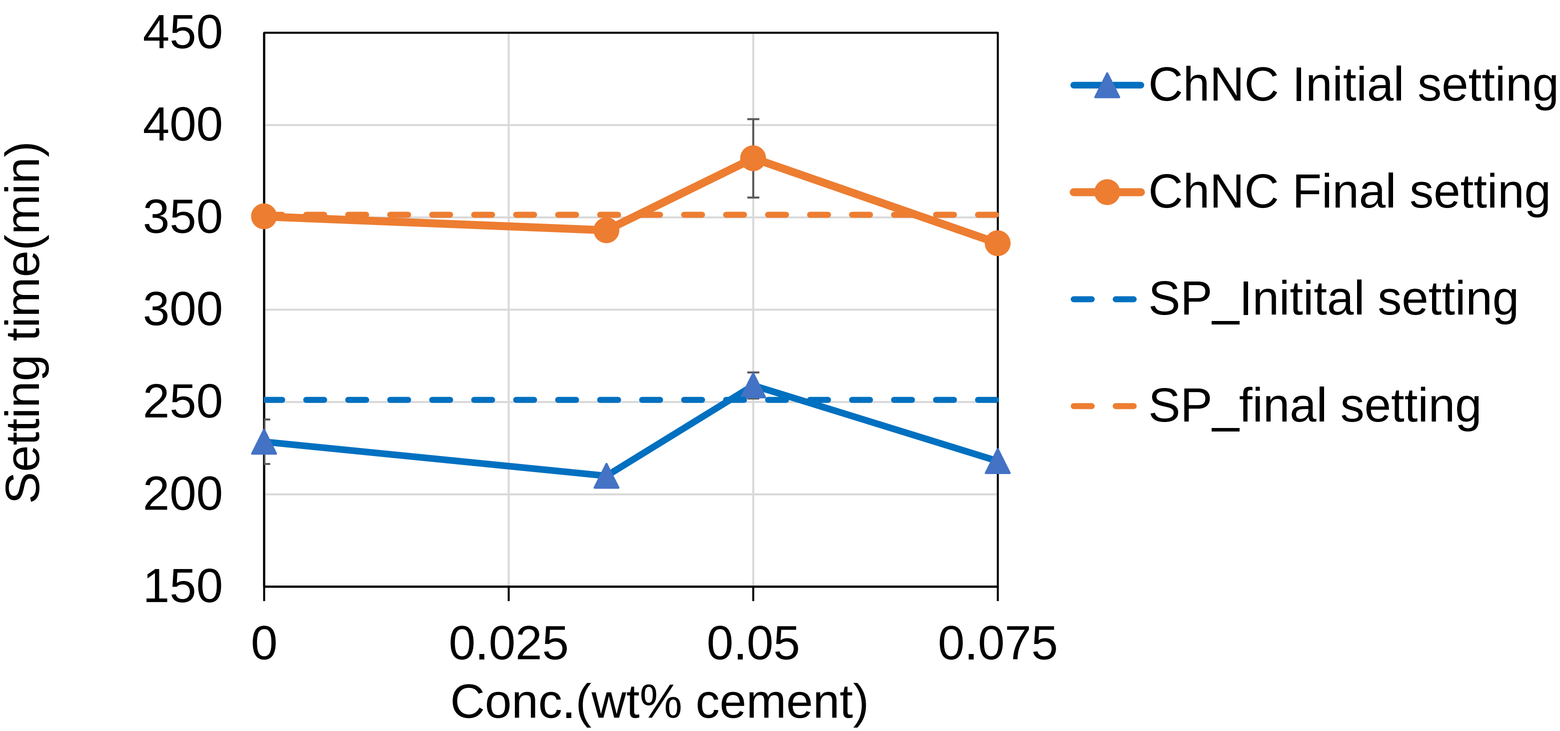
- ChNC & ChNF reduce workability due to their high specific surface area & OH groups
- ChNC: lower flow number with more ChNC
  - Max reduction: 0.1%wt ChNC by 26%
- ChNF: max reduction of  15% with 0.1%wt ChNF



# Initial & Final Setting Time


**ChNC**

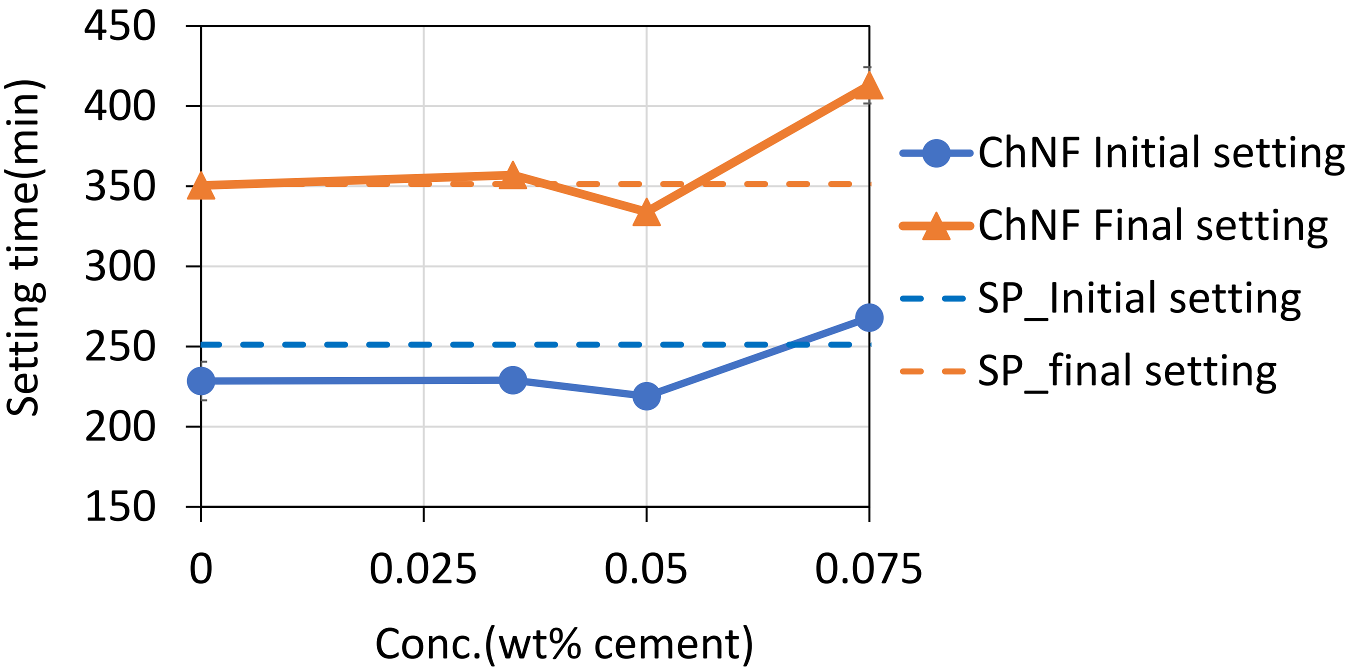
- 0.05wt% ChNC induce most delay
- Initial set delayed ~30min with 0.05%wt ChNC
- Final set delayed ~30 mins



