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Waterborne modifications to cellulose nanofibrils for biomaterials, coatings, and composites

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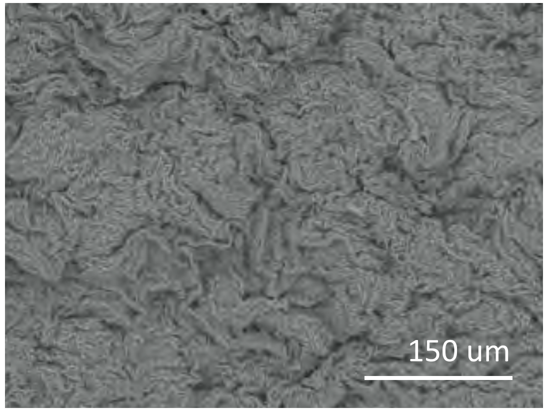
Challenges with using CNFs

Cellulose nanofibrils (CNFs)

Dewater or Dry



Challenges: High viscosity, low solids

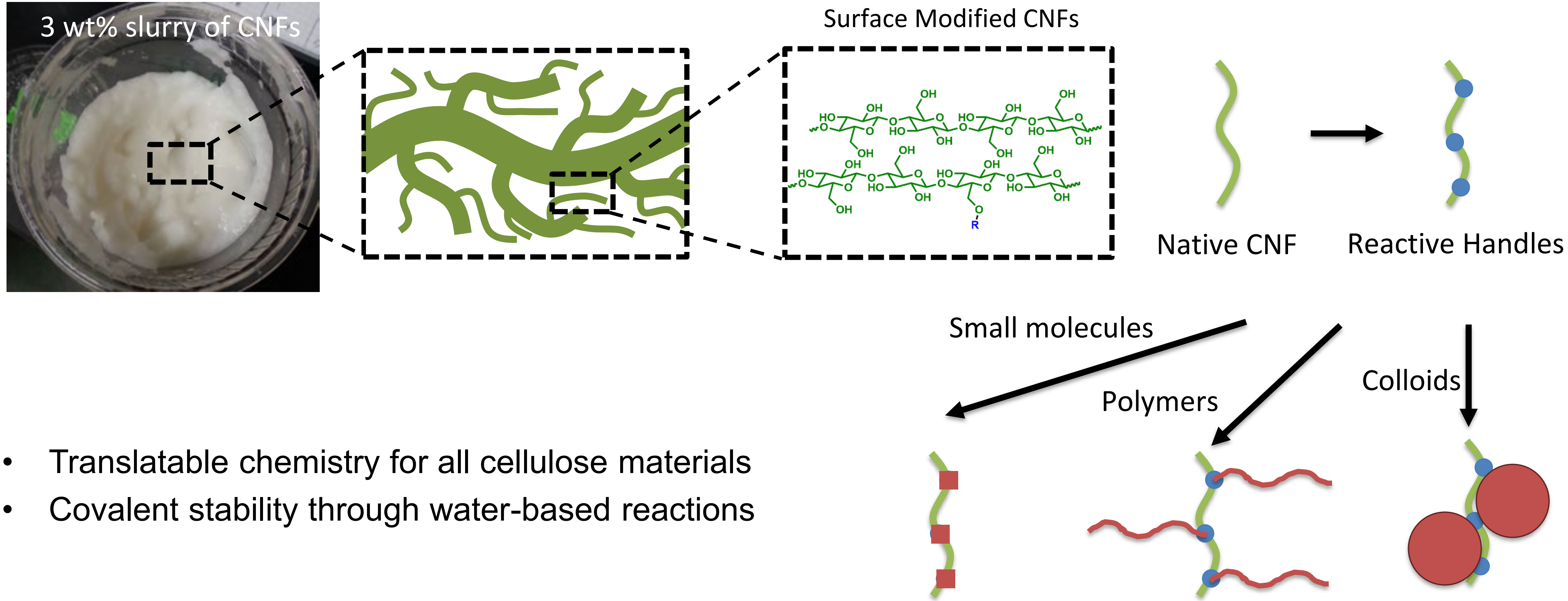
Challenges: Aggregation and hydrophilicity

Challenges: Dispersion and compatibility

Compound

Products with performance advantage

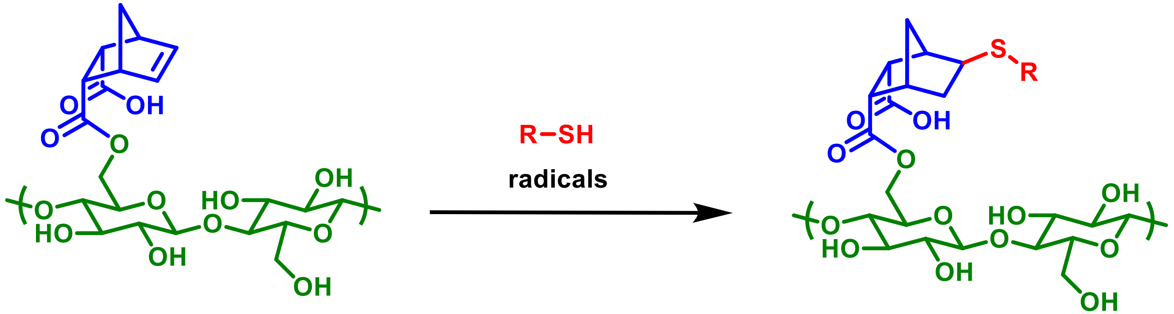
Modular modification of CNFs



- Translatable chemistry for all cellulose materials
- Covalent stability through water-based reactions

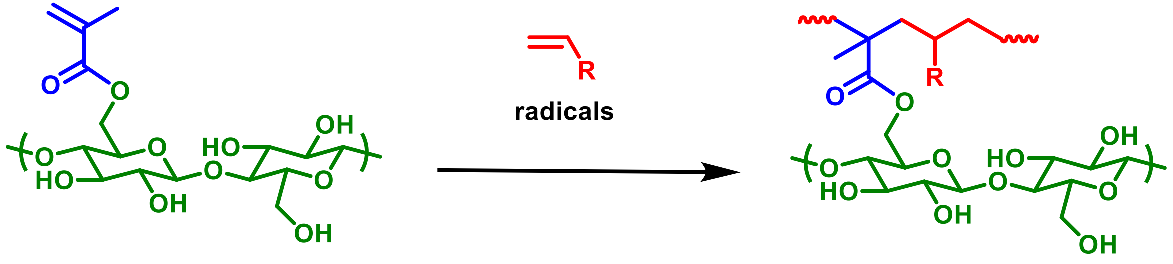
Kelly et al. Macromolecular Rapid Communications 2021
Fein et al. Carbohydrate Polymers 2020 - 115672
Fein et al. Carbohydrate Polymers 2020 – 117001
Dadoo et al. Cellulose 2021

Modular modification of CNFs



cCNF

Thiol-ene reaction

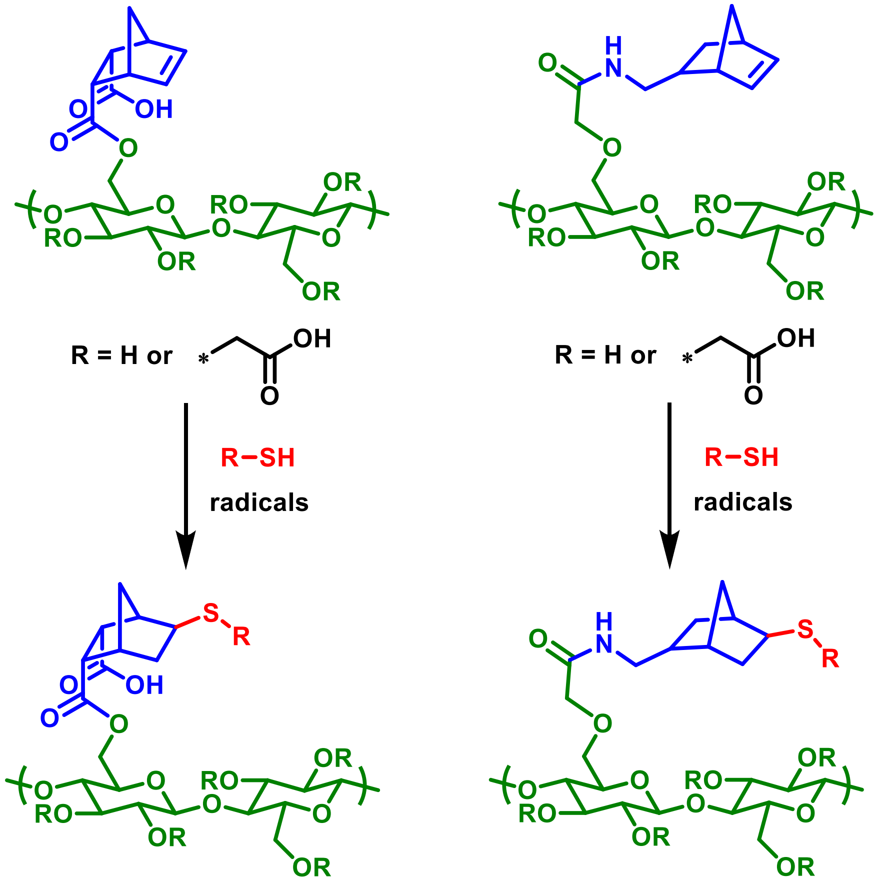


MetCNF

Radical polymerization

cCMC

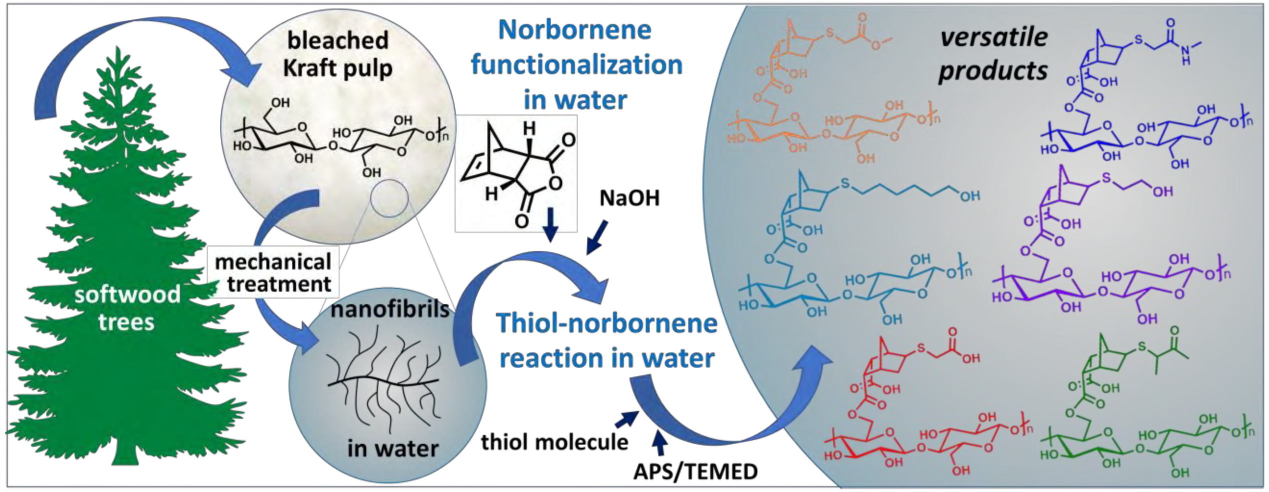
NorCMC

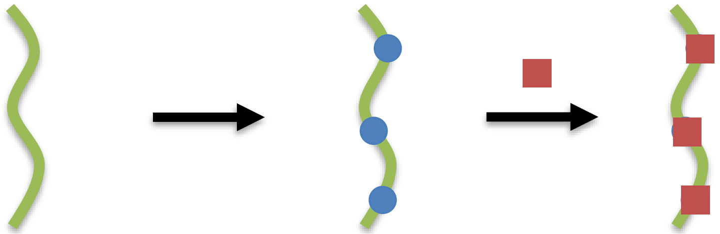


- Modifications performed in water
- Can occur on other polysaccharides and cellulose derivatives
- Orthogonal reactions possible
- All secondary reactions are possible in water
- Functional group tolerance

