Tailoring of Steel Fiber Surface by Coating Cellulose Nanocrystal for Ultra-High-Performance Concrete (UHPC)

Presenter: Weina Meng

Assistant Professor

Stevens Institute of Technology

Department of Civil, Environmental and Ocean Engineering

Advanced Concrete Technology (ACT) Lab

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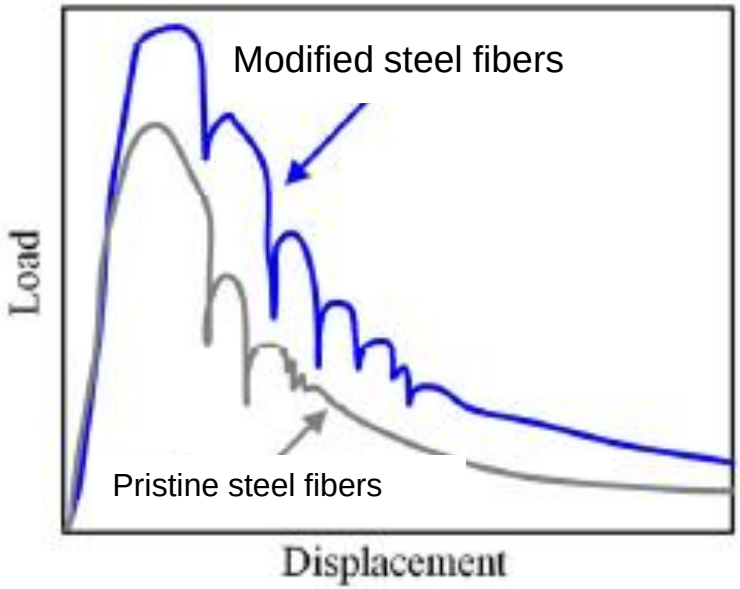
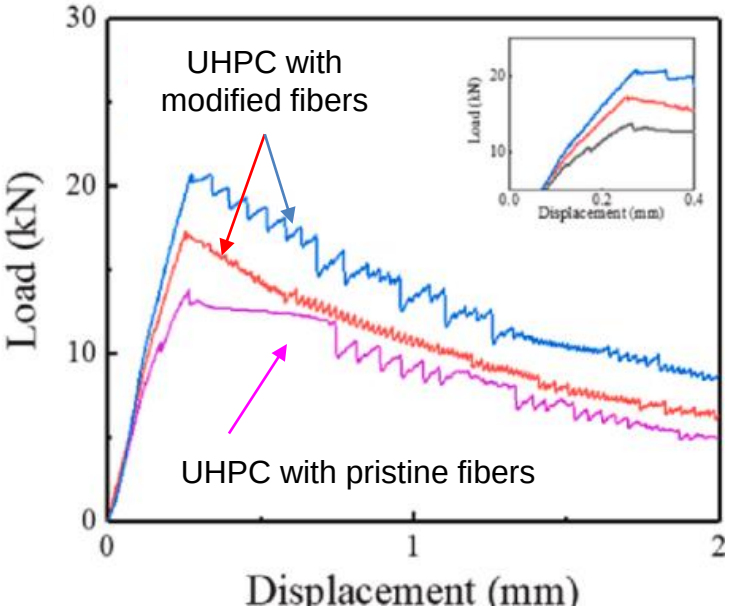
Flexural properties of UHPC need to be improved

- Higher flexural performance is needed to extend the its applications.
- Steel fibers surface modification is a promising method
  - ➢ Increase the fiber pull-out forces and energy [1]
  - ➢ Increase the flexural strength and toughness [2]



Single fiber pull out

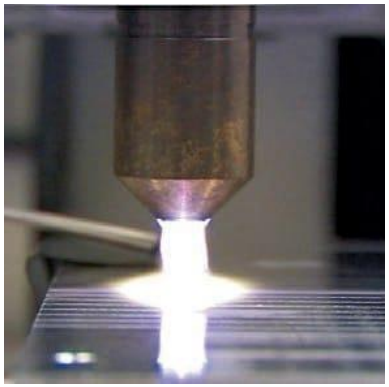


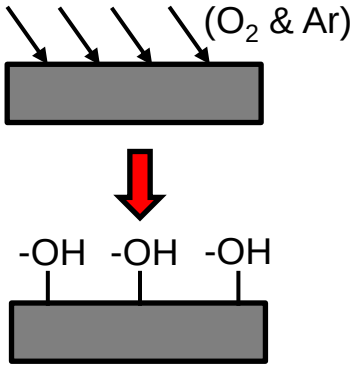
Three–points flexural tests

[1] Pi et al. *Cem Concr Compos.* 2019, 103, 1-10.
[2] Du et al. *Cem Concr Compos. 2023,* 137, 104926.

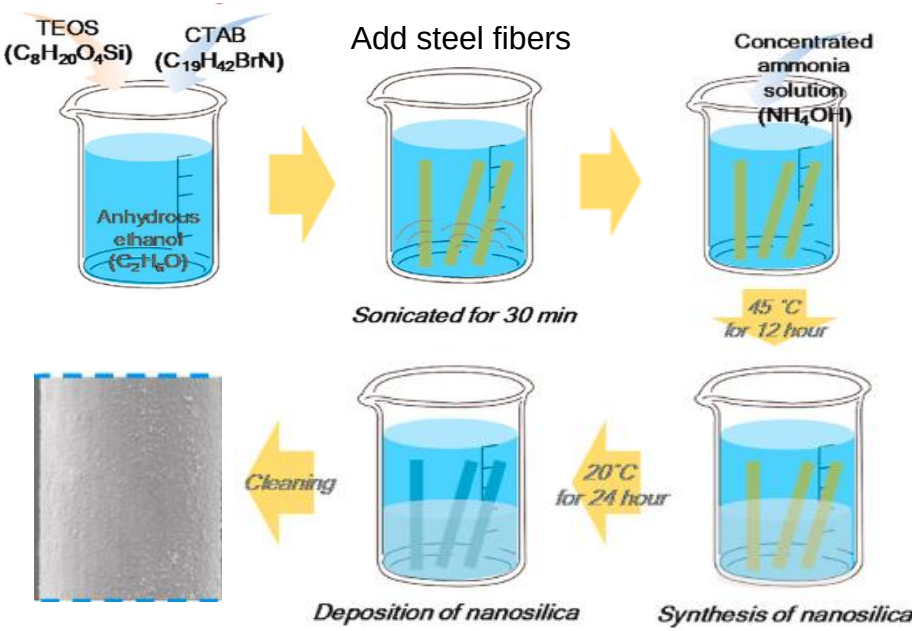
Current challenges for surface modification

- Plasma surface treatment (15% increase in flexural strength [1])
  - ➢ Equipment of plasma treatment is expensive.
  - ➢ Difficult for large-scale production.
- ZnPh surface coatings (20% increase in flexural strength [2])
  - ➢ Both Zn^{2+} and Ph^{2-} are pollutants for water and soil.
- Nano-SiO_2 surface coatings (25% increase in flexural strength [3])
  - ➢ The coating process is complicated and is hard for large-scale production.





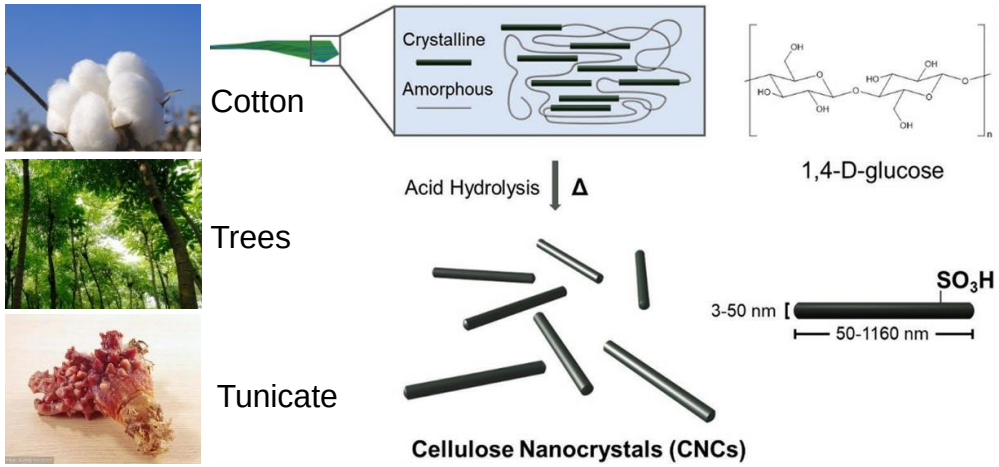
Plasma functionalized the steel surface with hydroxyl groups

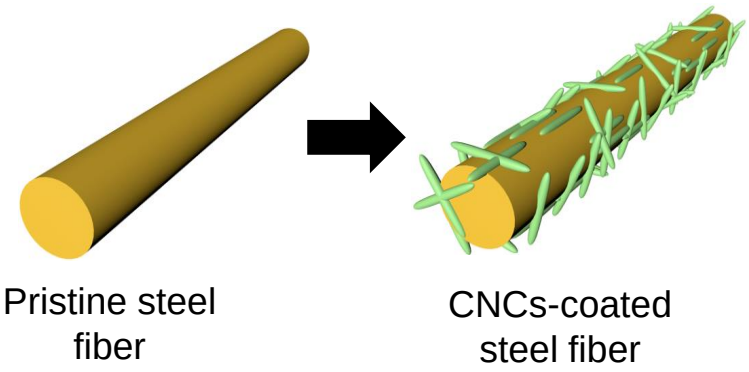


[1] Miller et al. *Cem. Concr. Compos.* 2019, 97, 24-32.
[2] Zhu et al. J. Mater. Civ. Eng. 2020, 32(10), 06020013
[3] Oh et al. Compos. B. Eng. 2021, 221, 109030.