# Initial & Final Setting Time

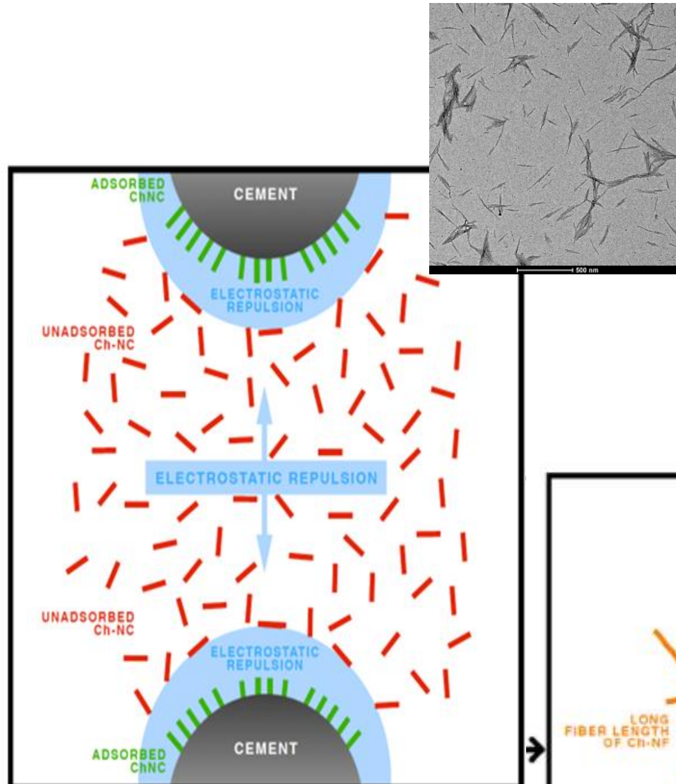

## ChNF

- 0.075wt% ChNF most delay
- Initial setting delayed 40min w/ 0.075wt%
- Final setting delayed 60 min w/ 0.075wt%ChNF

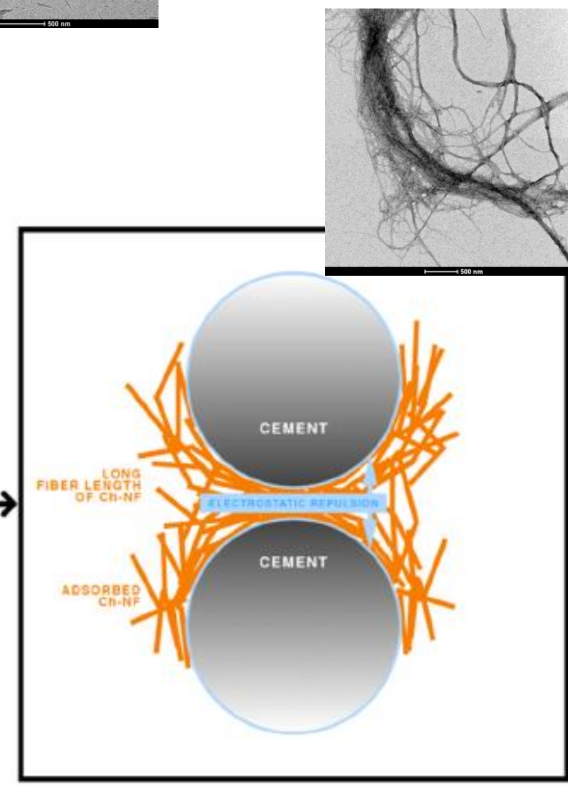


# Delayed Setting Time Mechanism

- With large <u>anionic surface charges</u>, ChNC and ChNF adsorbed on positively charged clinkers and hydrates
- Disperse them by <u>electrostatic repulsion</u> and delay setting time
- Morphology of ChNF vs ChNC may impose different physical restrictions among clinker particles