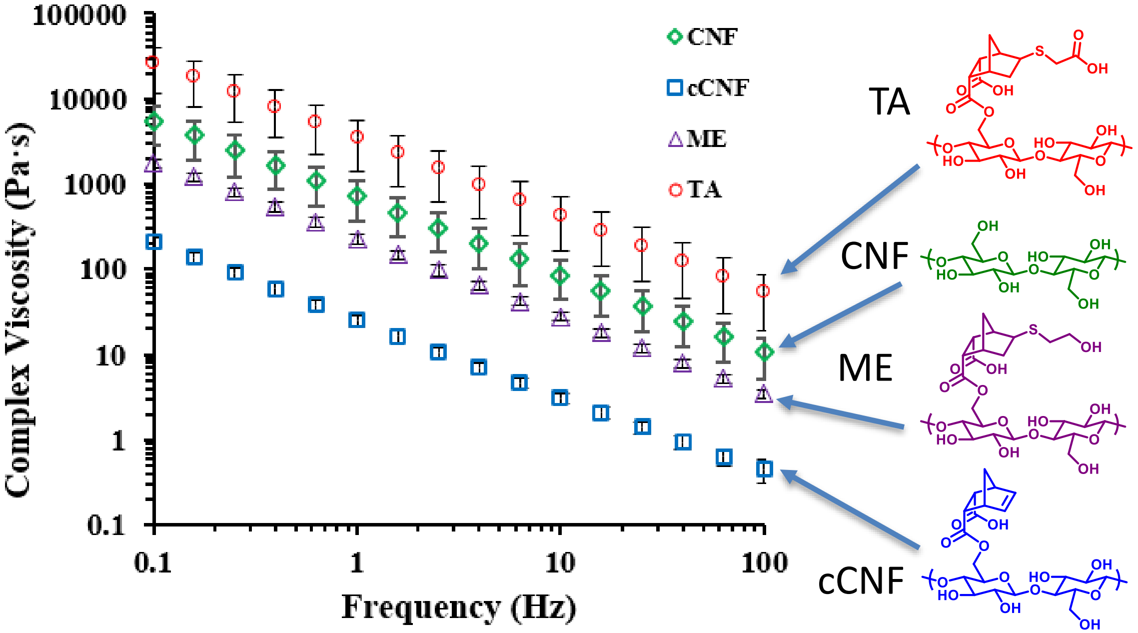
Morrison and Gramlich Carbohydrate Polymers 2023
McOscar and Gramlich Cellulose 2018
Ji et al. Bioprinting 2020
Dadoo et al. Macromolecular Bioscience 2017

Modular small molecule modifications





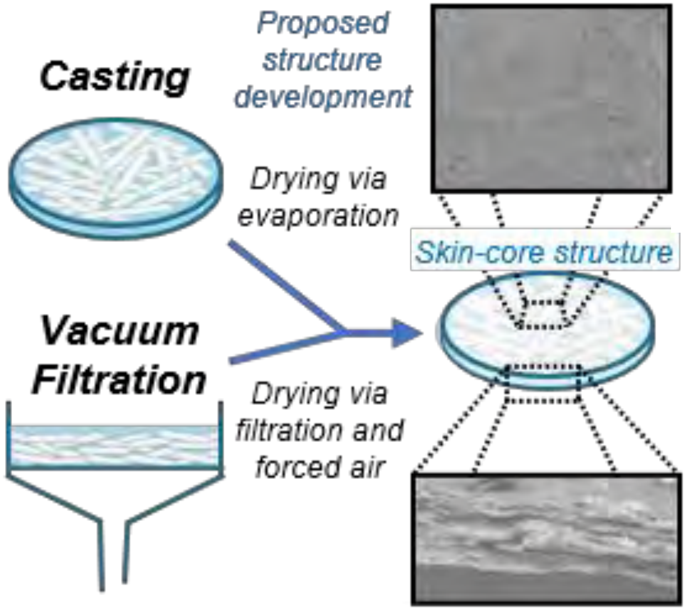
Small molecule thiol-ene

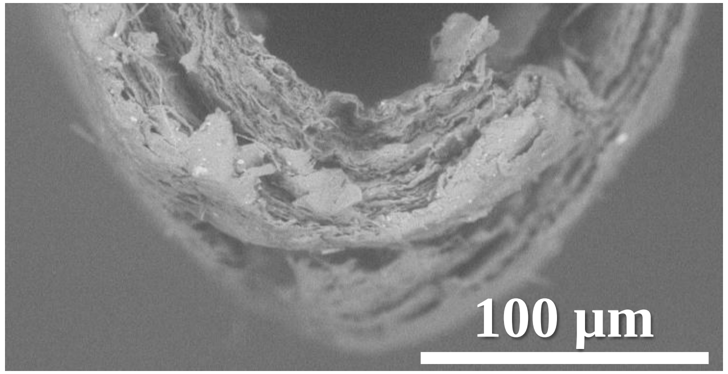


- Modifications can change suspension viscosity
- cCNF reduces viscosity by over an order of magnitude

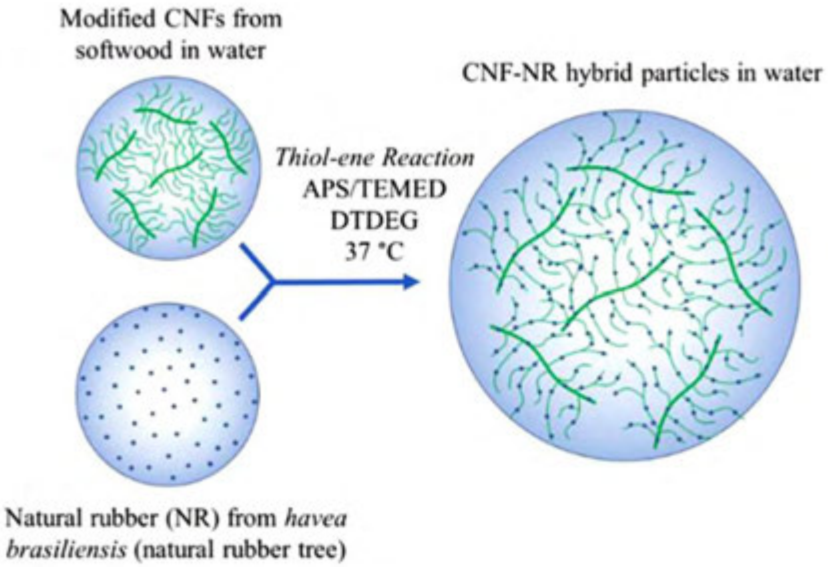
Fein et al. Carbohydrate Polymers 2020

Colloidal modifications for coatings

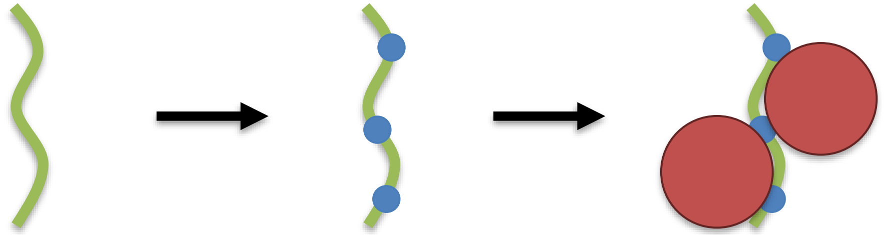




Layered structure



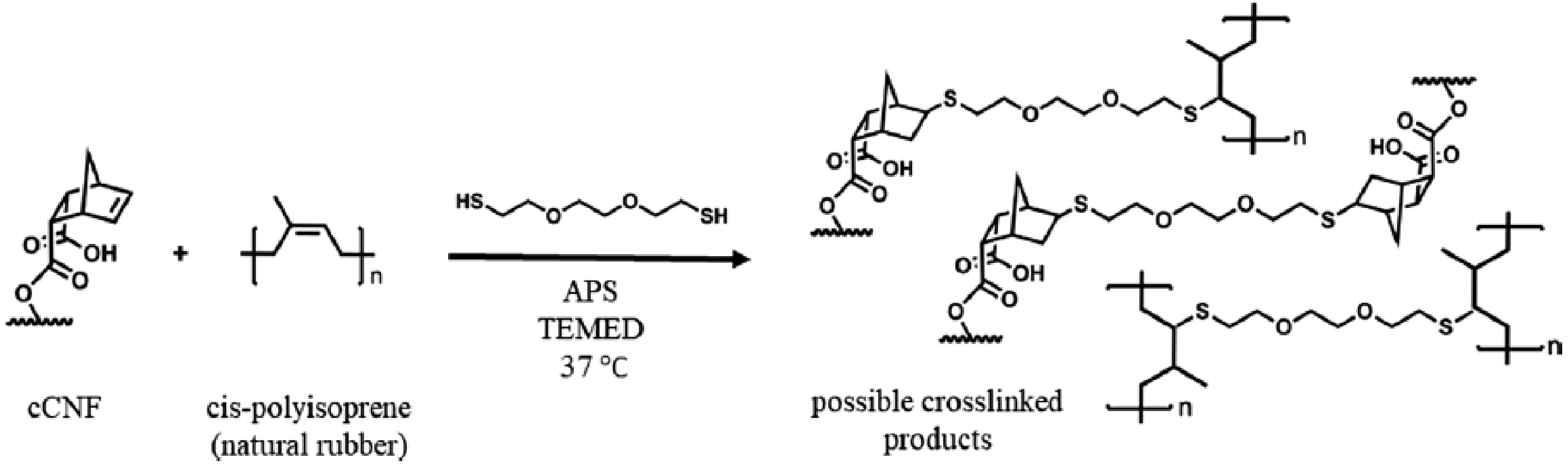
- CNF coatings and films formed through filtration
- Good grease and oxygen barrier
- Retains properties after folding
- Desire improved water barrier