Research objectives

- To enhance flexural behaviors of UHPC by coating the steel fibers with cellulose nanocrystal (CNCs)
- To evaluate the effect of CNCs coating on the key properties of UHPC
- To understand the underlying mechanisms



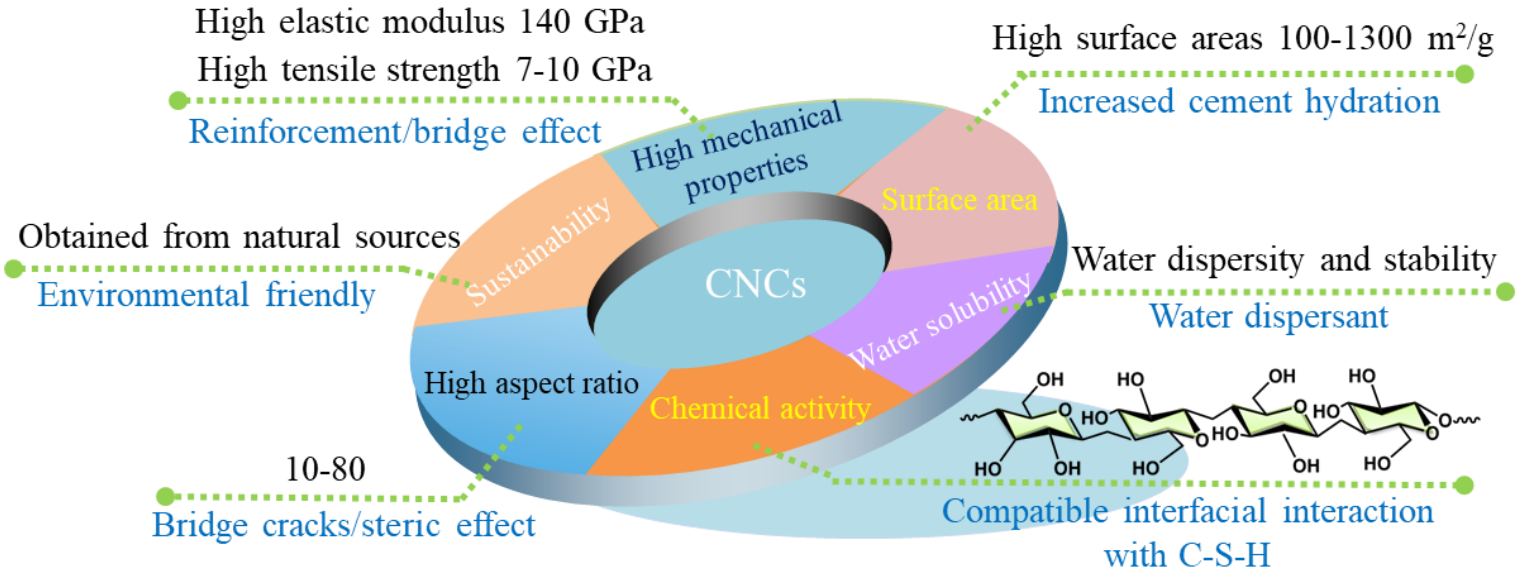


CNCs are environmentally friendly and cost-effective nanomaterials manufactured from natural sources

Andy et al. *Adv. Mater.* **2020**, 1905876.

Benefits of CNCs

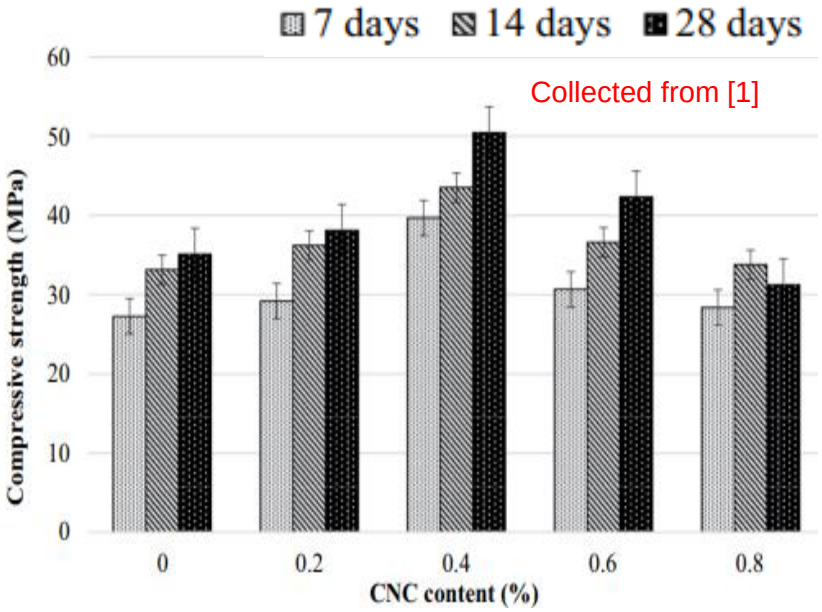
- CNCs are environmentally friendly (renewable, biodegradable, sustainable, low toxicity, and low cost)
- CNCs have abundant hydroxyl functional groups on the surface, therefore it can form strong bond with cement paste and promote the cement hydration.
- CNCs also exhibit large surface area, high aspect ratio, high elastic modulus and tensile strength, and low density.

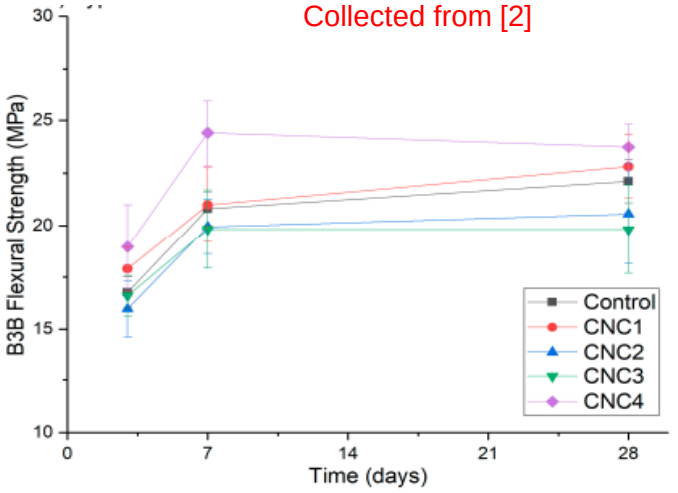


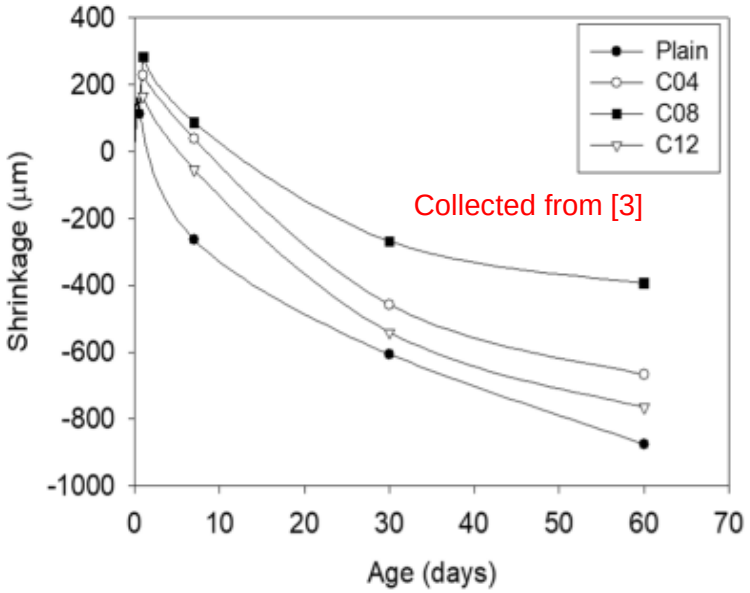
Cranston et al. *Chem. Mater.* 2017, 29, 4609−4631

Current usage of CNCs in concrete: direct addition

- By adding the optimum dosages of CNCs
  - ➢ Enhance the mechanical performance
  - ➢ Promote the cement hydration
  - ➢ Densify the microstructure
  - ➢ Reduce the autogenous shrinkage