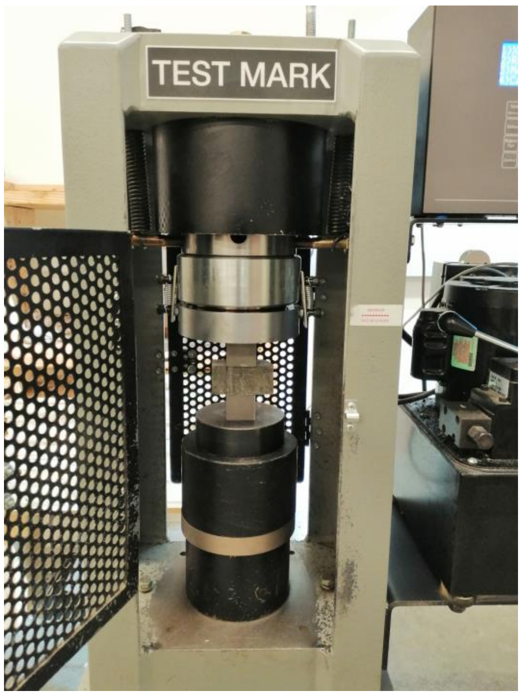

ChNC



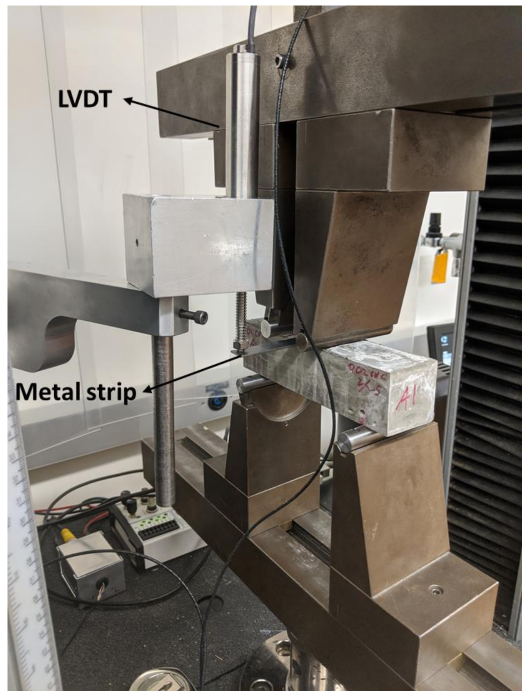

ChNF

# Tests for Mechanical Properties

**Compressive Strength Test**



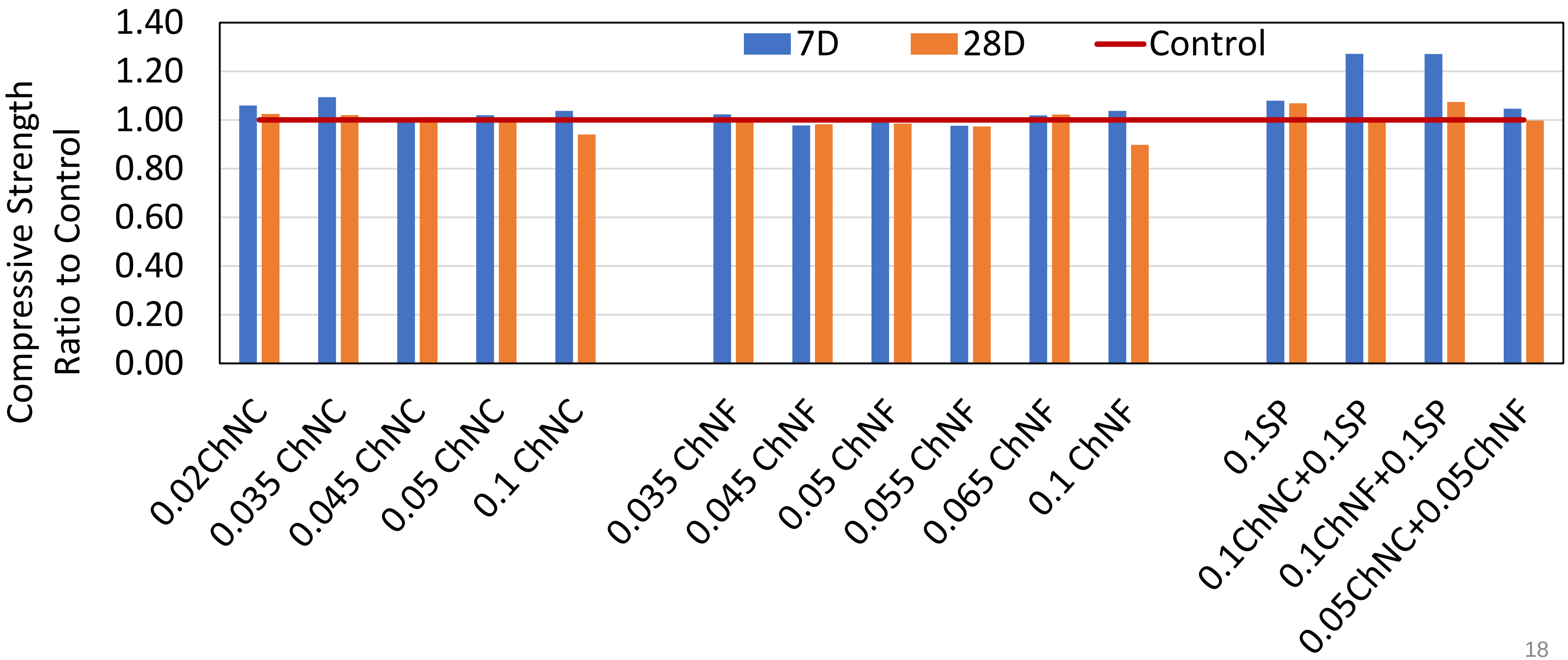

**Four Point Bending Test**




- Six beams for flexure test at 7 and 28d
- Mid-span deflection measured by LVDT
- Area under load-deflection for toughness
- 12 specimens from broken beams for compression test at 7 and 28d