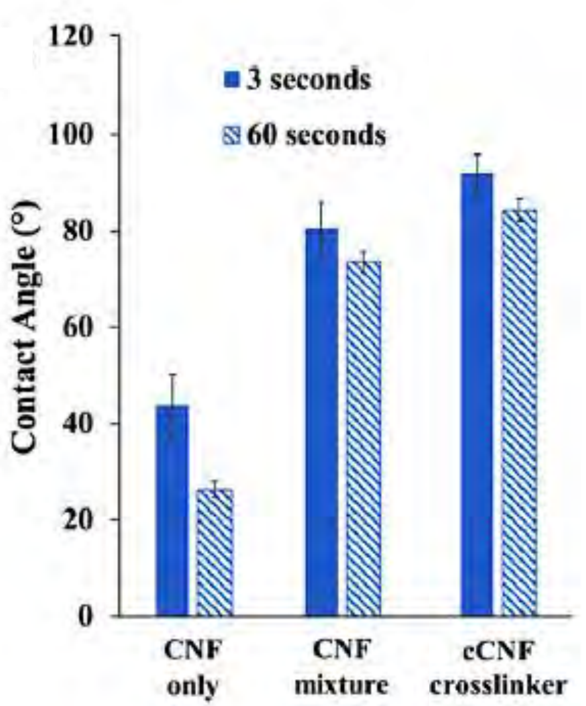


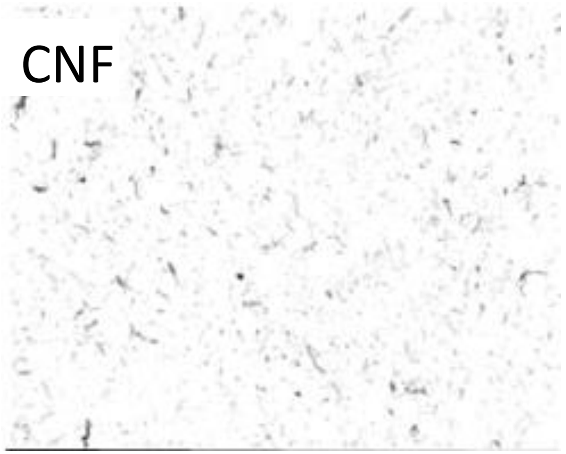
thiol-ene coupling reaction

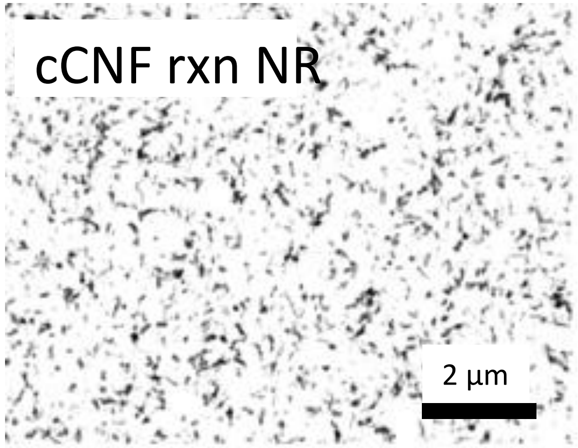
Fein et al. ACS Applied Polymers 2021

Coupling natural rubber improves dispersion





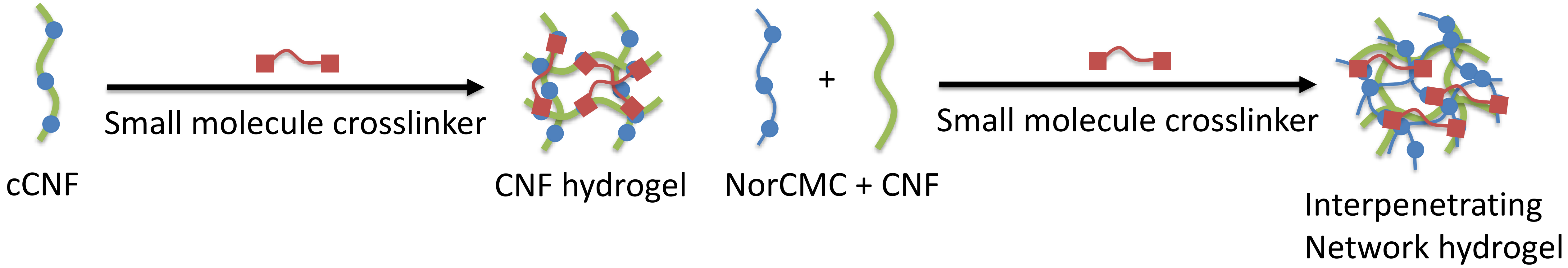


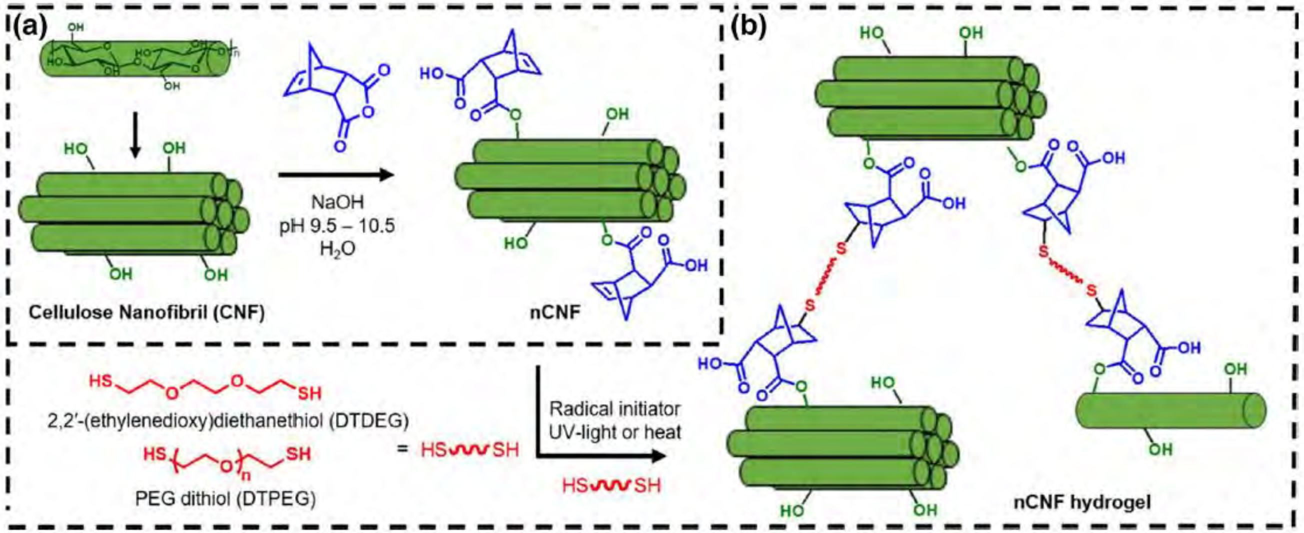


- Improved distribution of latex in coating
- Increased the contact angle compared to mixture

Fein et al. Carbohydrate Polymers 2020

Chemically crosslinked CNF hydrogels

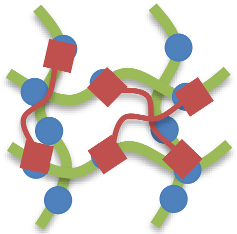




- Hydrogels for biomedical applications
- Various dithiols crosslink through thiol-ene
- Provide mechanical robustness
- Control mechanical properties

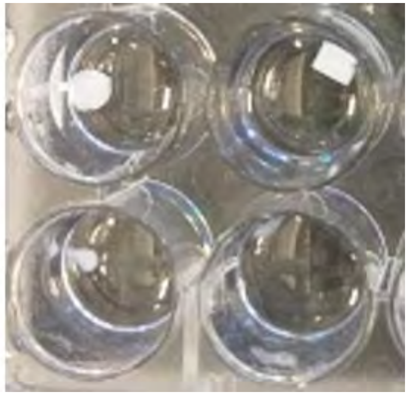
Dadoo et al. Cellulose 2021
Morrison and Gramlich Carbohydrate Polymers 2023

Stability and stiffness control

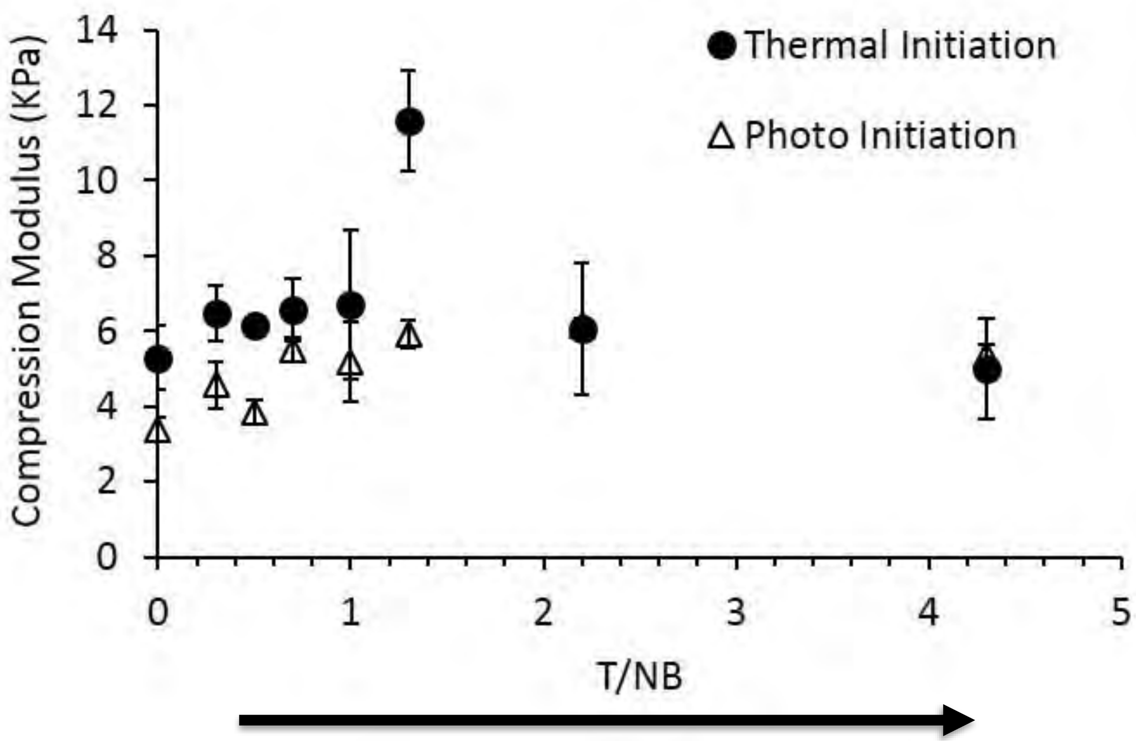


Covalently crosslinked hydrogel

With crosslinker



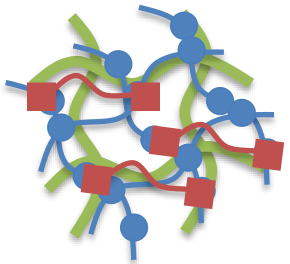
Without crosslinker



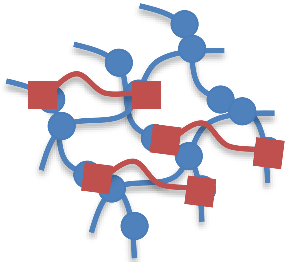
Increasing concentration of crosslinker

- Crosslinked hydrogels are stabilized
- Different thiol-ene initialization possible
- Control over the compression modulus