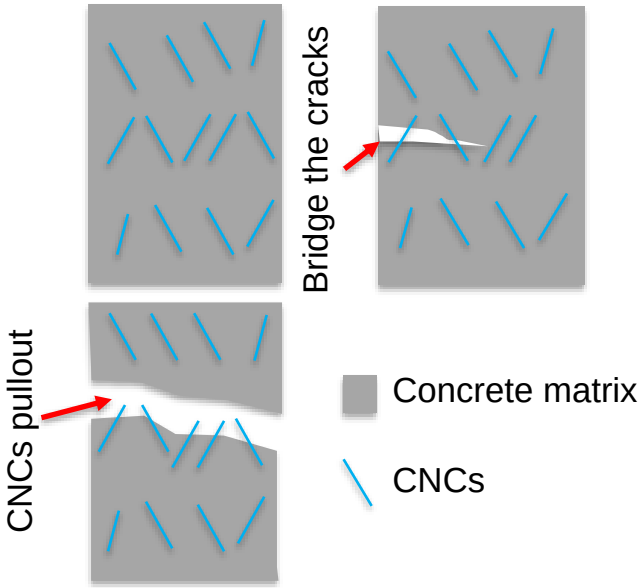




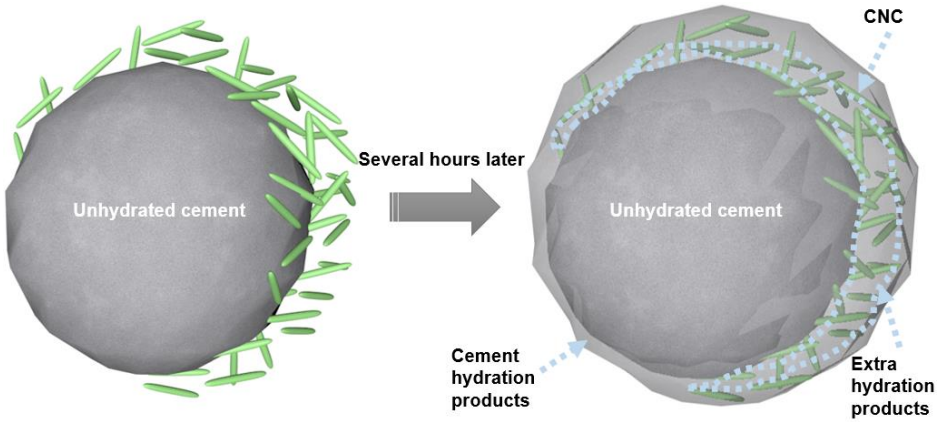
[1] Mazlan et al. *Sci. Rep.* 2020, 10(1), 6412.
[2] Fu et al. *Polymers.* 2017, 9(9), 424.
[3] Lee et al. *Appl. Sci.* 2019, 9(3), 426.

Enhancement mechanisms by CNCs

- Bridge effect
  - ➢ CNCs acts as nano-size fibers to bridge the cracks.
- Internal curing effect
  - ➢ (1) CNCs are hydrophilic and hygroscopic; (2) short circuit diffusion effect.



Bridge effect

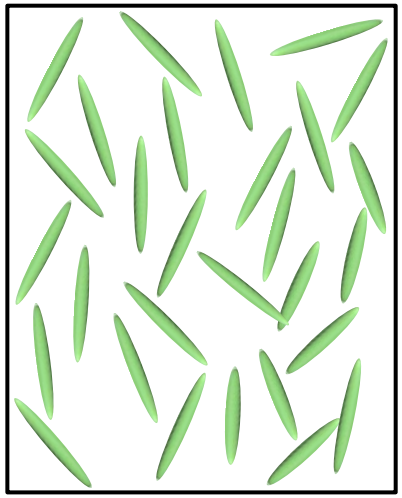


Internal curing effect

[1] Zhong et al. *Nanotechnol. Rev.* 2022, 11(1), 2673-2713.
[2] Lee et al. Constr Build Mater. 2020, 238, 117754.

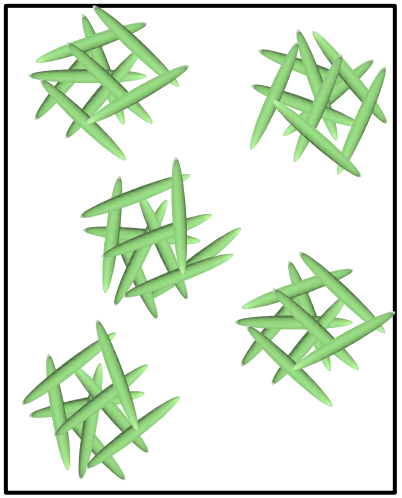
Current problems of using CNCs in UHPC

- The content of CNCs can be used in concrete application is low (around 0.5%, by mass).
- High CNCs concentration leads to the agglomeration, which compromises the mechanical properties.

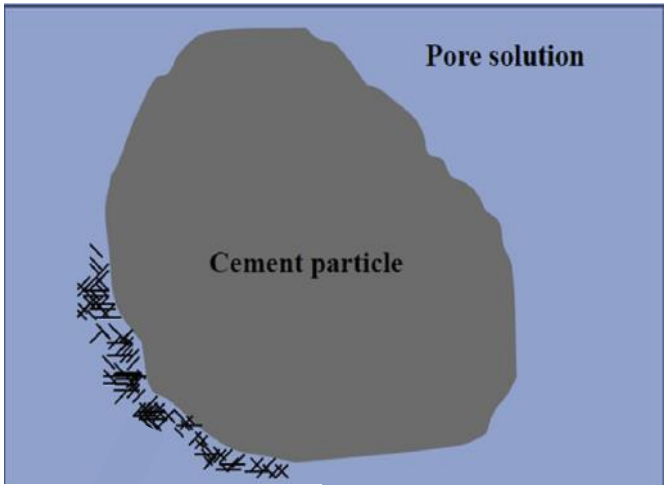


Well-dispersed CNCs in aqueous solution

High concentration



Agglomeration of CNCs in aqueous solution

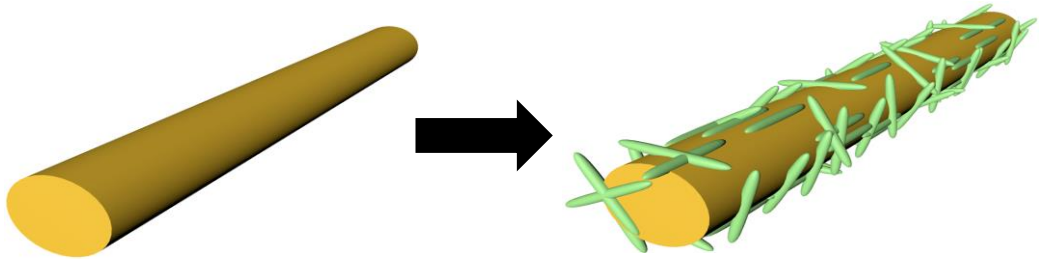


Agglomeration of CNCs on cement particles

Cao et al. Constr Build Mater. 2016, 119, 71-79.

Significance of this research

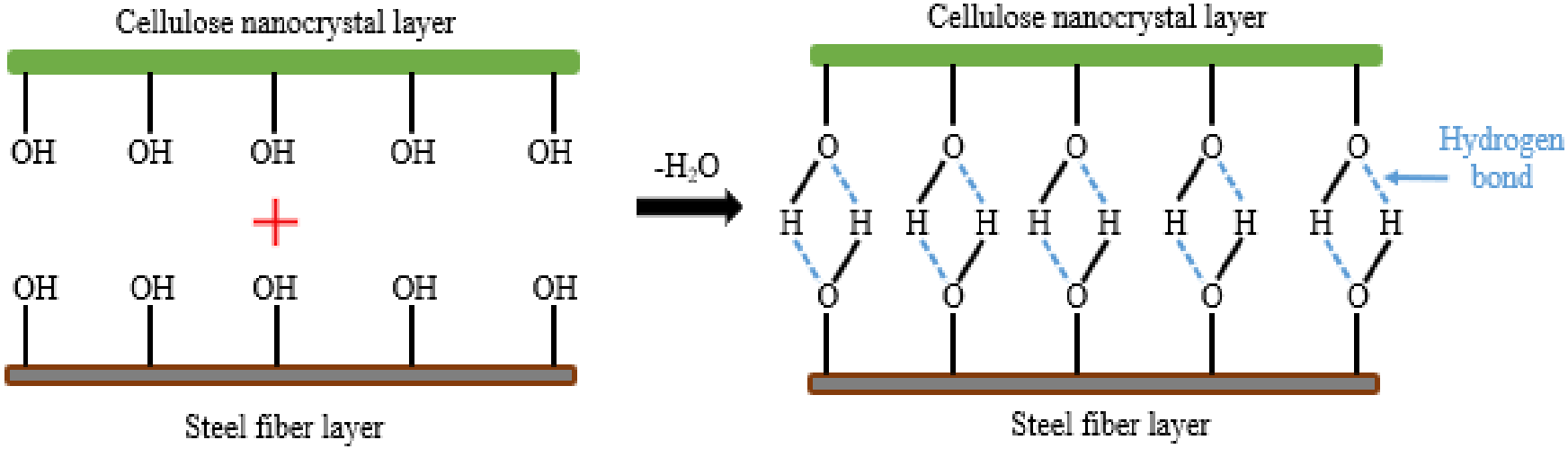
- Coat the CNCs on fibers is a better way to utilize the nano materials.
  - ➢ CNCs coating can mitigate the agglomeration of CNCs in cement pore solution.
- This study proposes an effective method to coat CNCs on surface of steel fibers to improve the flexural performance of UHPC:
  - ➢ CNCs is assumed significantly enhance the ITZ between the steel fibers and UHPC matrix, thus improve the bonding properties and flexural strength.