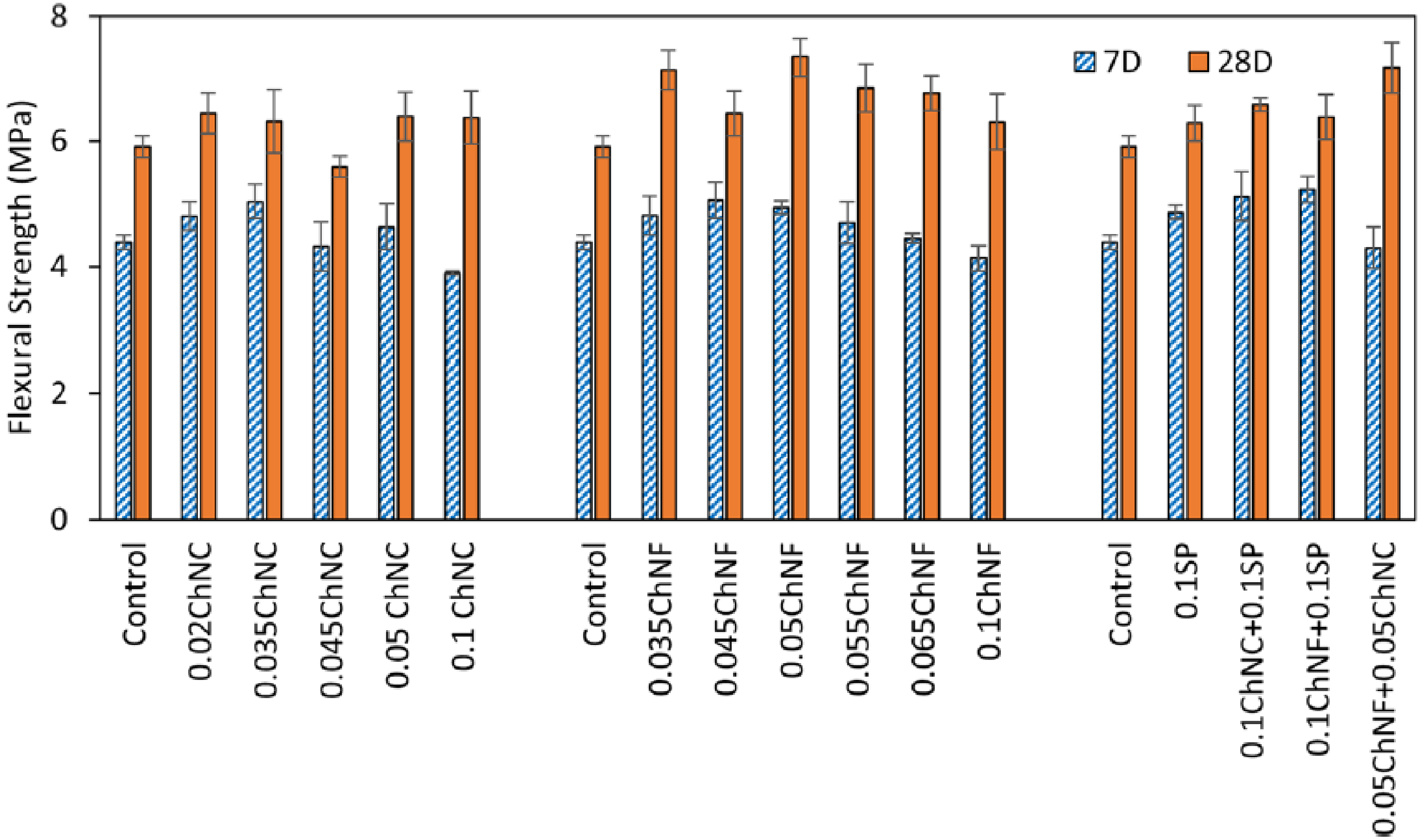
# Compressive Strength Results

- **ChNC**
  - 7d: max +9% w/ 0.035 wt% (p-value=0.023)
  - 28d: max +2.5% with 0.02wt% (p-value=0.004)
- **ChNF**
  - 7d: max +4% w/ 0.1%wt      (p-value=0.049)
- **Max among all 0.1 wt% ChNF + 0.1 wt% SP**
  - 7d: +25% and 28d: 7%, for