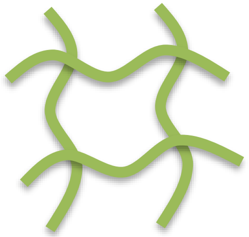
Interpenetrating network synergy



Interpenetrating Network hydrogel

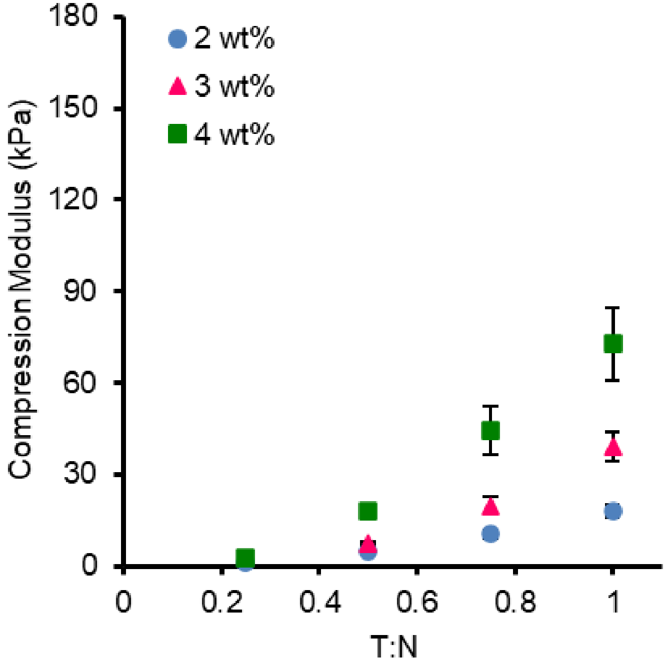


NorCMC Chemically crosslinked

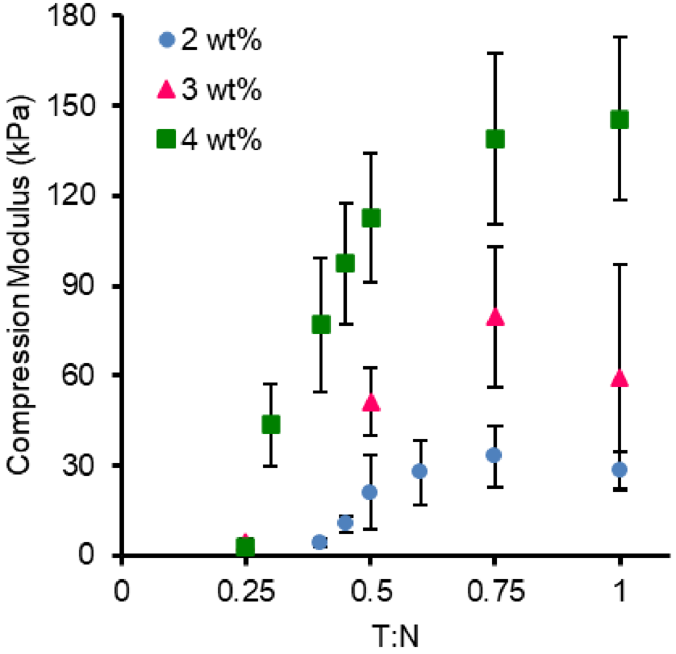


CNFs Physically crosslinked

100% NorCMC

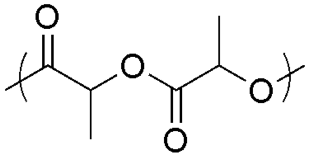


50% NorCMC + 50% CNFs



- Synergistic interactions between CNF and NorCMC network increase modulus
- Can be tuned to different stiffness for desired application

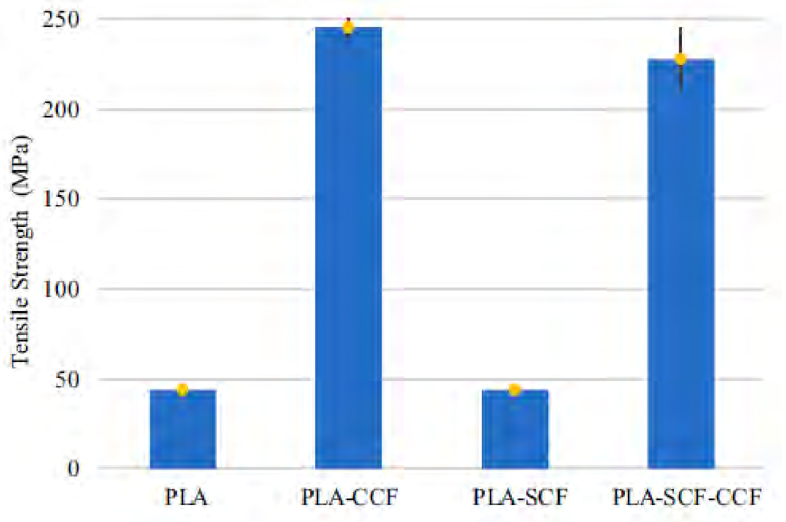
Strengthening PLA with CNFs



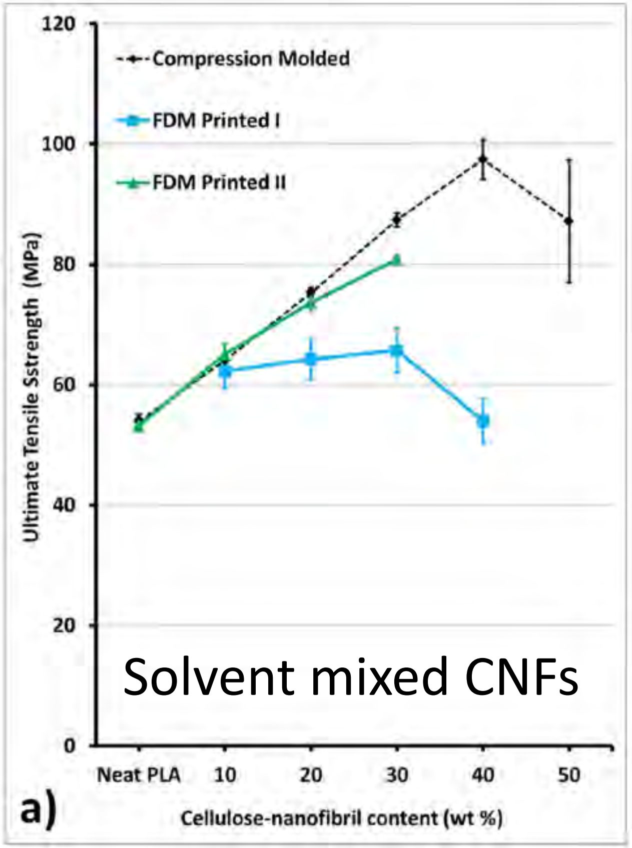
Polylactide

Disposable items

Solvent mixed carbon fibers



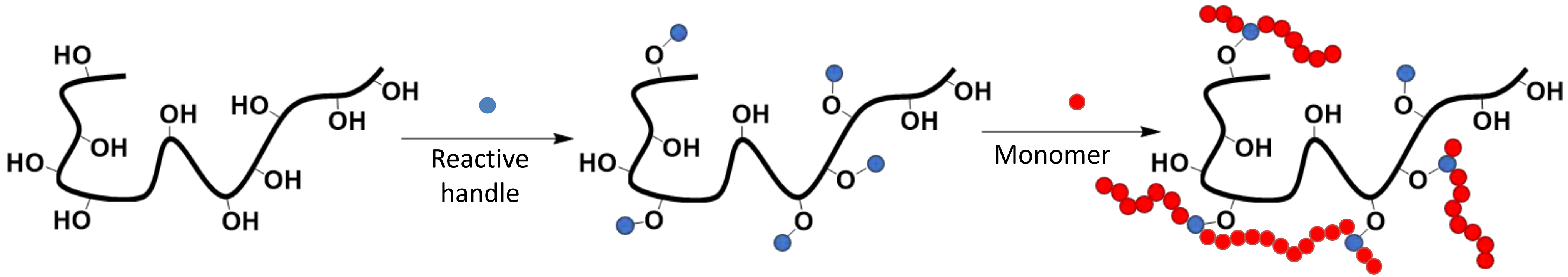
Rimasauskas et al. Composites Part C 2021

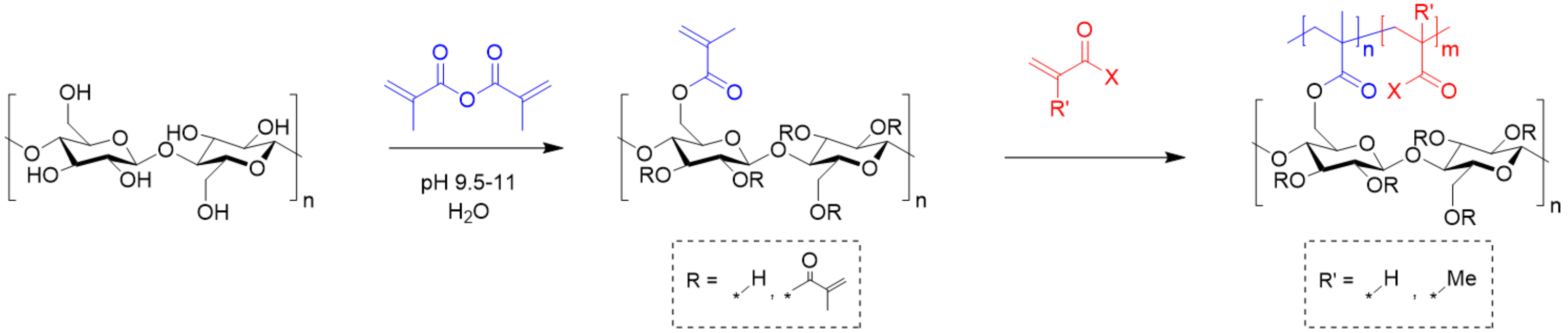


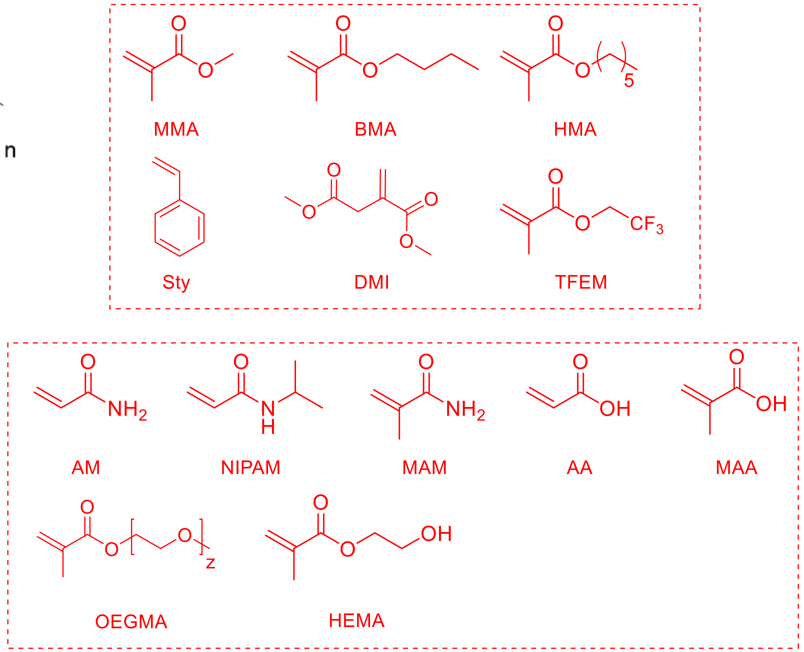
Tekinalp et al. Composites Part B 2019

- Polylactide or poly(lactic acid) (PLA) is renewably sourced
- Requires reinforcement for durable goods applications
- Incorporate fibers and fibrils without solvent casting