Schematic diagram of CNCs-coated steel fibers

Coat CNCs on steel fibers

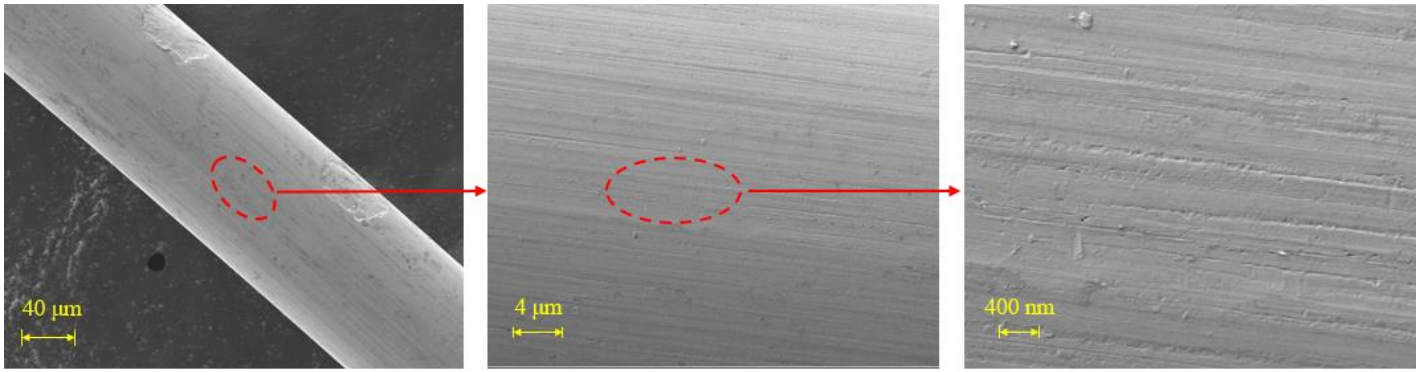
- Step 1: Pretreatment
  - ➢ Pristine steel fibers were immersed in NaOH solution (solid content: 20%) for 30 min to enhance the surface activity.
  - ➢ Steel fibers were washed with the deionized water and ethyl alcohol was used to remove the residual NaOH solution.
- Step 2: CNCs coating process
  - ➢ Pretreated steel fibers were immersed into the CNCs suspension for 1 h, and then dried in an oven at 40 ℃ for 24 h.



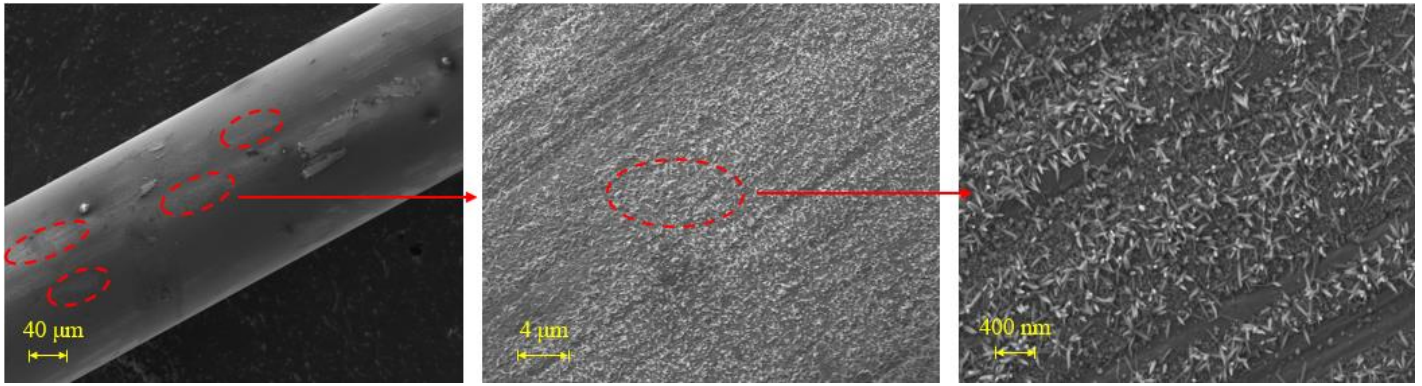
Zhong et al. *Nanotechnol. Rev*. 2022, 11(1), 2673-2713

SEM observation

- Pristine steel fibers: the surface is smooth
- CNCs-coated steel fibers: CNCs particles are well coated and uniformly covered on surfaces.



Pristine steel fibers

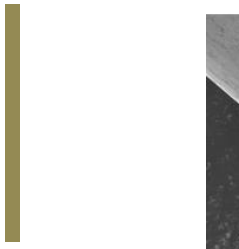


CNCs-coated steel fibers

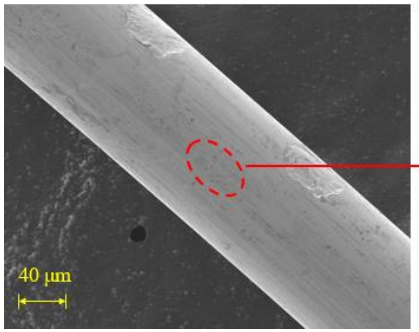
EDS observations

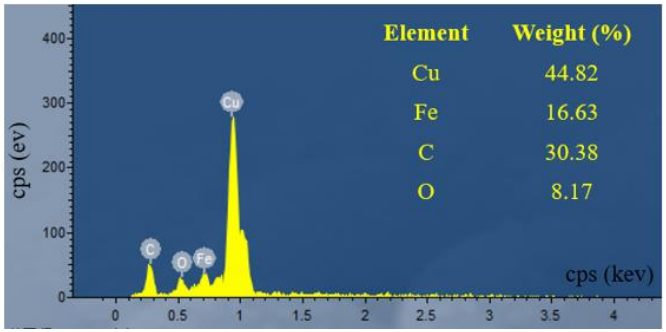
- Pristine steel fibers: only 8.17% oxygen is detected on the surface.
- CNCs-coated steel fibers: the oxygen content is increased to 26.16%.
- The increased oxygen is from hydroxyl groups in CNCs.

Surface of pristine fibers →



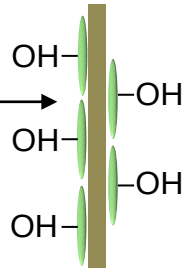
No reactive groups on surface of pristine steel fibers



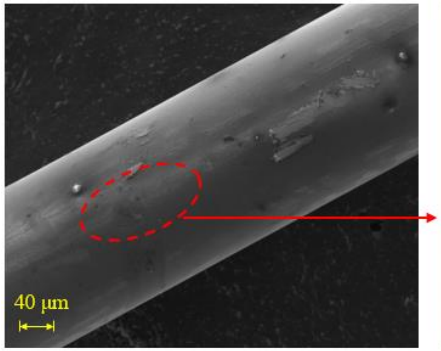


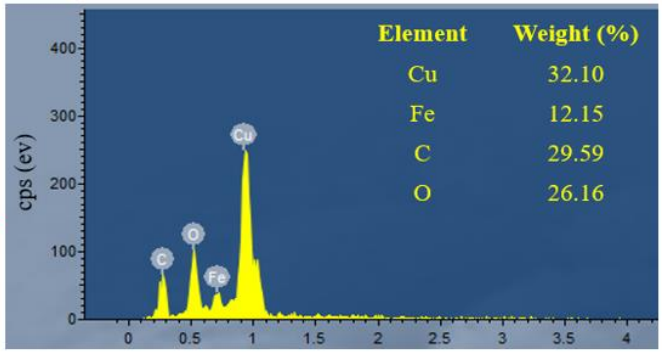
Pristine steel fibers

Surface of CNCs-coated fibers →



Plenty of –OH groups from CNCs are grafted on surface of steel fibers

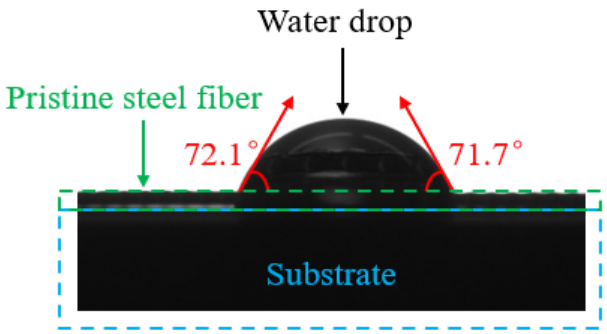




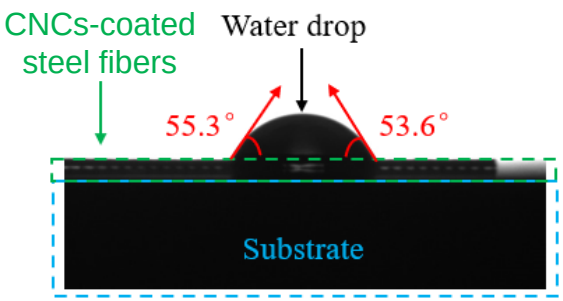
CNCs-coated steel fibers

Contact angle results

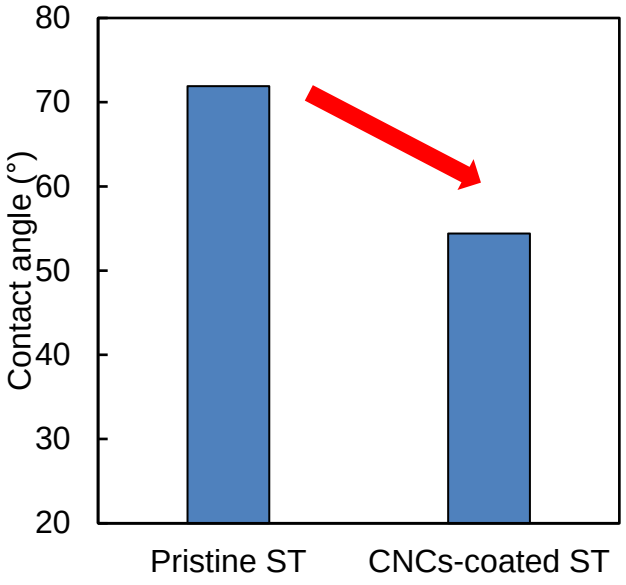
- Pristine steel fibers: the contact angle is 71.9°.
- CNCs-coated steel fibers: the contact angle is 54.5°.
- CNCs are hydrophilic, improve the hydrophilicity of steel fibers.