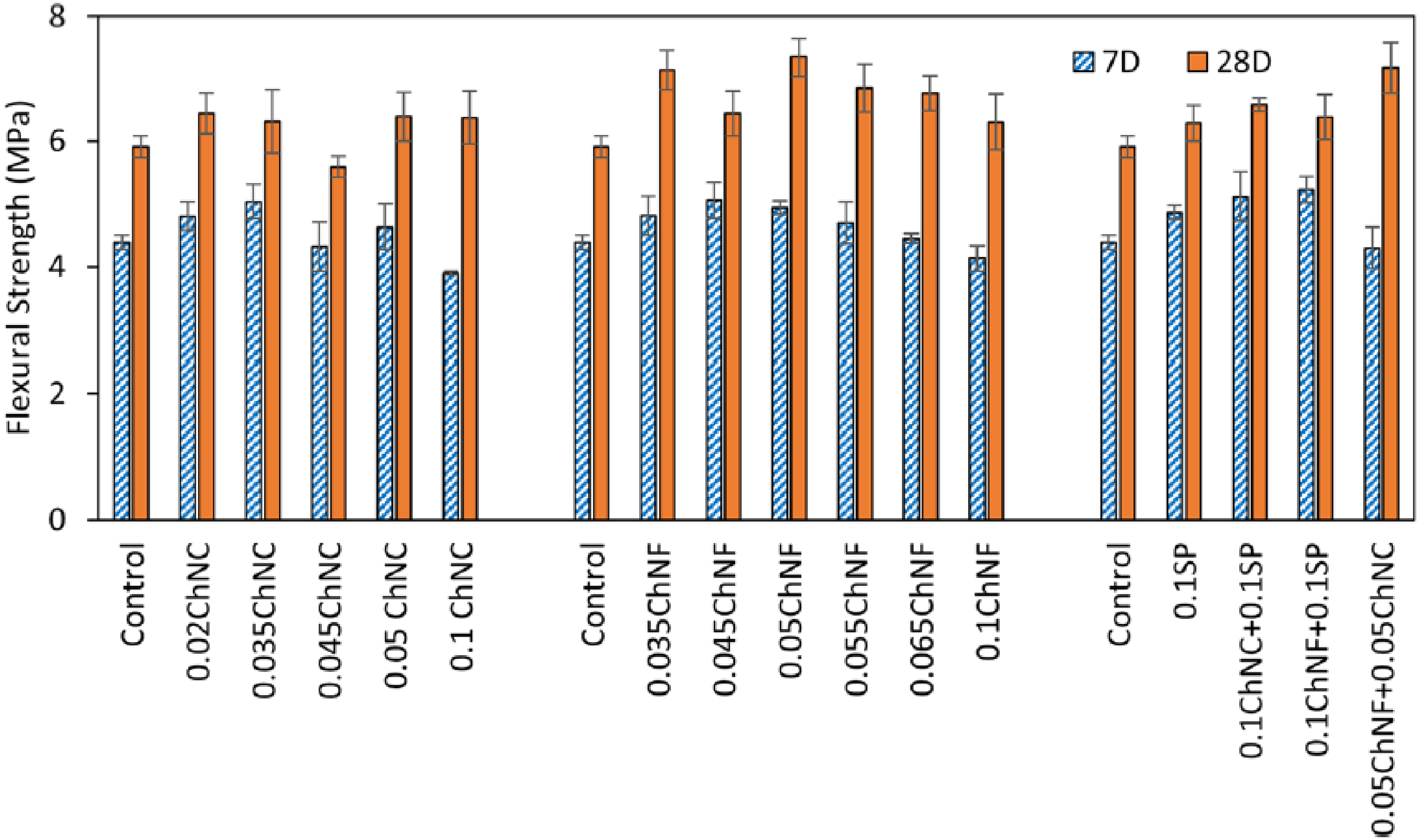
# Flexural Strengths Results

- **ChNC**
- 7d: max 15% w/ 0.035 wt% (p-value= 0.0007)
- 28d: 7~9% increase

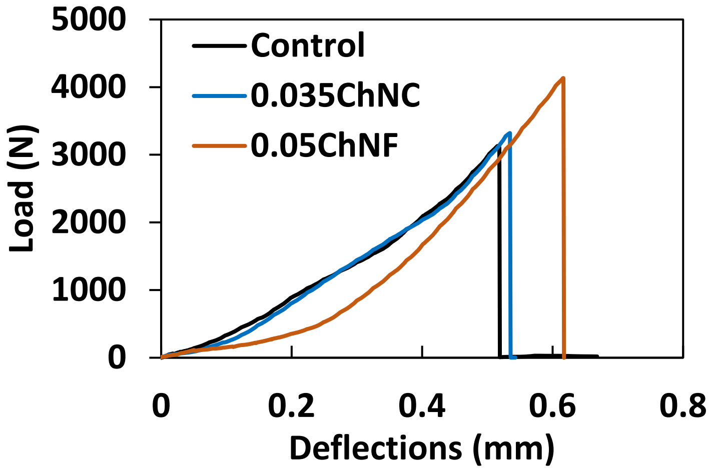


# Flexural Strengths Results

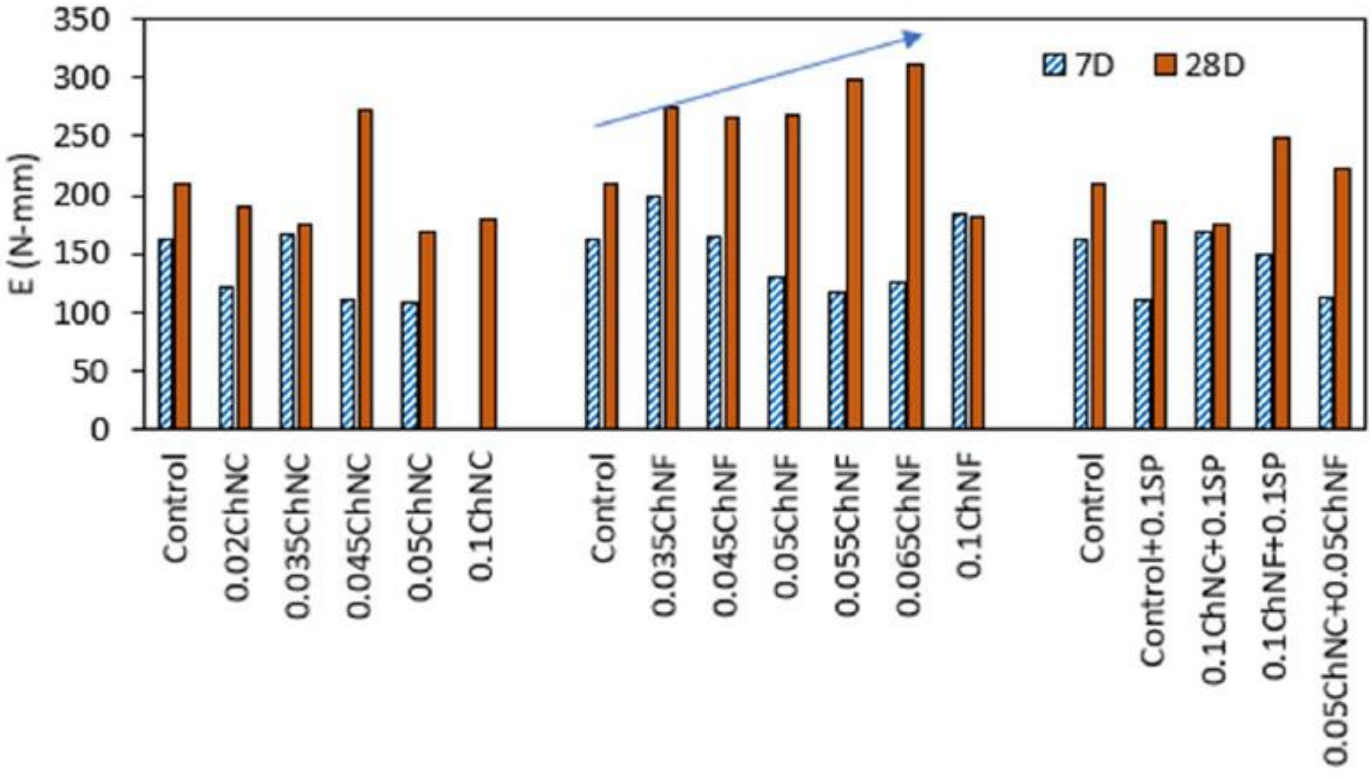
- **ChNF**
  - bell-shaped curves 7 & 28 days
  - 28d: +20% w/ 0.05 wt%
- **ChNF+ChNC mix**
  - 28d: +17%
- **At equal doses, ChNF better than ChNC**