Grafting-through polymerization



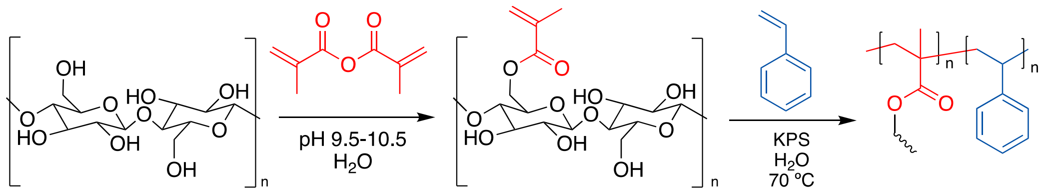




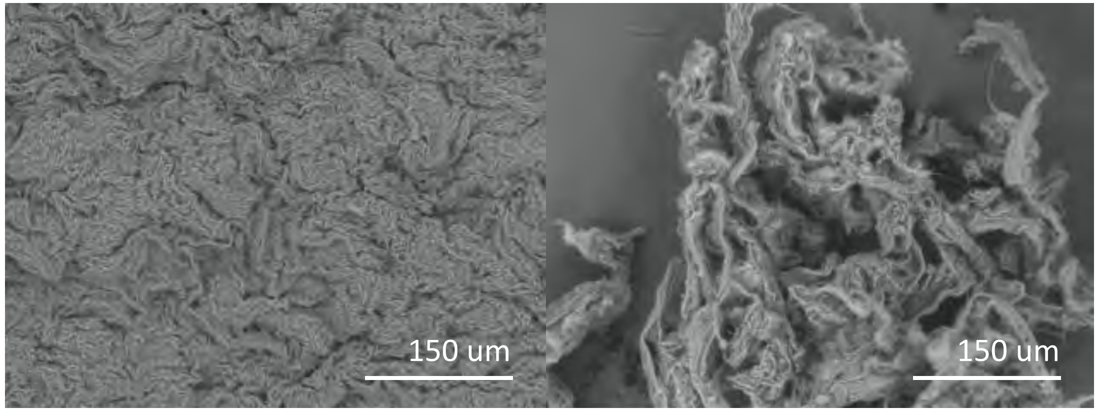
- Works on wood, pulp, CNF, wheat straw, flax, etc.
- Hydrophobic and hydrophilic monomers can be attached
- Can tune to polymer matrix

Kelly et al. Macromolecular Rapid Communications 2021

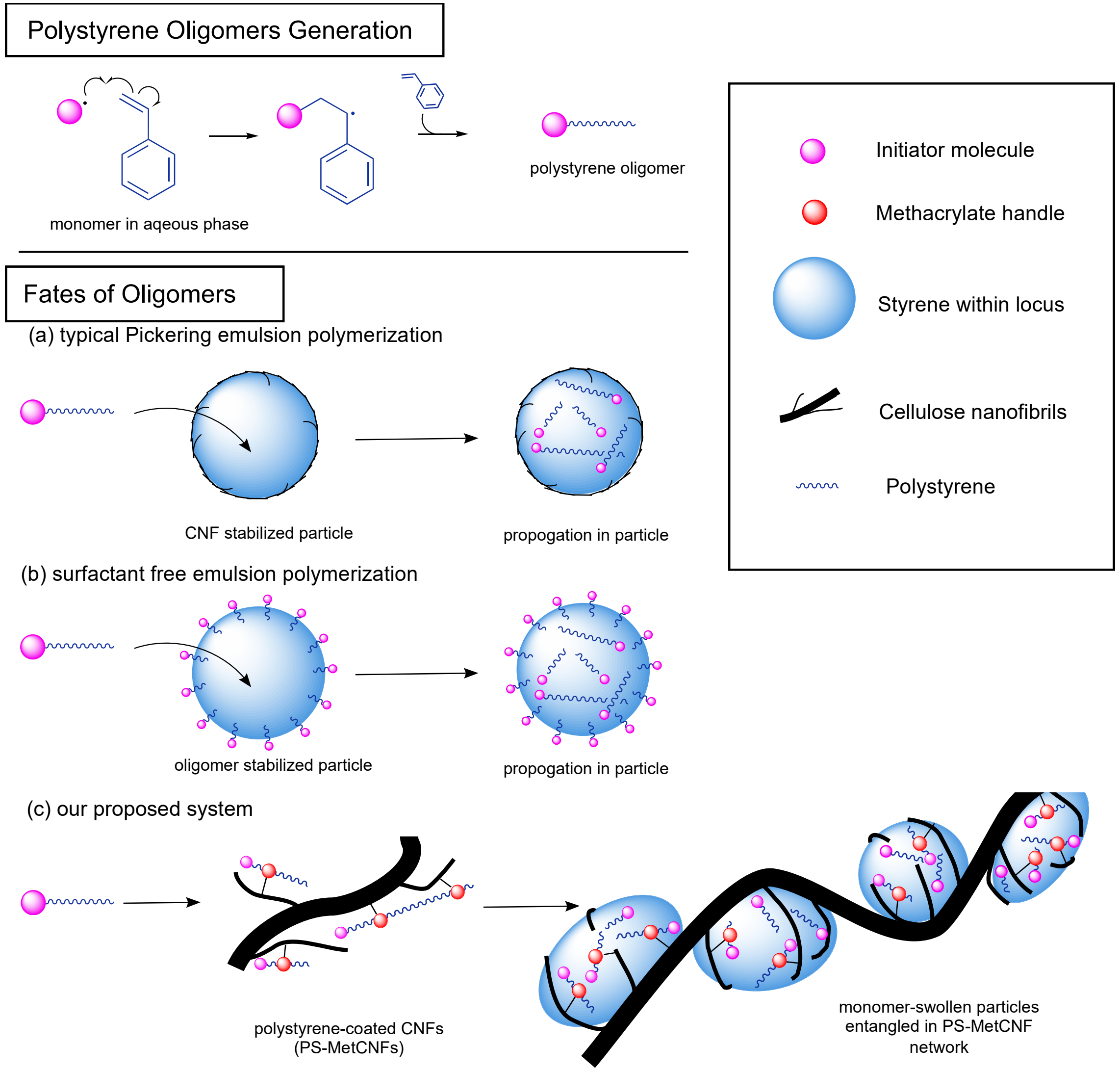
Surfactant free-emulsion polymerization



Unmodified CNF | PS-CNF



- Hydrophobic monomers can retain fibril morphology oven drying
- Complex emulsion behavior



Driscoll and Gramlich Langmuir 2023

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Creating and testing PLA reinforcements

Aqueous Modification

Drying

Dried Powder

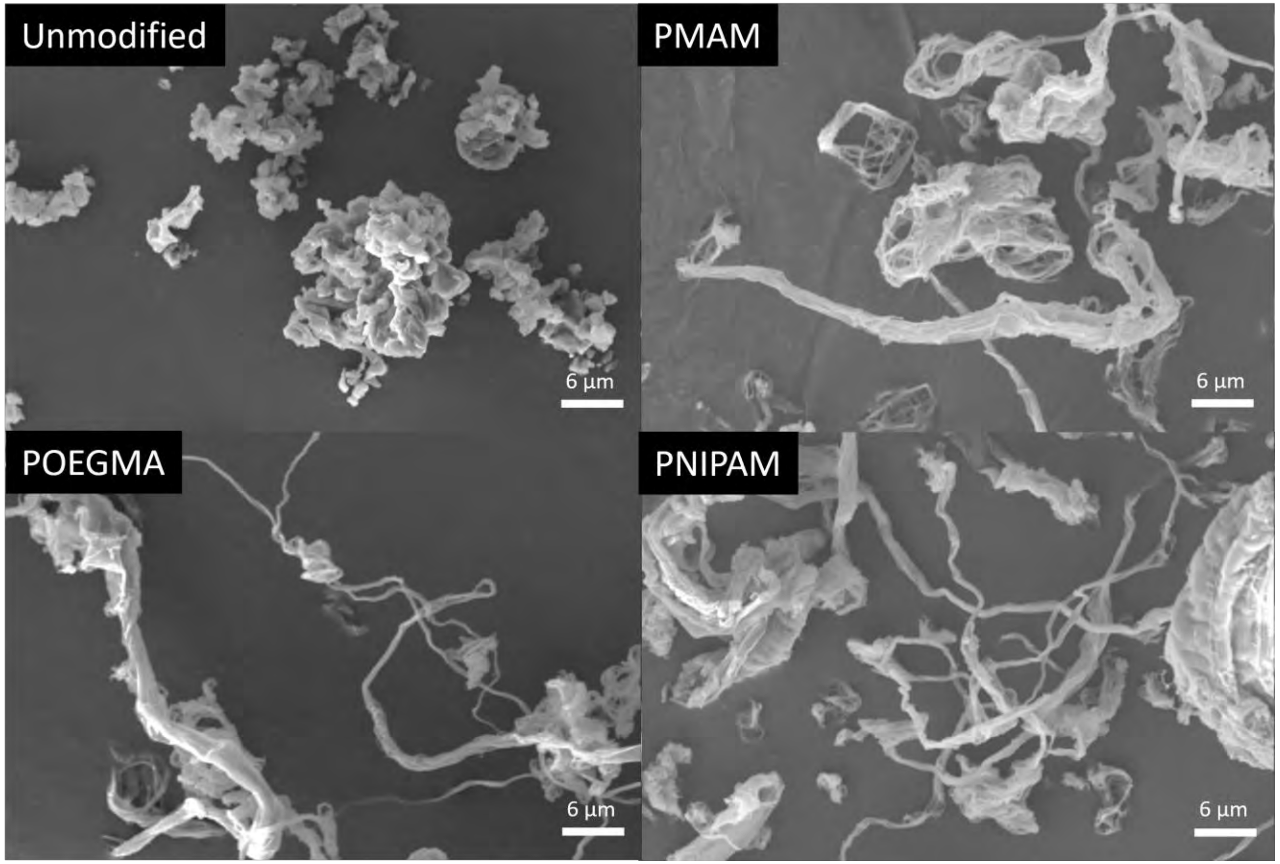
Melt Mixing

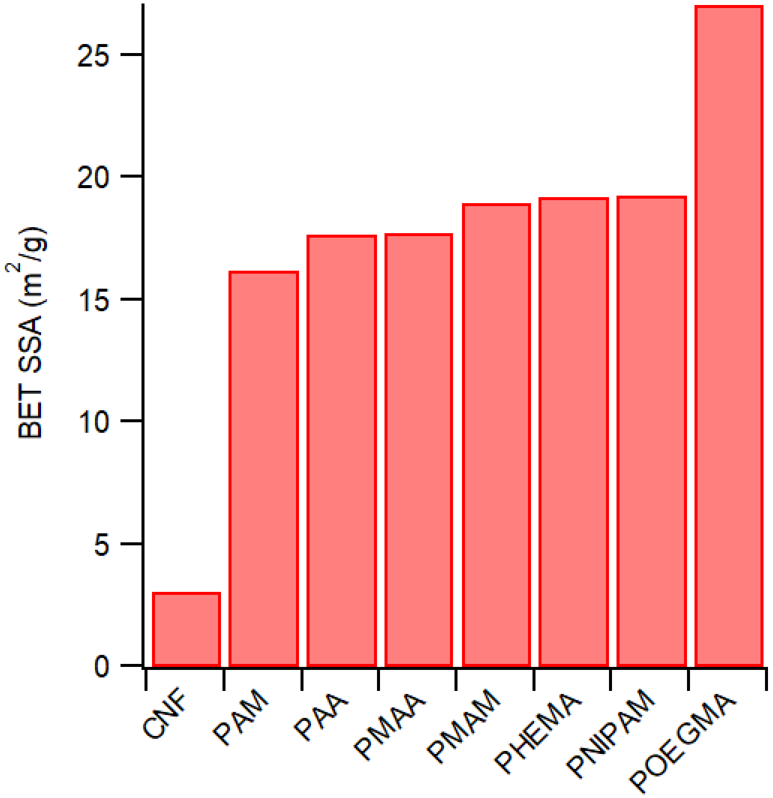
Composite

- Water soluble polymers can be used to create reinforcements
- Understand how polymer coating affects spray drying process
- Understand how polymer coating affects composite properties