Pristine steel fibers



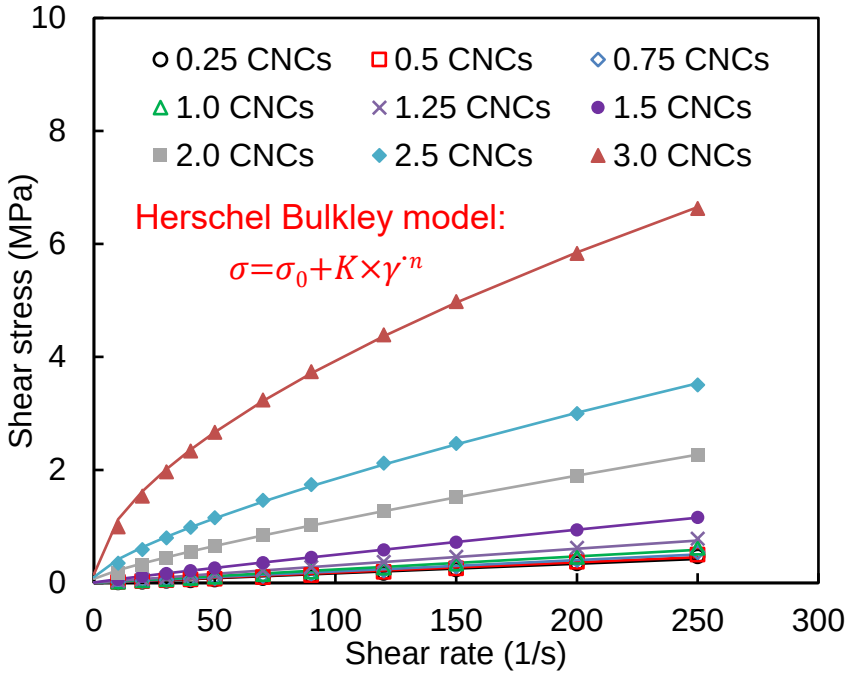
CNCs-coated steel fibers

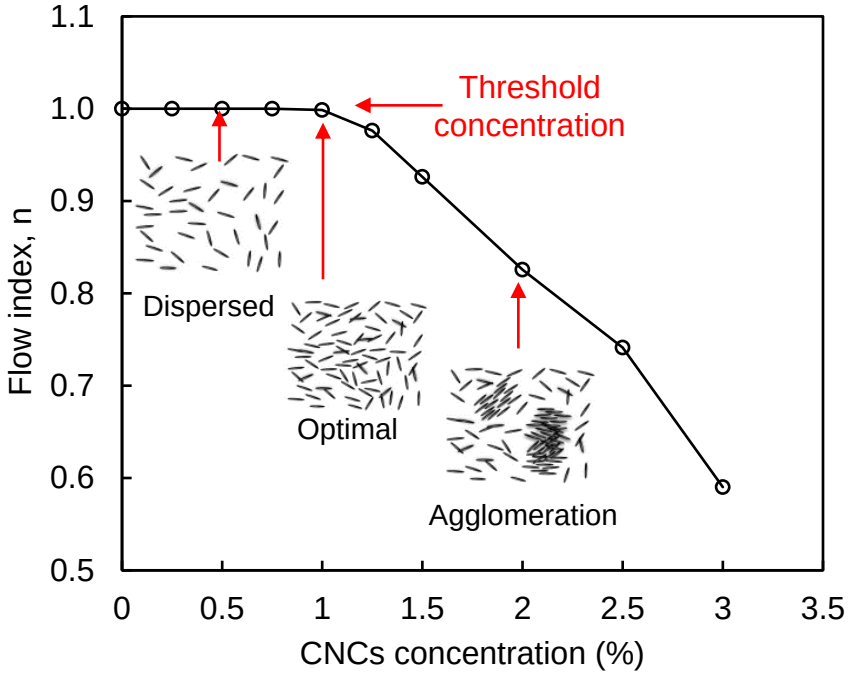


The improvement of the hydrophilicity of the steel fiber surface is expected to densify ITZ of the fiber and cement matrix

Preliminary determination of CNCs concentration

- The flow index (n) is an indicator of CNCs agglomeration [1], which is determined by Herschel Bulkley model.
- As CNCs concentration is above 1.0%, the CNCs particles start to agglomerate in tap water.
- The preliminary threshold concentration of CNCs is 1.0%.





[1] Cao, Y. (2016). The relationship between cellulose nanocrystal dispersion and strength.
Note: K is the consistency and n is the flow index.

UHPC mixture design

- UHPC mixture design is shown in the table (kg/m^3)
- Control is the UHPC with pristine steel fibers.
- CSF is the UHPC with CNCs-coated steel fibers.

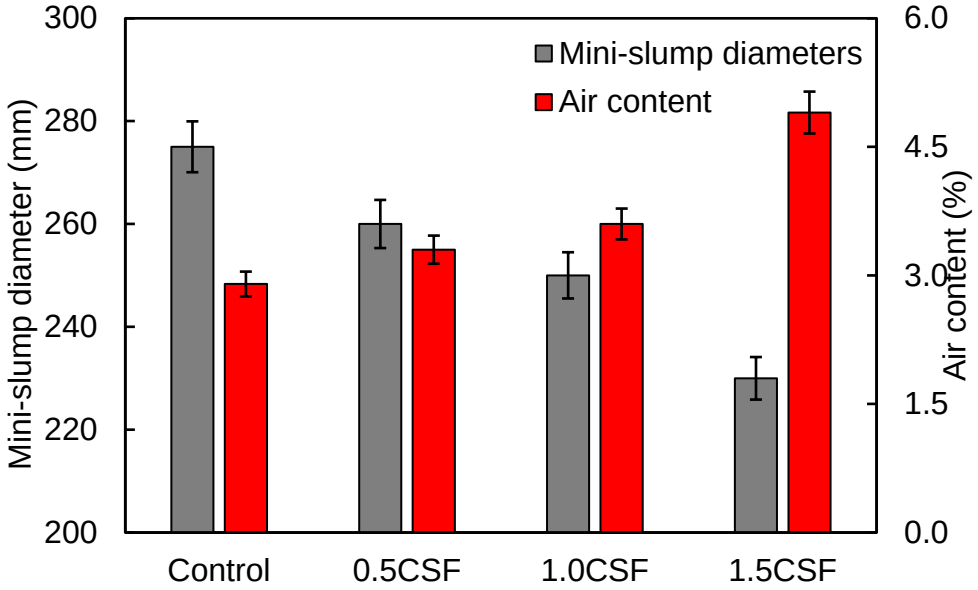
Mixture	Cement	Slag	River sand	HRWR	Water	PSF	CSF	CNCs
Control	459.0	633.9	965.4	8.0	248.1	156.0	-	0
0.5CSF	459.0	633.9	965.4	8.0	248.1	-	156.0	2.5
1.0CSF	459.0	633.9	965.4	8.0	248.1	-	156.0	5.0
1.5CSF	459.0	633.9	965.4	8.0	248.1	-	156.0	7.5

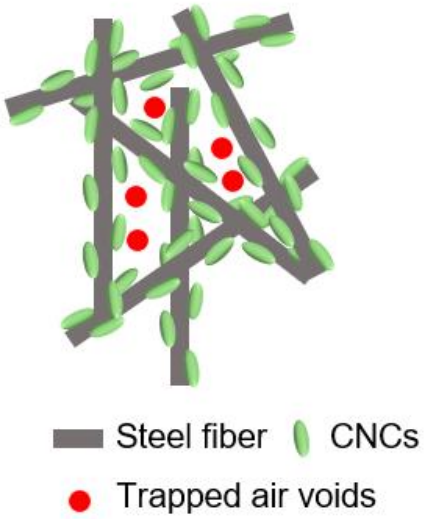
Note: HRWR is high-range water reducer; PSF is pristine steel fibers; CSF is CNCs-coated steel fibers.

e.g., 0.5CSF represents the mixture with the steel fibers treated by CNCs suspension at 0.5% concentration.

Workability

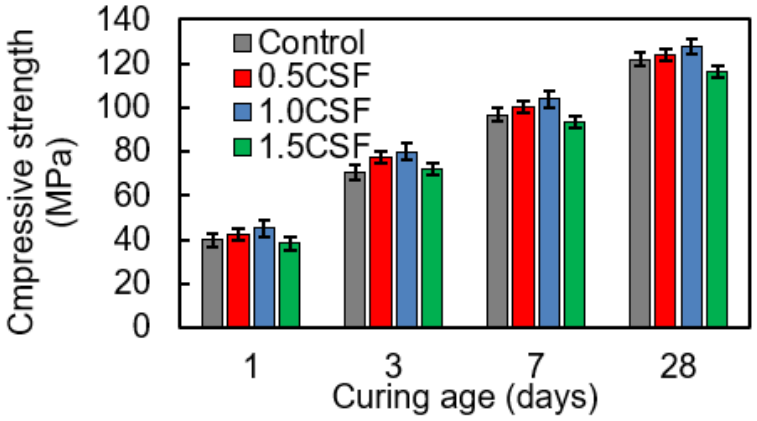
- CNCs-coated steel fibers reduces the flowability and increases the air content of UHPC mixtures
- Mechanisms:
  - The CNCs prone to absorb free water which reduces the water for lubrication.
  - The agglomeration of CNCs-coated steel fibers traps the air voids, thus increasing the air contents (especially for 1.5CSF).