# Fracture Energy Results




- **ChNF**
  - ChNF enhance fracture energy
  - Max 49% w/ 0.065 wt% ChNF at 28d
- **ChNC**
  - 0.045 %wt ChNC improve fracture energy by ~30%



# Dispersion of ChNM in Mortar Beams

## Total Organic Carbon (TOC)

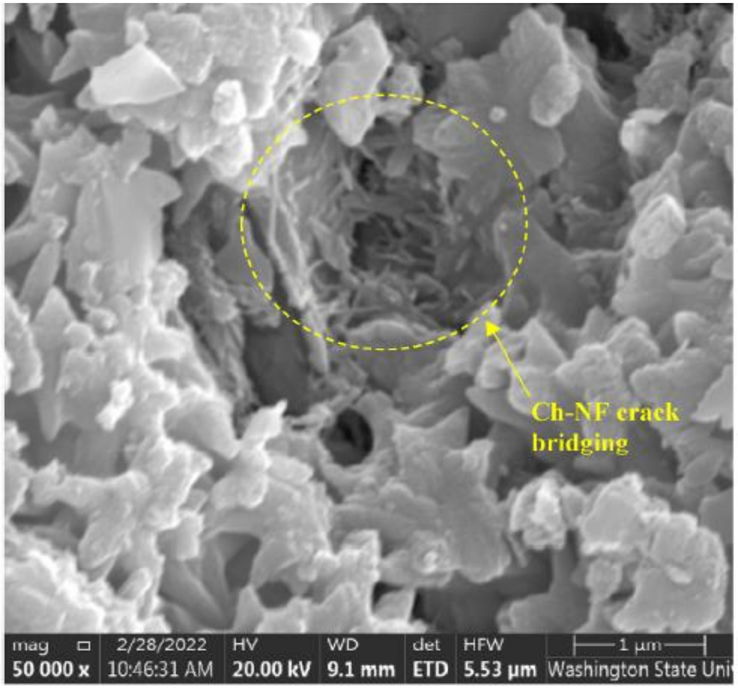
- Organic carbon content evaluated for three samples from bottom portion of beams after flexural test
- Chitin-mortar samples possess significantly more organic carbon than control
- ChNMs present in beams fracture surface
- ChNMs dispersed well in beam supporting improvements seen in flexural strength

| **Mix** | **Total Organic %Carbon** |
|---|---|
| Control | 0.0027 |
| 0.05ChNC | 0.0607 |
| 0.05ChNF | 0.1233 |

Total organic %Carbon in specimens from the broken beam face

# Possible Mechanisms

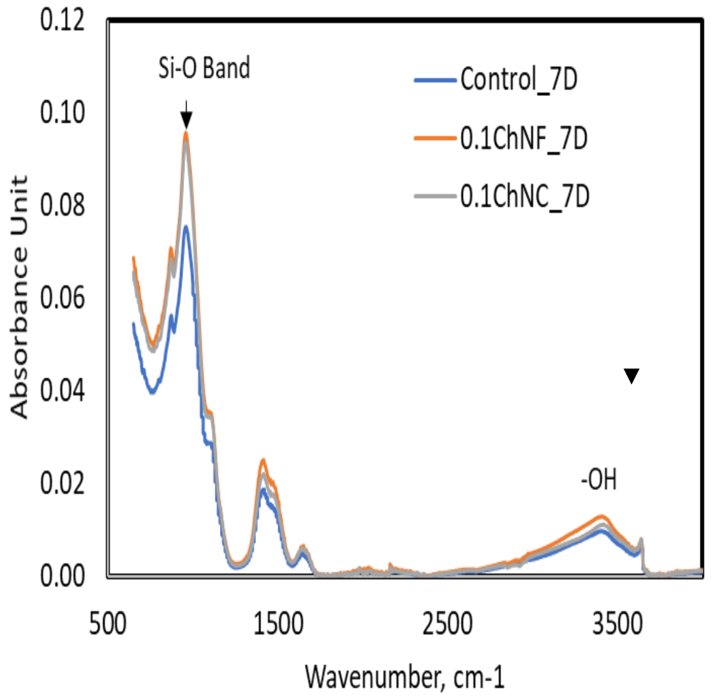
- ChNMs filler role under compression, but a more significant enhancement of composite strength seen under tension
- Possible reason bridging of nano cracks and pores, delay in crack propagation before peak load
- Better flexural performance with ChNF over ChNC for same dose attributed to greater length, higher aspect ratios, and fiber-like structure of ChNFs