Kelly et al. ACS Applied Polymer Materials 2023

Polymer modification prevents aggregation

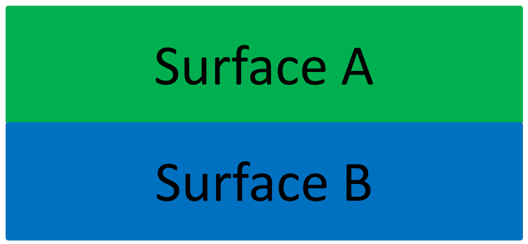




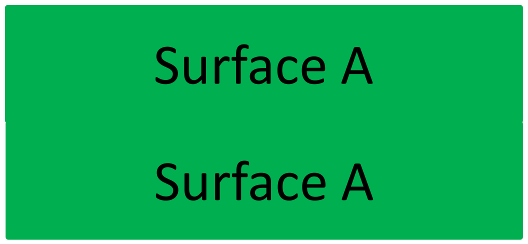
- Polymer coating blocks hydrogen bonding
- Increased surface area

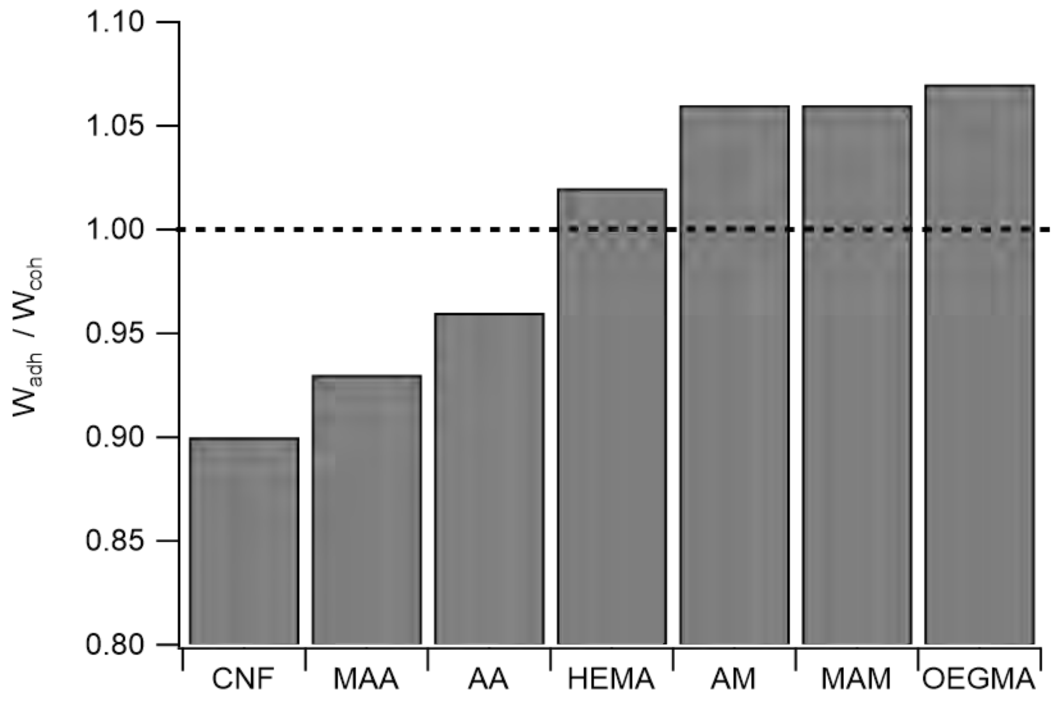
Kelly et al. ACS Applied Polymer Materials 2023

Surface energy analysis for targeted modifications



$$cos\ prefered\ 1 < \frac{W_{adh}}{W_{coh}} < 1\ adh\ prefered$$

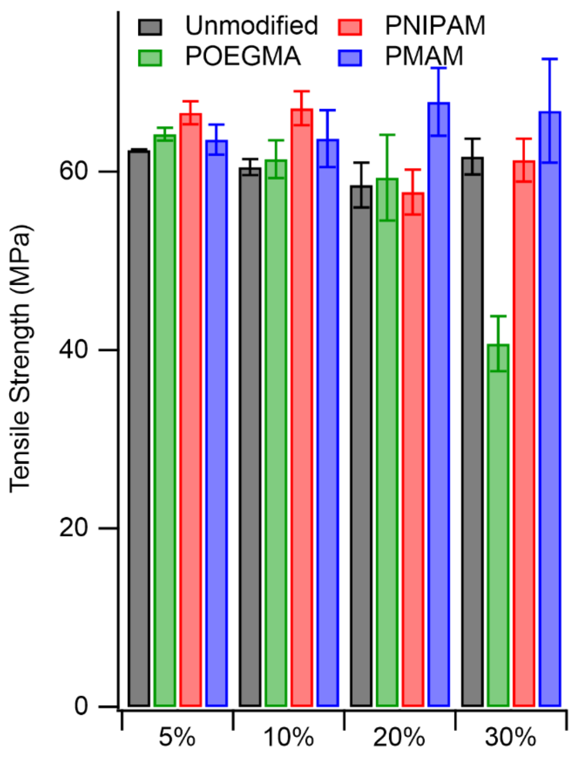


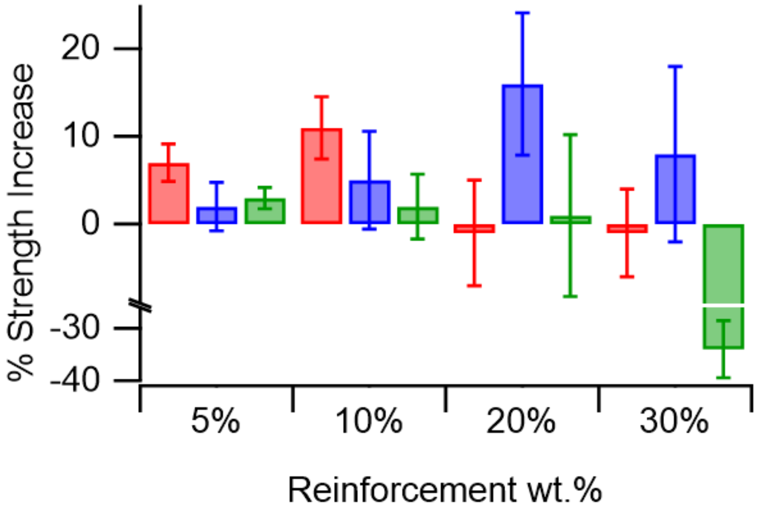


- Work of cohesion reduced after modification
- NIPAM could not be measured
- Targeted three modifications for compounding

Kelly et al. ACS Applied Polymer Materials 2023

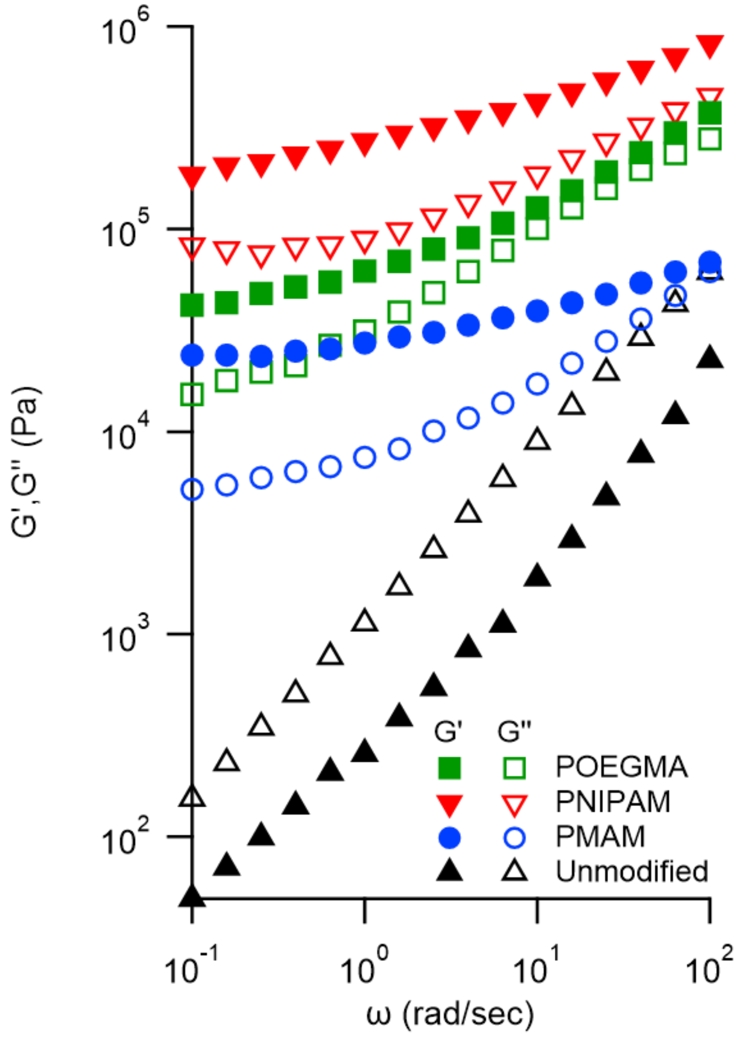
Improved composite properties





PLA composites

- PNIPAM and PMAM improved strength
- POEGMA plasticized the PLA and reduced strength
- Elastic response in melt