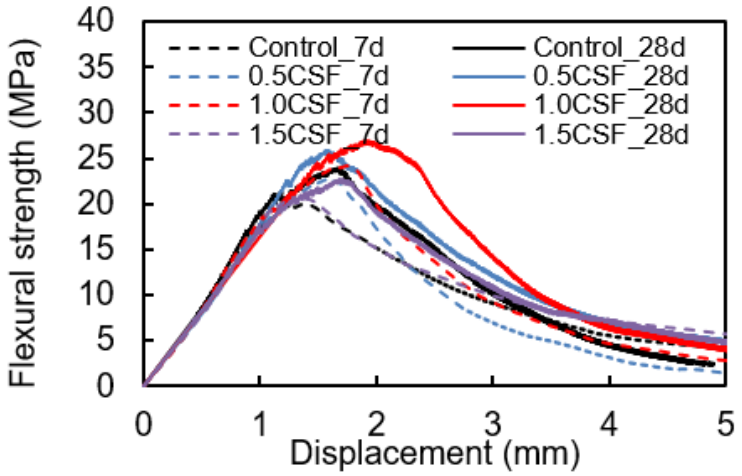


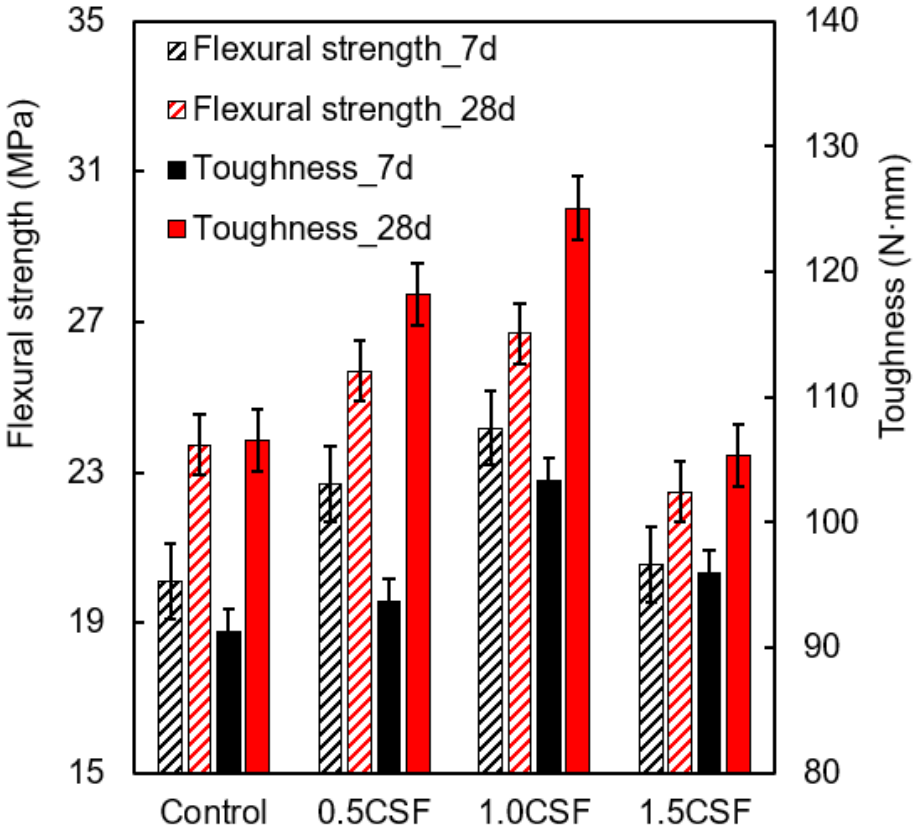


Mechanical properties

- As the concentration of CNCs suspension increases, the mechanical properties first increase and then decrease.
- The optimal concentration of CNCs coating suspension is validated to be 1.0%.

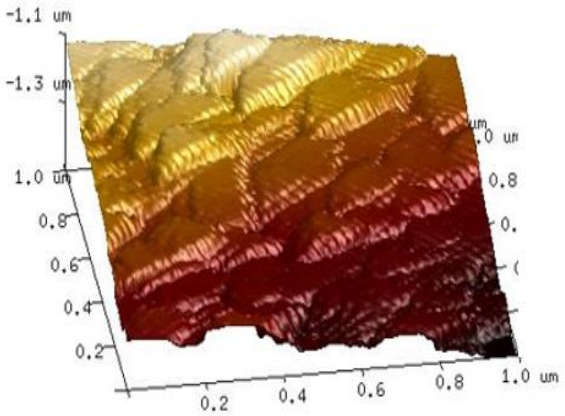




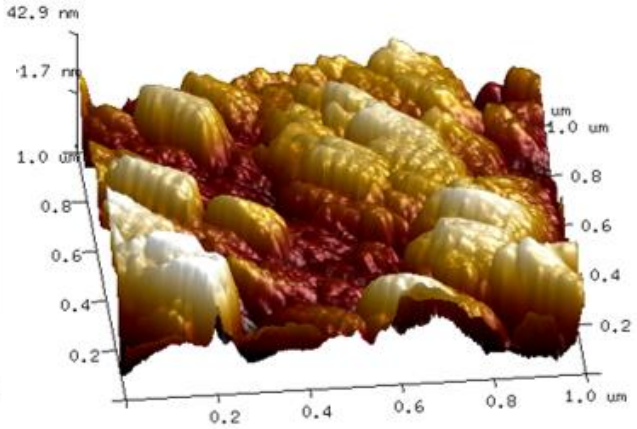


Enhancement mechanism: physical interlock (micro)

- Pristine steel fibers: the average roughness is 5.7 nm.
- CNCs-coated steel fibers: the average roughness is 20.1 nm.
- The increased average roughness of steel fiber surface increases the mechanical interlock, improve the bonding between fibers and matrix.

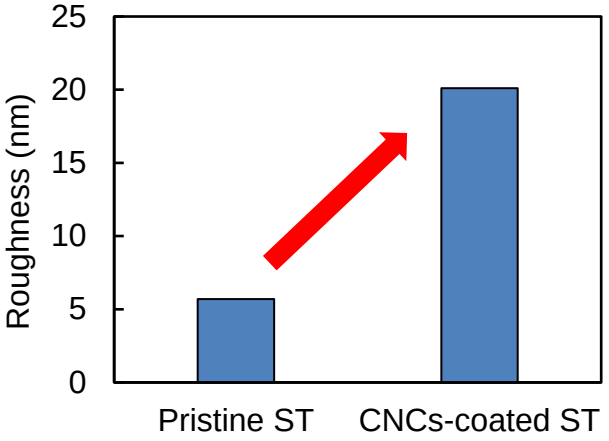


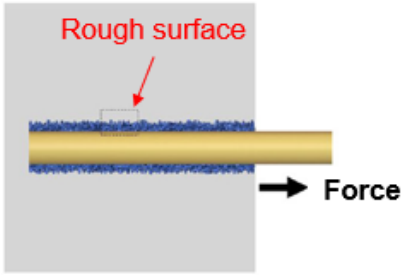
Pristine steel fibers



CNCs-coated steel fibers

AFM results

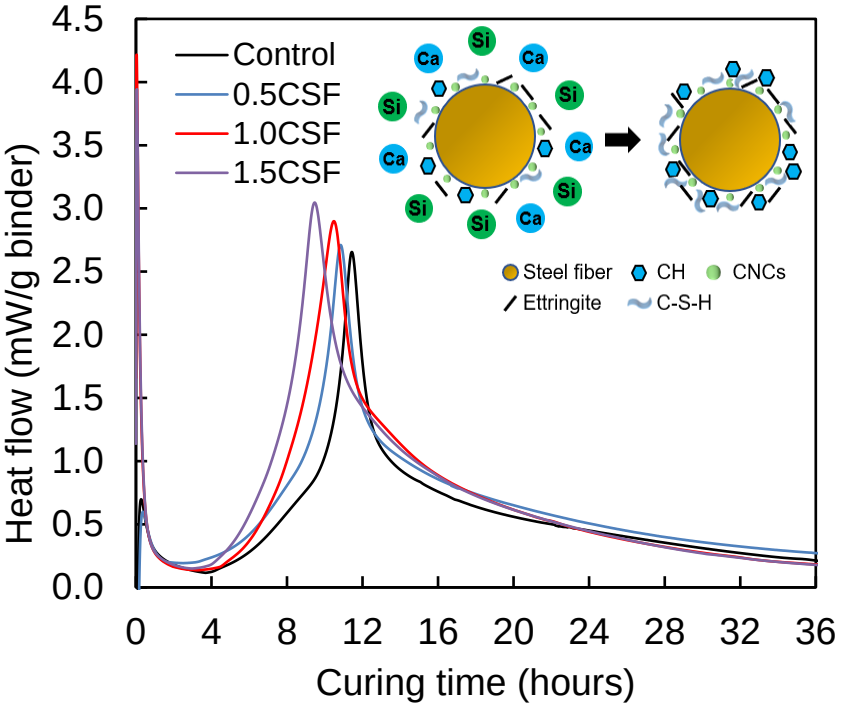




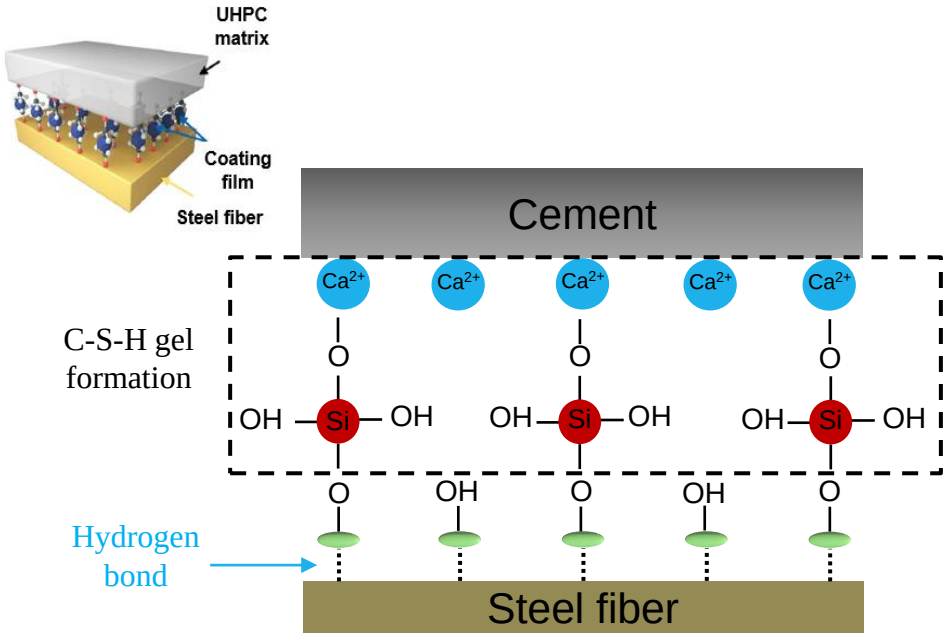
Mechanical lock

Enhancement mechanism: chemical reaction (micro)

- The CNCs-coating film promotes and accelerates the hydration.
- Mechanism:
  - The -OH group on CNCs-coated steel fibers reacts with Si^{2+} ions and Ca^{2+} ions to form more C-S-H gel in the ITZ [1].