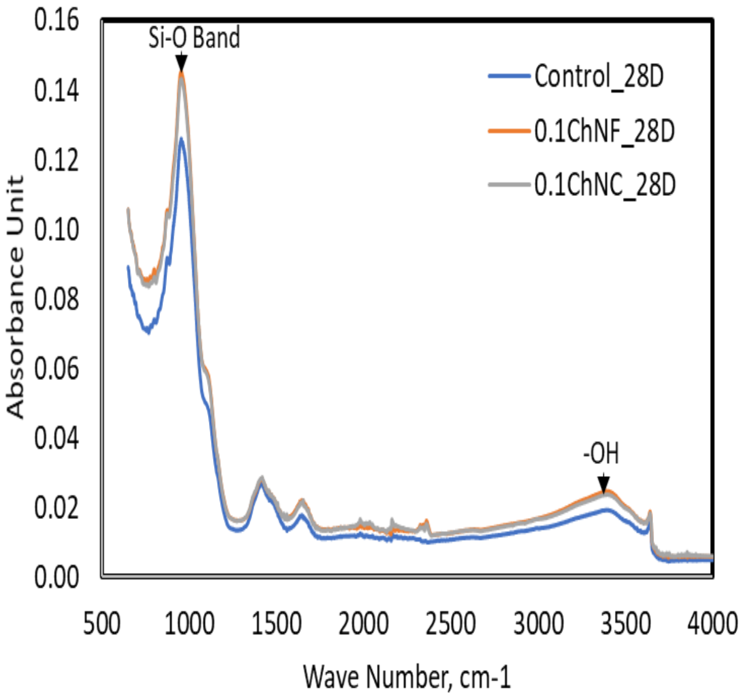


# FTIR of ChNM-Mortar

- **Shifting of Si–O stretching band** to higher wavenumber **evidence of polymerization** of silicate group. Higher peaks for both 7 and 28D at this wavenumber for ChNC and ChNF.
- Region **3400 to 3700 cm$^{-1}$ reflects change occurring in cement–water system** due to hydration. Higher and wider peak for ChNC and ChNF compared to control at 7 and 28d

7 day




28 day

# Impact on Silica Chains in C-S-H Structure

## Solid-State $^{29}Si$ nuclear magnetic resonance

- Assess number of bonds between adjacent silicate tetrahedrons in 7d and 28d samples

$$Polymerization\ degree\ (PD) = \frac{Q^2}{Q^1}$$

$$Degree\ of\ Hydration\ (DH) = \frac{Q^1 + Q^2}{Q^0 + Q^1 + Q^2}$$

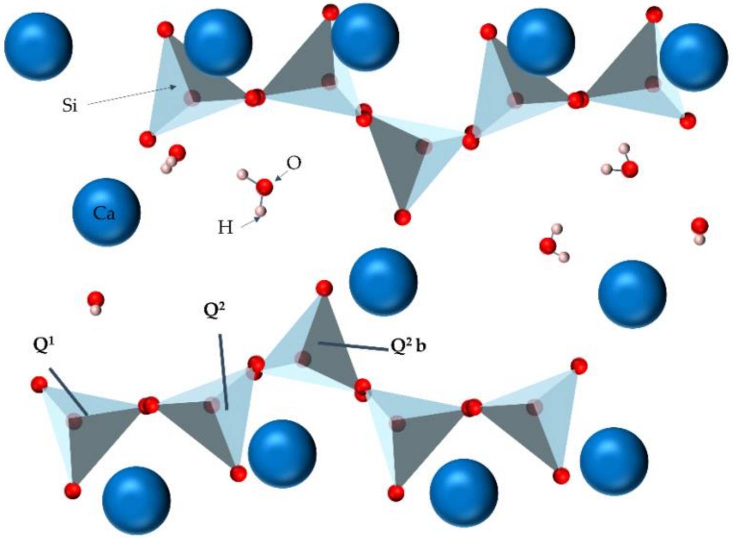
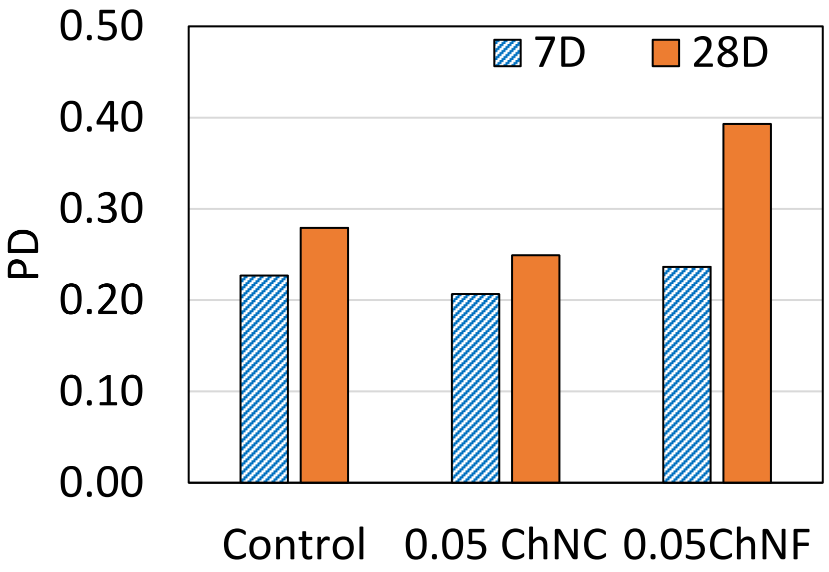
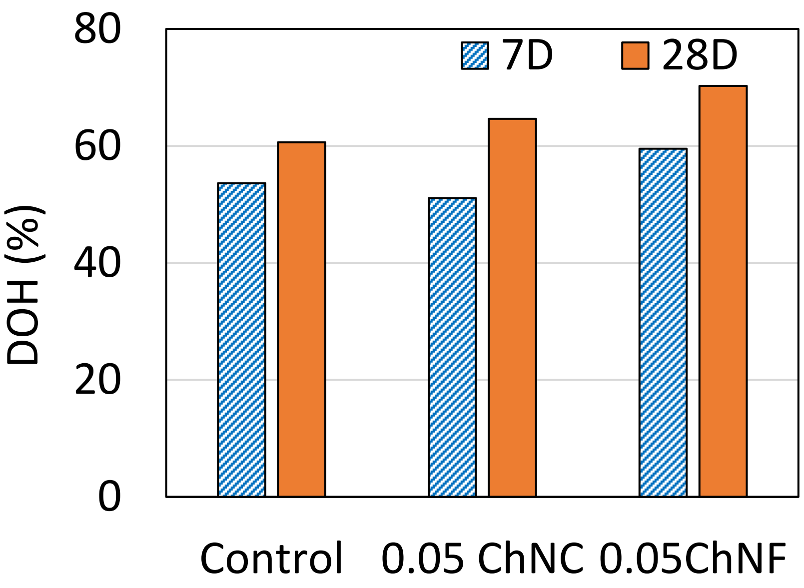