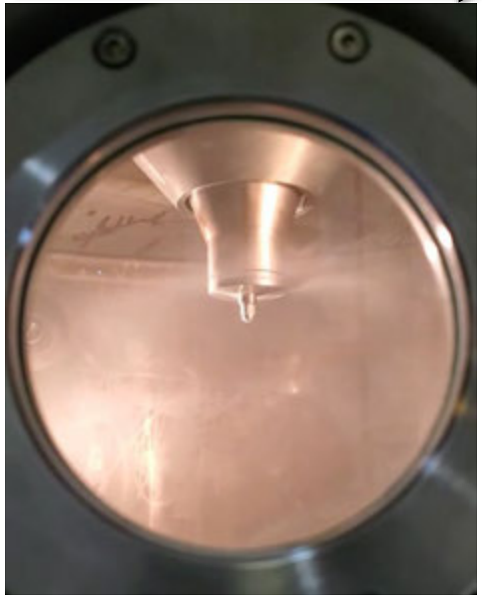
Rheology

Kelly et al. ACS Applied Polymer Materials 2023

Increasing to pilot scale

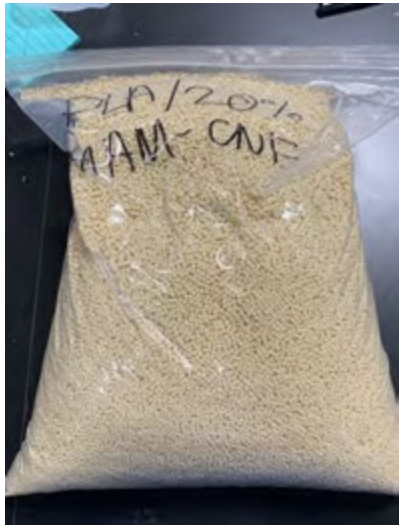
Aqueous Modification

Drying



Dried Powder

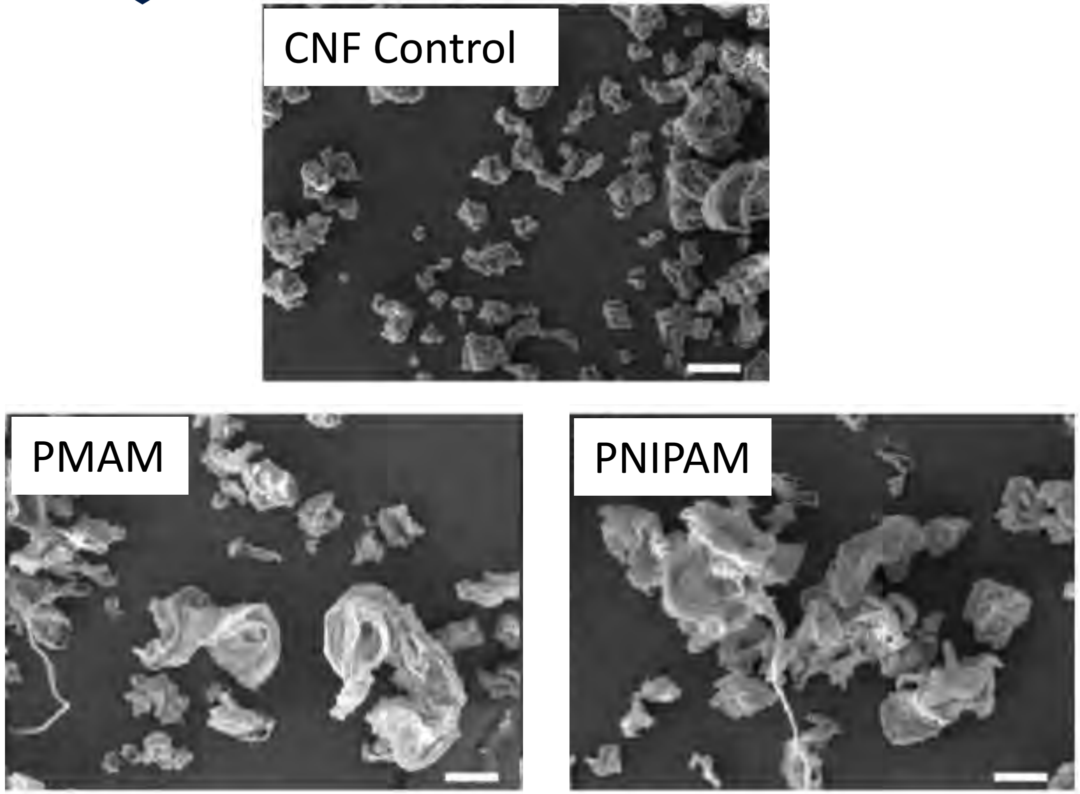
Melt Mixing



Composite

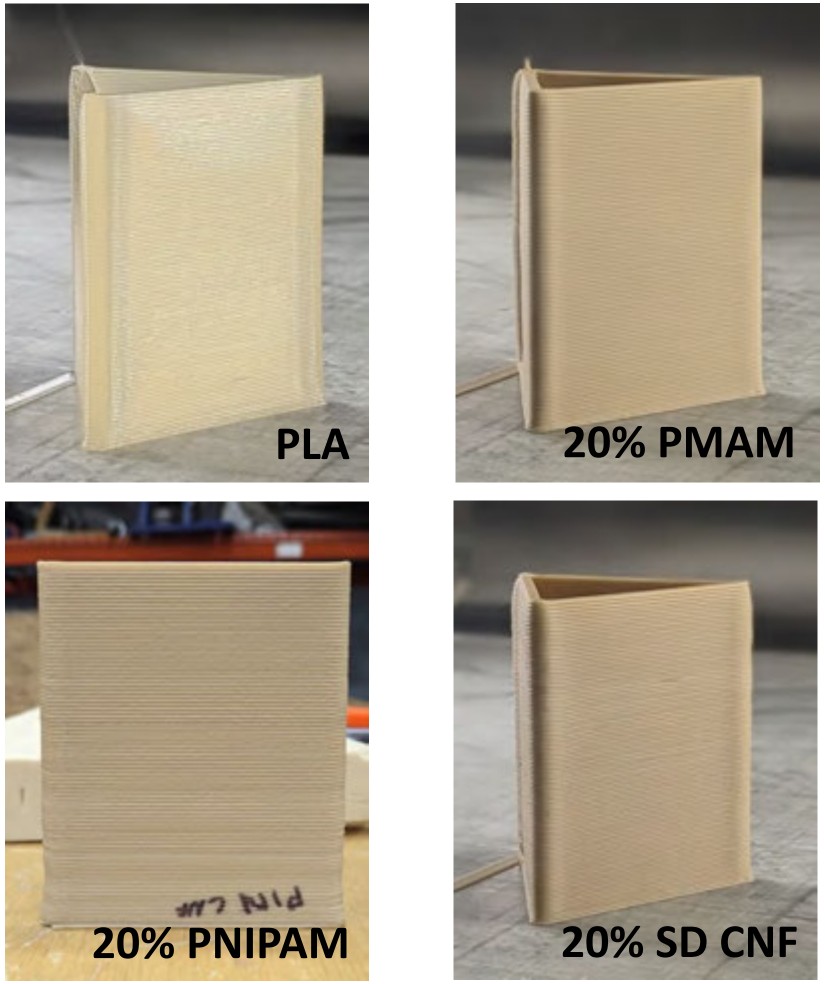
- Created nearly a kilogram of reinforcement
- Compound at 20 wt% reinforcement