Isothermal calorimetry analysis

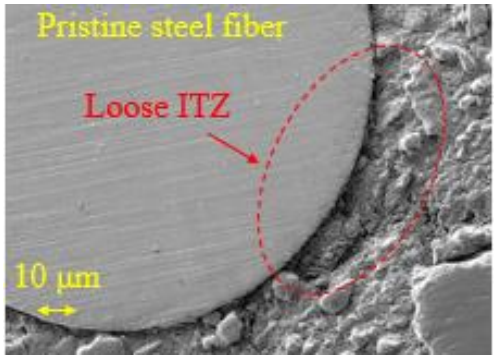


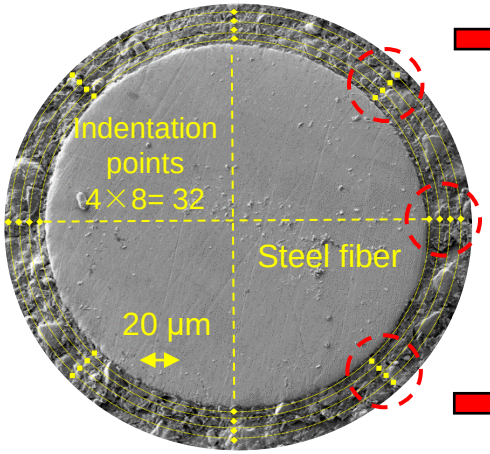
Chemical reaction on ITZ

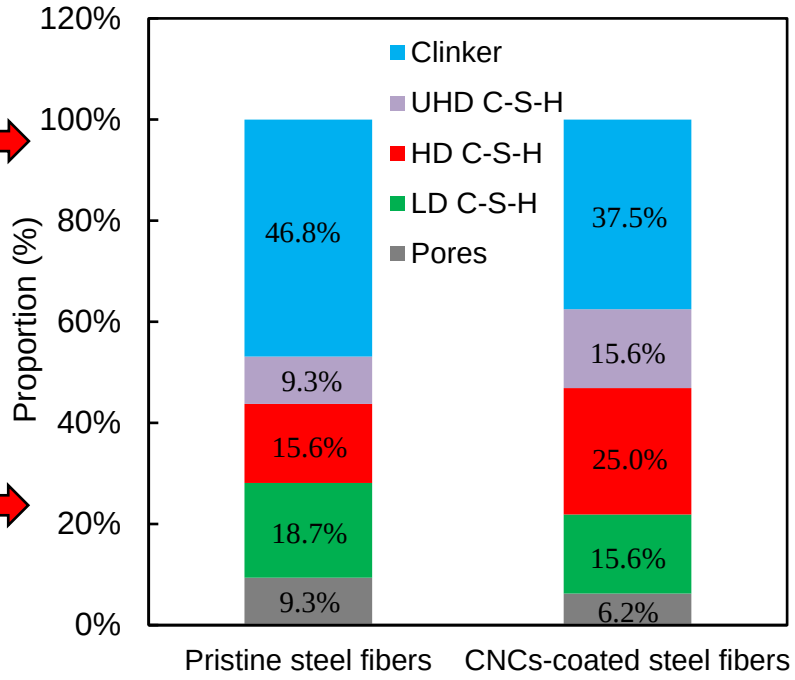
[1] Zhang et al. *Compos. B. Eng.* 2019, 162, 500-507.

Interfacial transition zone (ITZ) analysis (micro)

- Qualitative analysis – SEM observation
  - ➢ The ITZ between CNCs-coated steel fiber and matrix is denser than the ITZ between pristine steel fiber and matrix.
- Quantitative analysis - Nanoindentation
  - ➢ More HD C-S-H and UHD C-S-H phase as well as less pores are found in the ITZ between CNCs-coated steel fiber and matrix.