Figure from Tang, S., Wang, Y., Geng, Z., Xu, X., Yu, W., & Chen, J. (2021). Structure, fractality, mechanics and durability of calcium silicate hydrates. *Fractal and Fractional*, *5*(2), 47.

# Solid-State $^{29}$Si Results

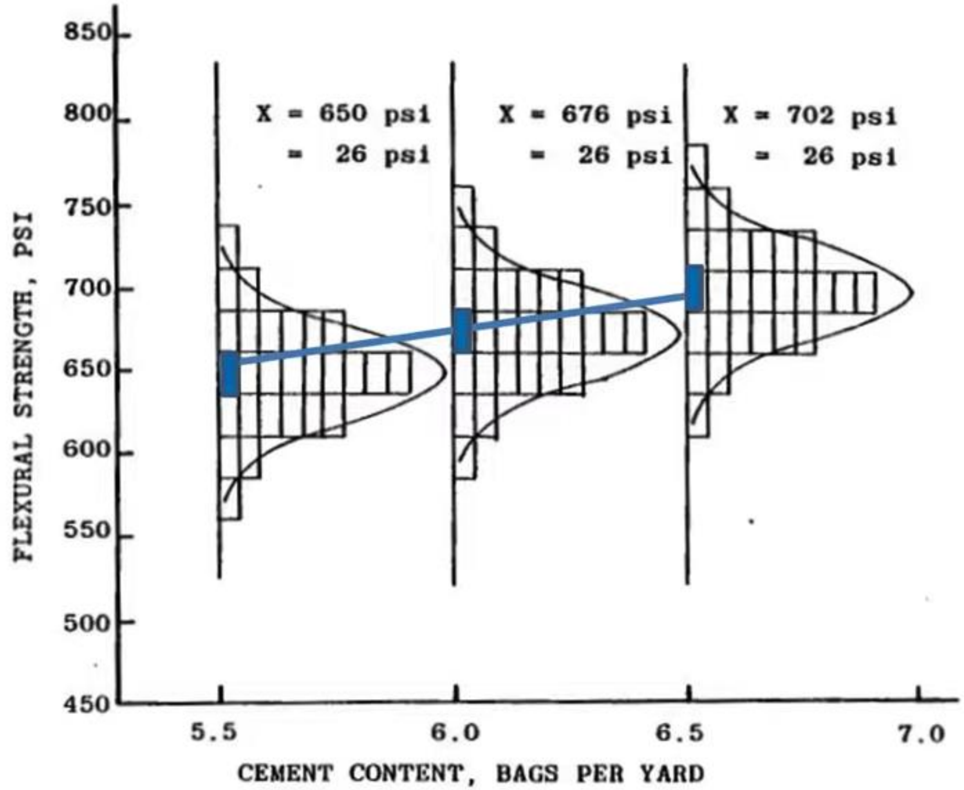
- **ChNC**: DOH improved at 28d by 7%
- **ChNF**: 28d PD and DOH improved by 41% and 16% compared to control



# A Promise for Cement Reduction?

"… heavy volumes of traffic, higher structural capacity can be achieved by increasing the bending resistance of the pavement..."[1]




Source: Charlie Greer

[1] Snyder, M B, et al. "Towards Sustainable Pavement Systems. A Reference Document.," n.d., 458.

# Conclusions

- Chitin nanomaterials improved flexural strength and fracture energy of mortar without adversely affecting compressive strength of others
  - ChNF improved flexural strength up to 24% (optimal dose 0.05 wt%)
  - ChNC optimal dose lower (0.035 wt%) with a max 9% improvement over control
  - FTIR showed more silicates and less amount of portlandite with ChNMs on 28d
  - NMR showed higher 28d polymerization in C-S-H and higher 28D DOH
- ChNMs may bridge nano/micropores and delay crack growth. This effect more pronounced in ChNF due to their higher length and aspect ratio

# Conclusions-Cont’d

- ChNMs induced slight reduction to flow of mortar
- 0.05%wt ChNC and 0.075%wt ChNF delayed final set time by 30 and 40 min
- Chitin from seafood waste show excellent potential for nanocrystals and nanofibers for cementitious systems
- Working on scaling up to concrete, studying impact on microstructure and durability

# Thank you!!

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- Haider, M., Jian, G., Zhong, T., Li, H., Fernandez, C. A., Fifield, L. S., ... & Nassiri, S. (2022). Insights into setting time, rheological and mechanical properties of chitin nanocrystals-and chitin nanofibers-cement paste. *Cement and Concrete Composites*, 104623.
- Nassiri, S., Chen, Z., Jian, G., Zhong, T., Haider, M. M., Li, H., ... & Wolcott, M. (2021). Comparison of unique effects of two contrasting types of cellulose nanomaterials on setting time, rheology, and compressive strength of cement paste. *Cement and Concrete Composites*, *123*, 104201.
- Zhong, T., Jian, G., Chen, Z., Wolcott, M., Nassiri, S., & Fernandez, C. A. (2022). Interfacial interactions and reinforcing mechanisms of cellulose and chitin nanomaterials and starch derivatives for cement and concrete strength and durability enhancement: A review. *Nanotechnology Reviews*, *11*(1), 2673-2713.