Creating composites for printing



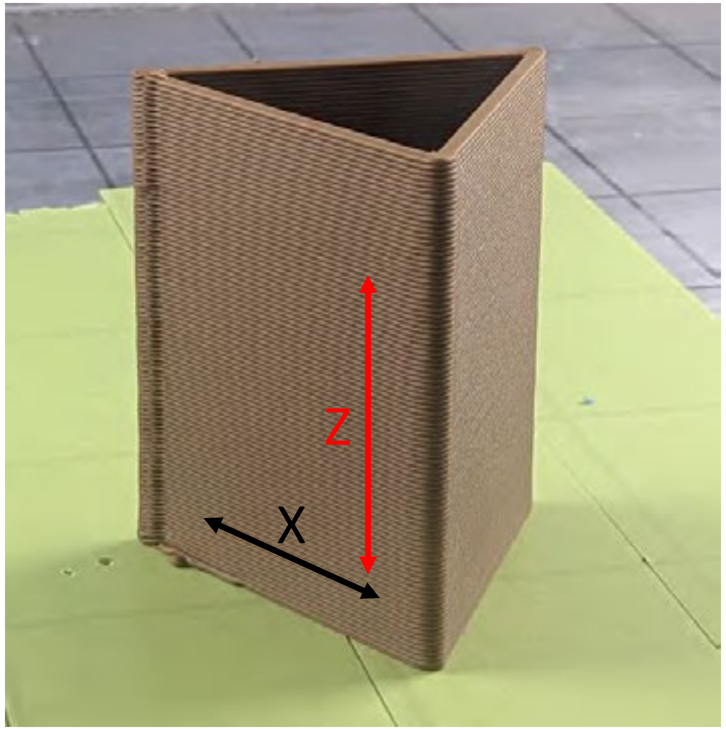
Scale bar = 6 µm

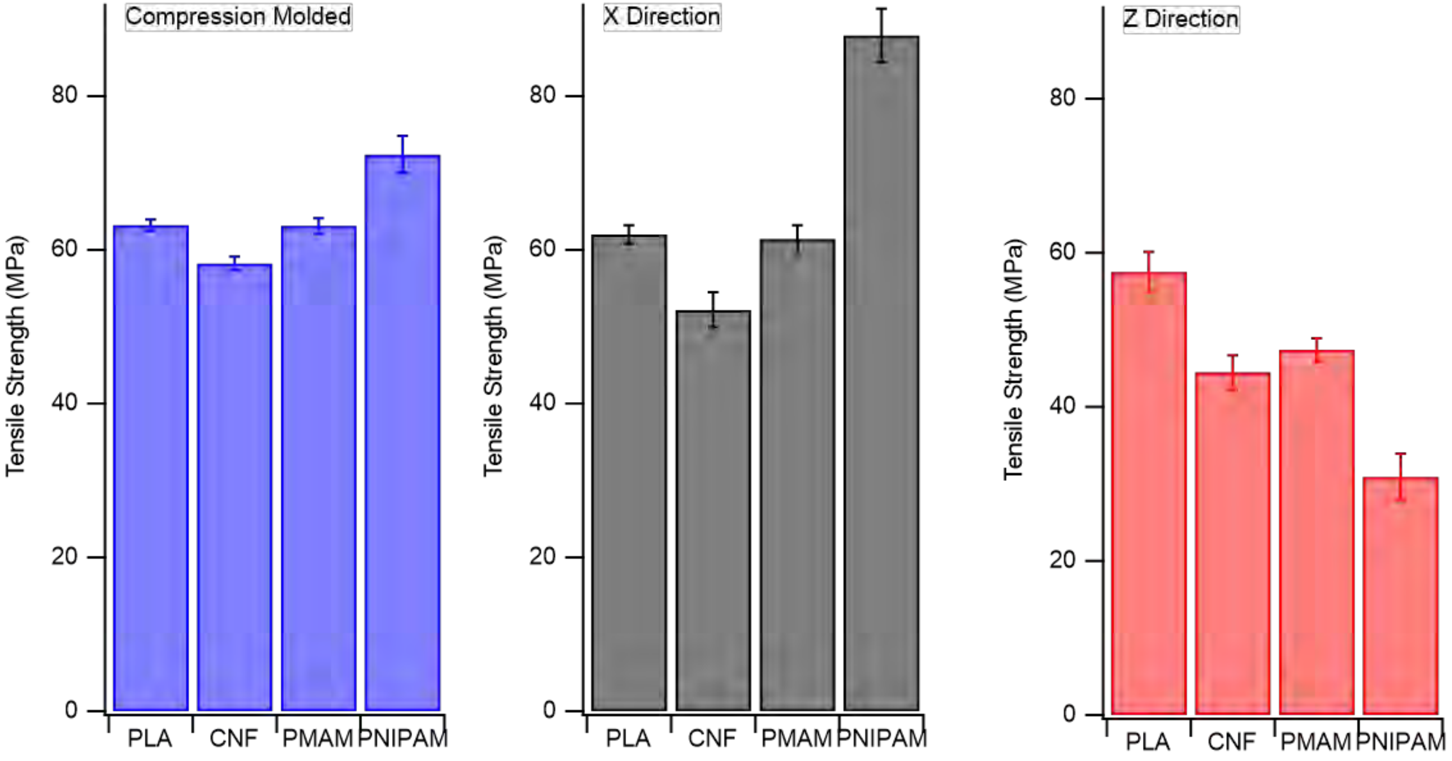

3D Print



- Pilot spray drying gives different morphology
- Can be compounded and printed

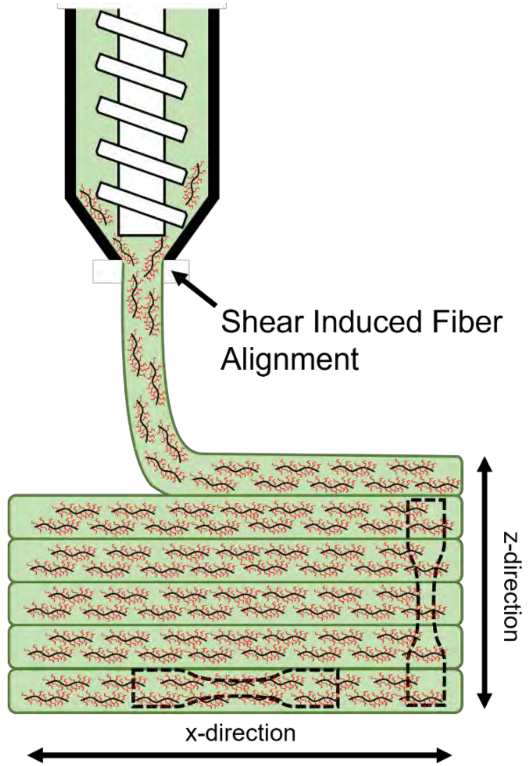
Significant strength improvements

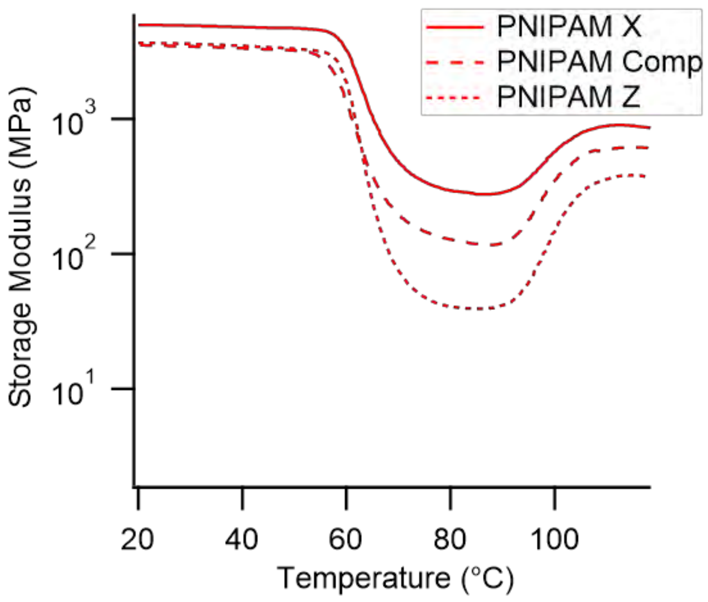


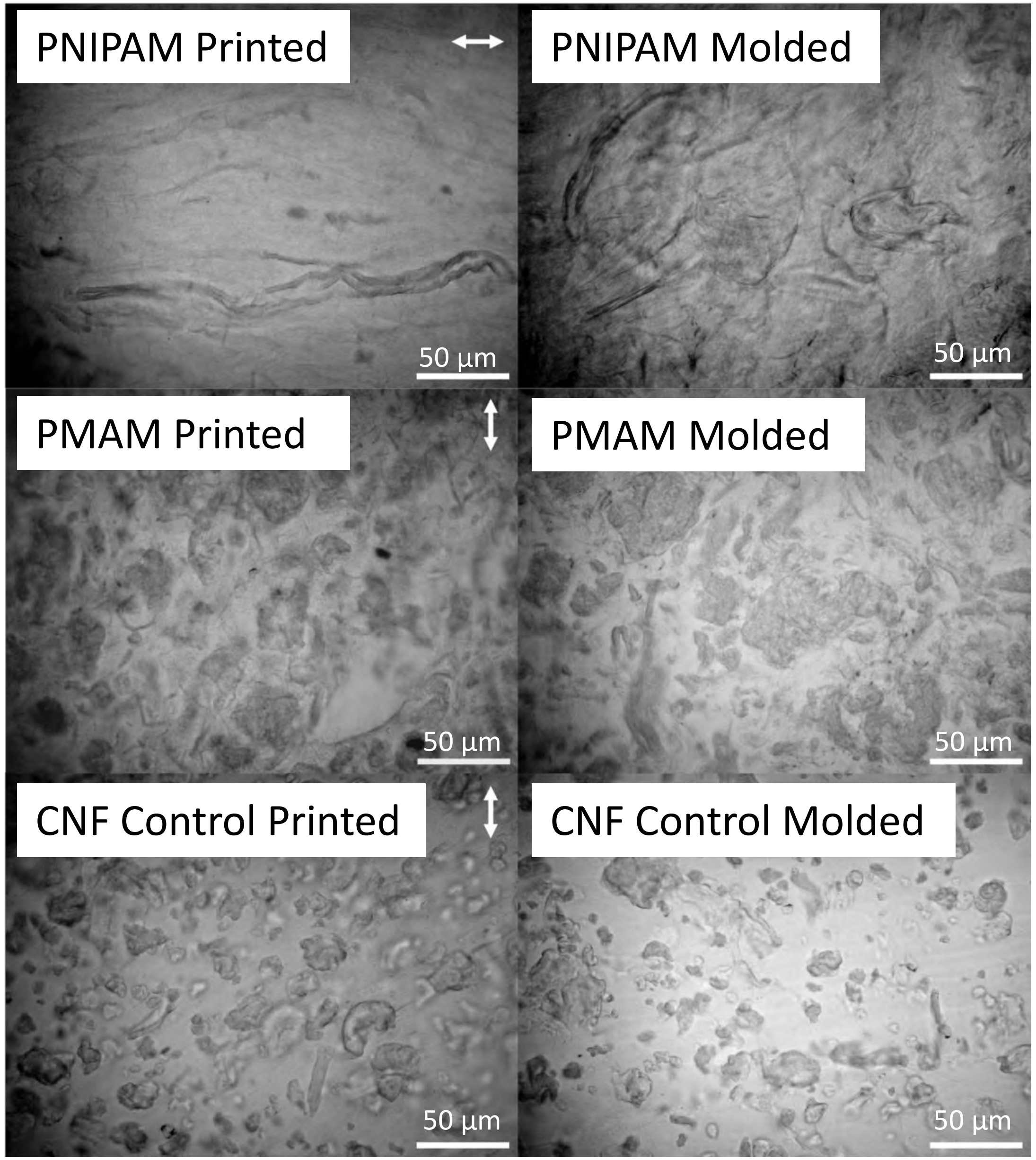


- Potential alignment of fibers or fibrils in print direction

Printing aligns fibers for PNIPAM modified



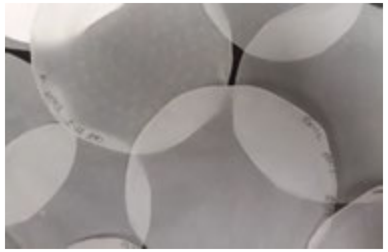




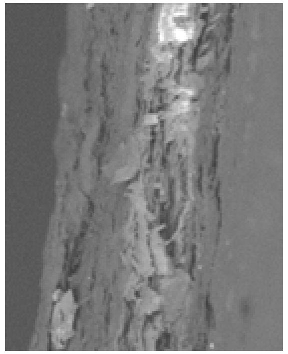
- Shear aligns fibers
- PNIPAM surface chemistry enables interactions with matrix
- Tune surface energy for new thermoplastics

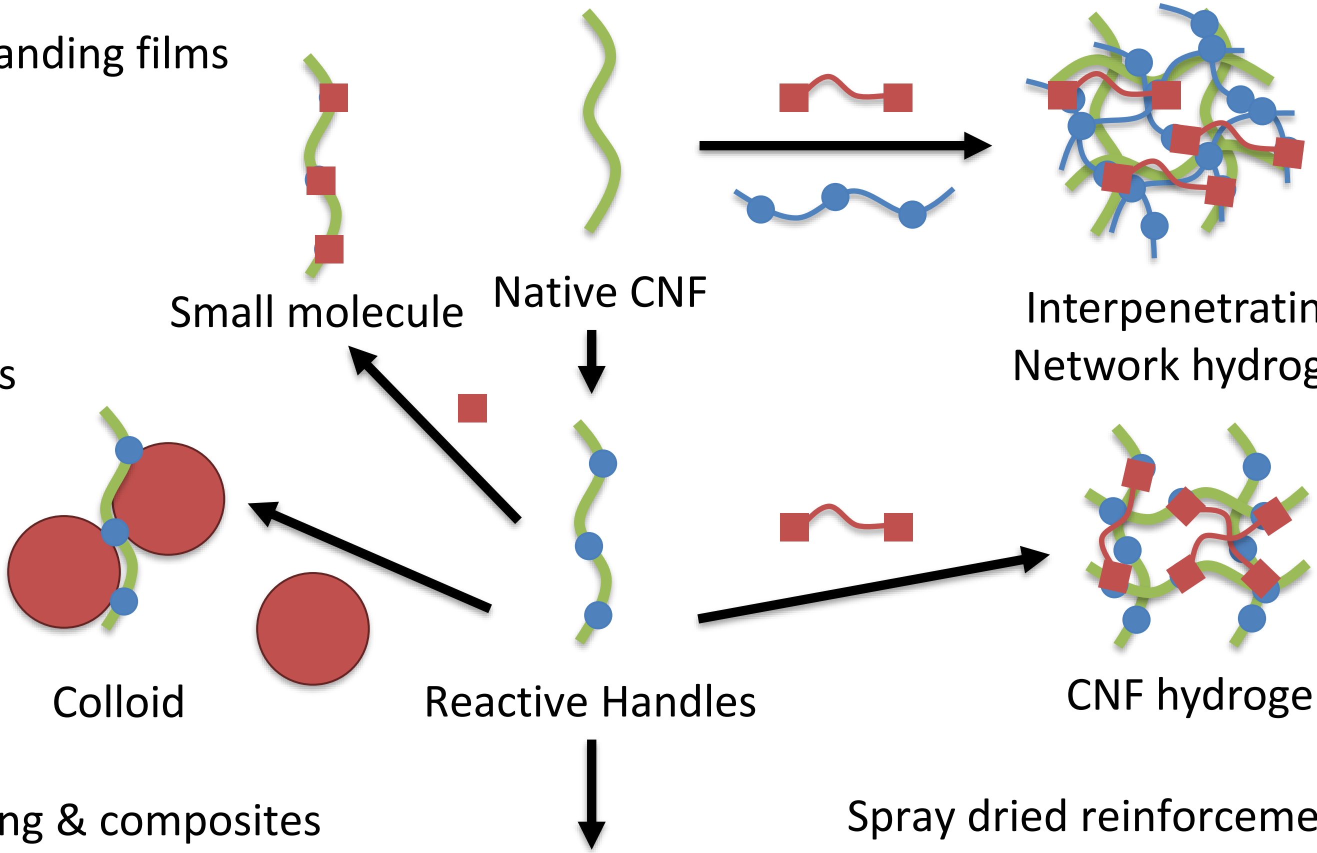
Conclusions

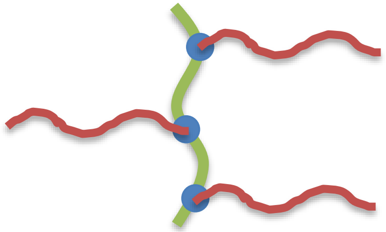
Rheology modification & free-standing films



Hydrophobicity & paper coatings

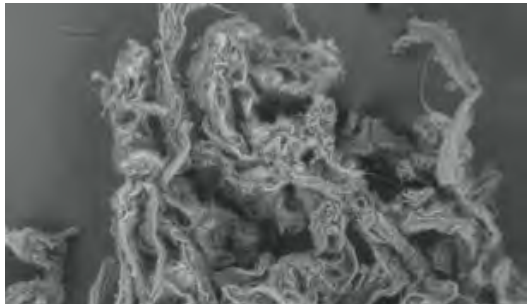






Stiffness control & biomaterial hydrogels

Retaining fibrils with air drying & composites



Spray dried reinforcements & strong composites

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Acknowledgements

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Current Gramlich Group

CNF Composites

Dr. Siamak Shams Es-haghi

Dr. Katie Coperhaver

Dr. Doug Gardner

Dr. Meghan Lamm

ADVANCED STRUCTURES & composites center

OAK RIDGE National Laboratory

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