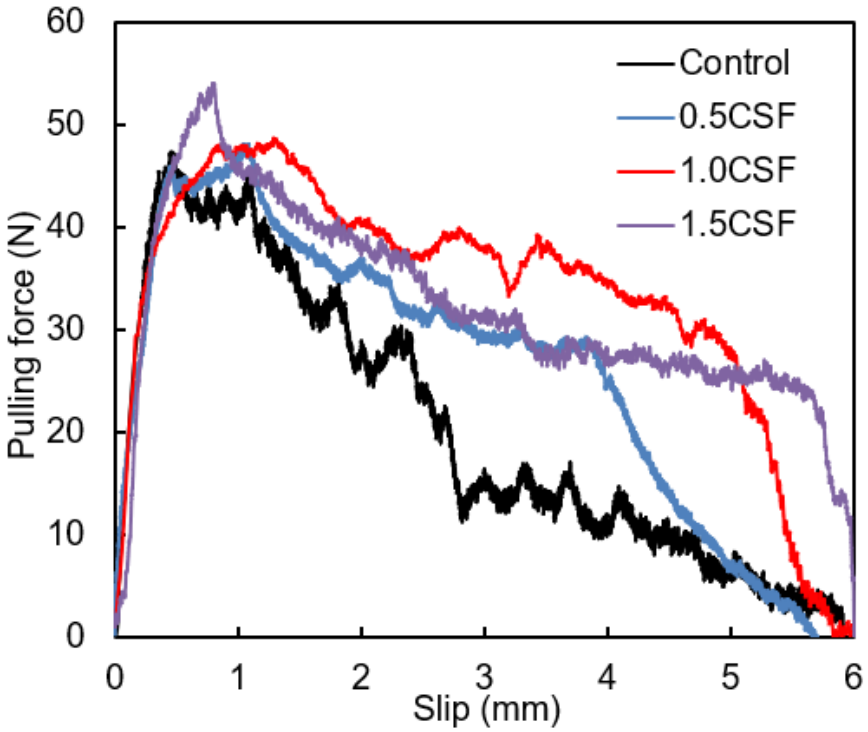


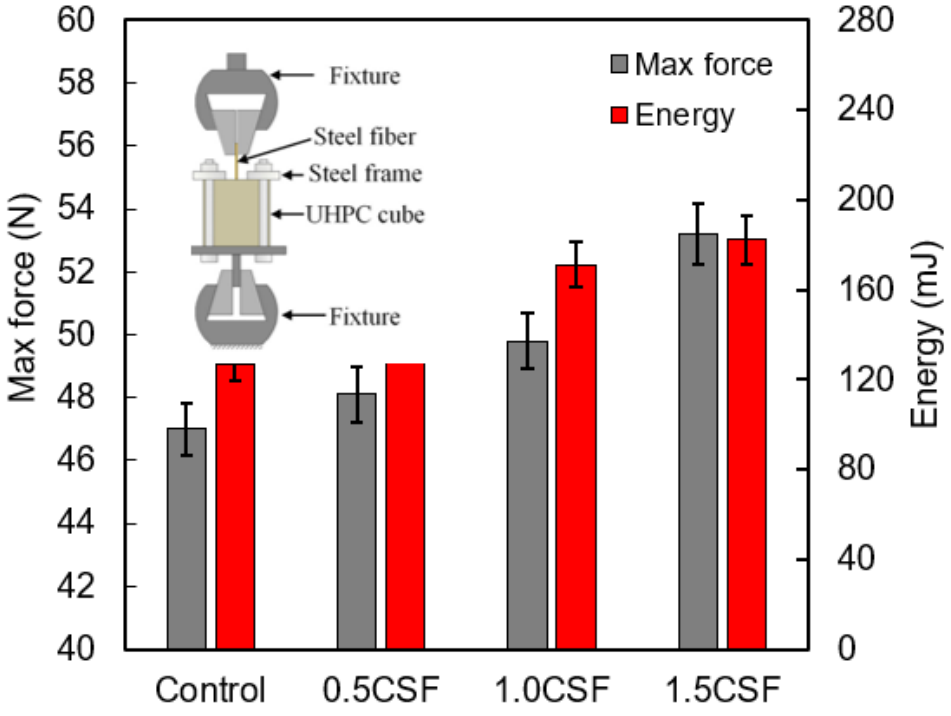




Bonding between fiber and matrix

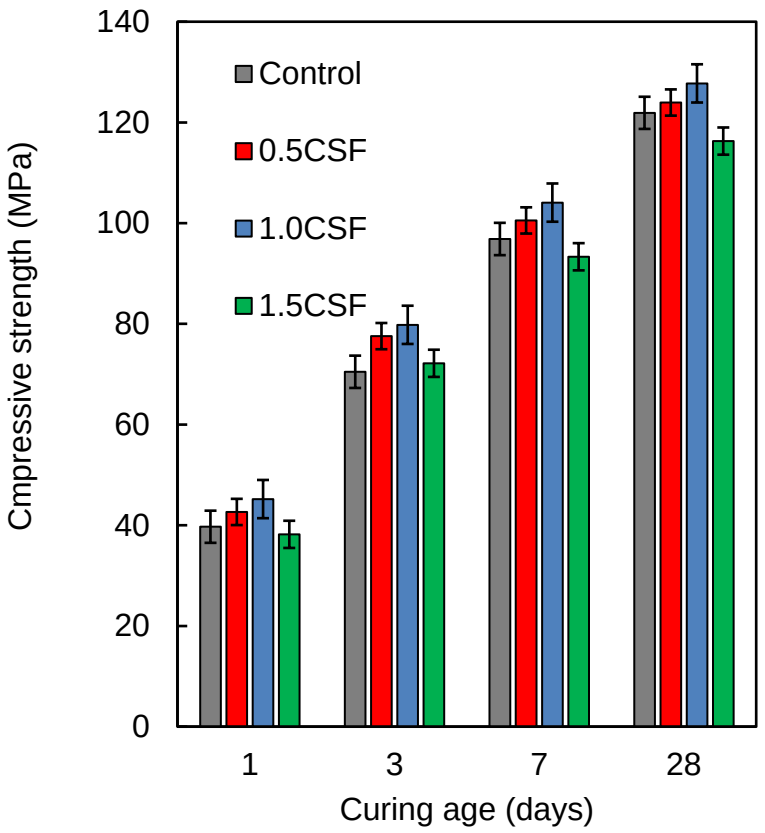
- The CNCs-coating film increases the fiber pull-out force and energy.
- Mechanism:
  - ➢ Increased surface roughness
  - ➢ Densified interfacial transition zone due to the chemical reaction

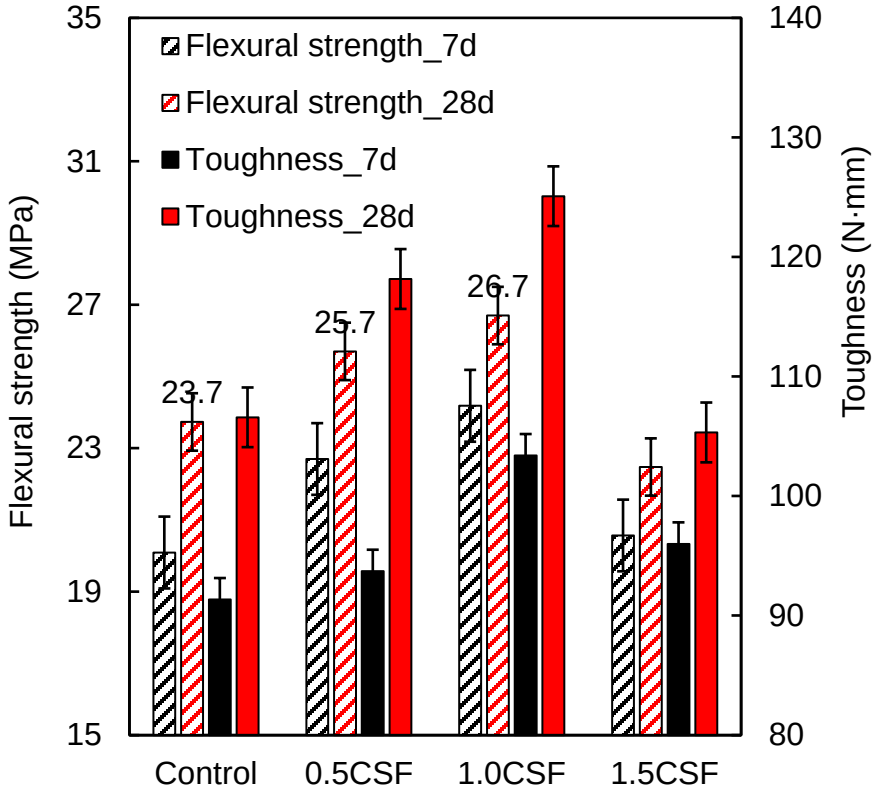




Strength reduced as bonding is improved?

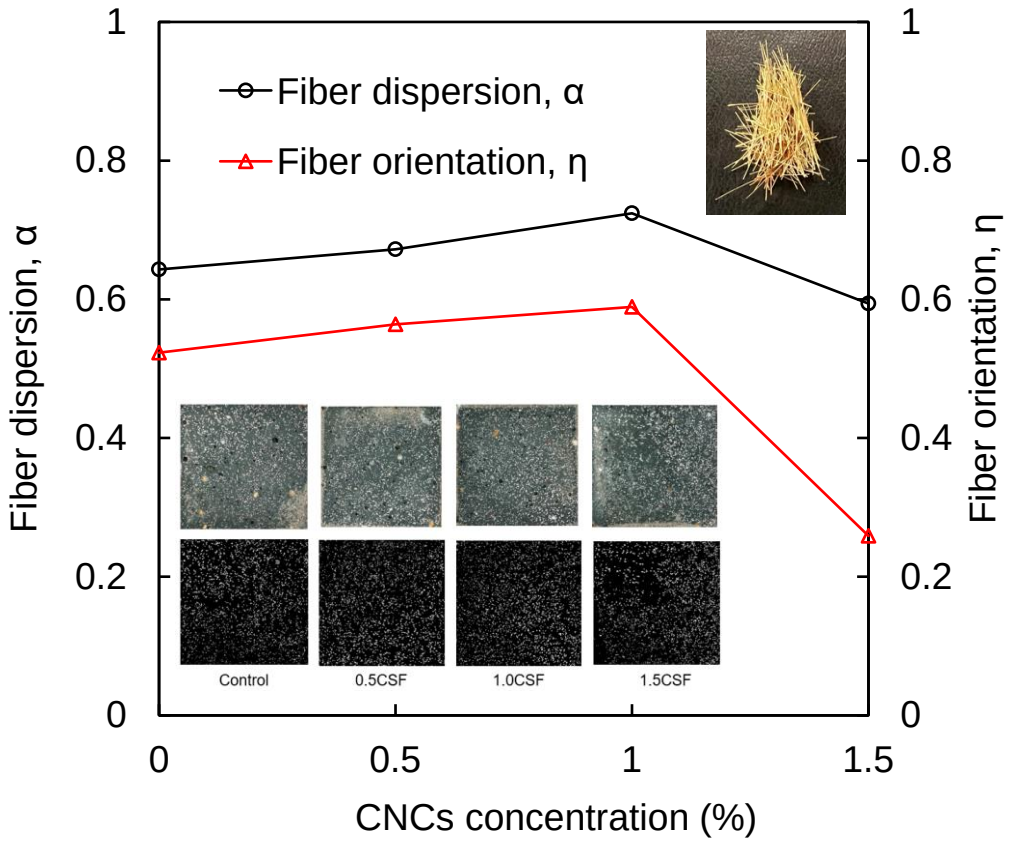
- Both compressive strength and flexural properties reduced when CNCs suspension concentration is great than 1%.

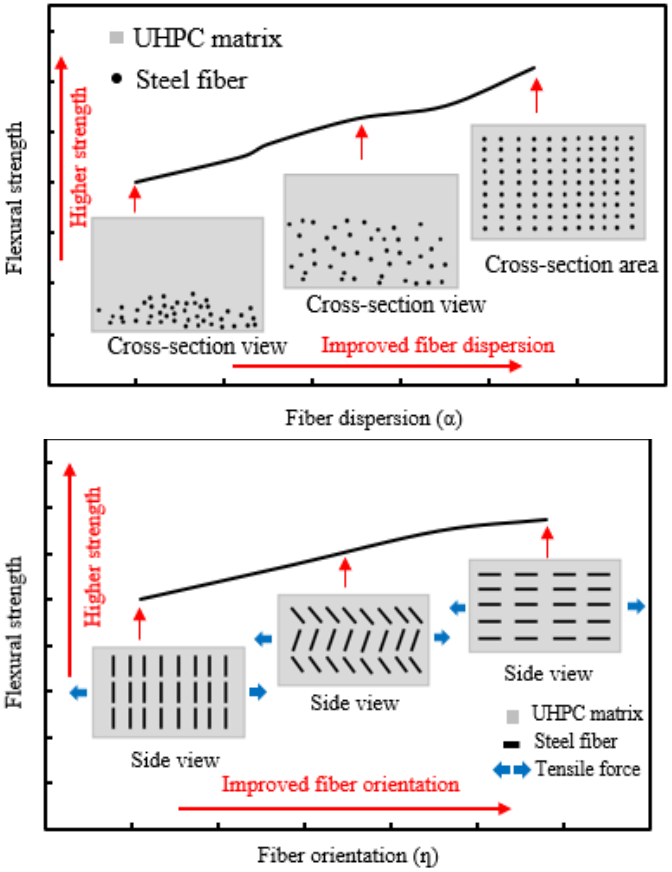




Why strength reduced?

- When the concentration of CNCs suspension exceeds 1.0%, the fiber dispersion and orientation coefficient are significantly reduced.
- The agglomeration of CNCs-coated steel fibers leads to the reduction of the mechanical strength of UHPC mixtures.





Conclusions

- Rheological properties of CNCs coating suspension can be used to preliminarily determine the threshold CNCs concentration.
- The microscale characterization, including SEM-EDS, AFM, FTIR, and contact angle, proved CNCs is well coated on steel fiber surface.
- Steel fibers treated by CNCs suspension with optimum concentration of 1% enhances mechanical performance of UHPC due to the promoted hydration and increased bond performance between steel fibers and matrix.
- Steel fibers treated by CNCs suspension with greater than 1% reduces mechanical performance of UHPC due to agglomeration of steel fibers.

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weina.meng@stevens.edu