

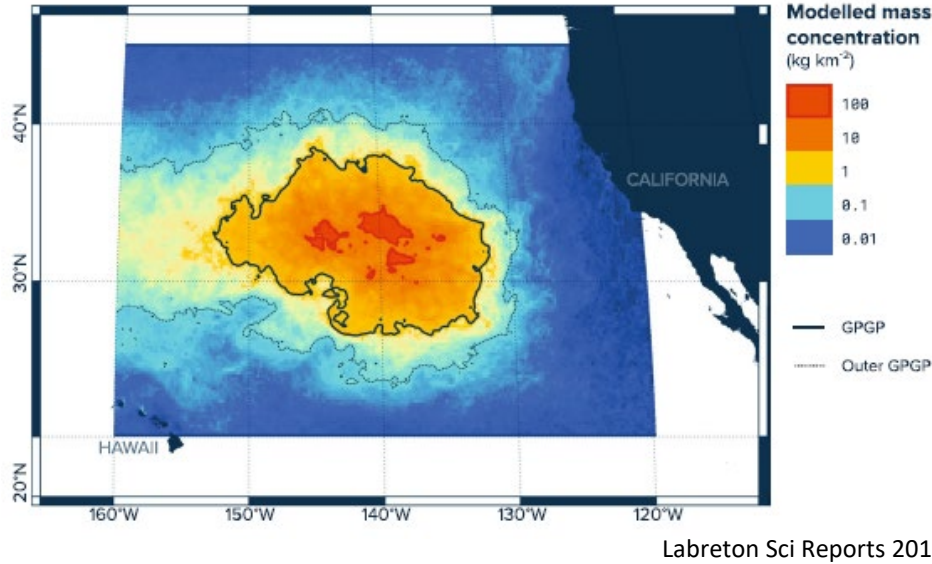
Aqueous polymer modifications to cellulose nanofibrils to create poly(lactic acid) composites

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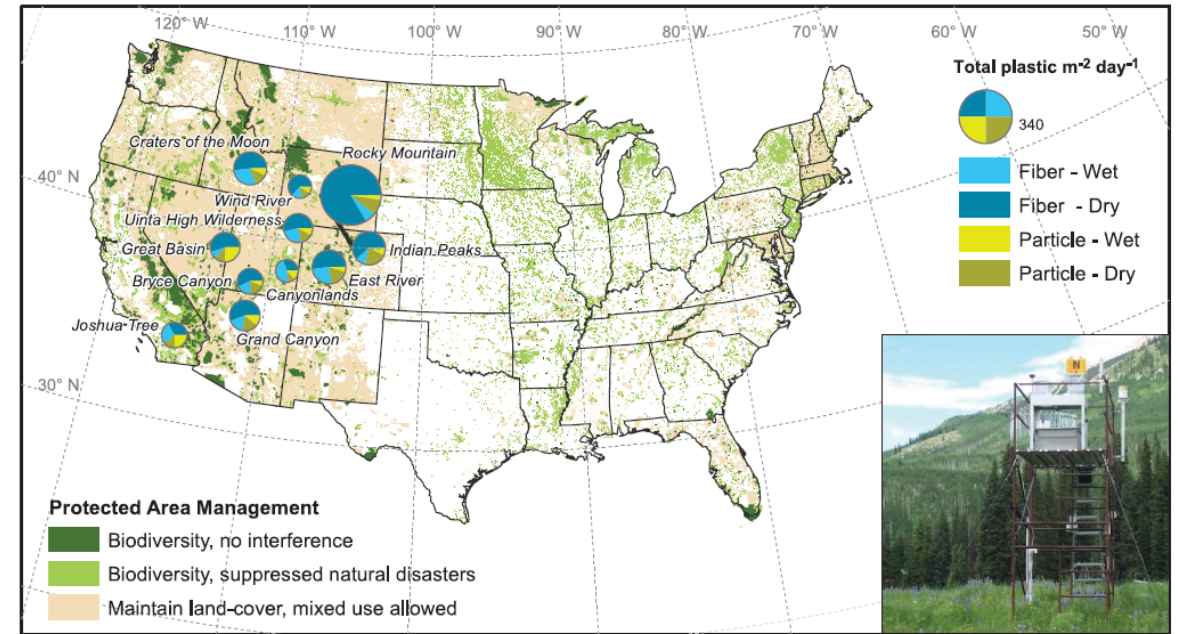
The Need for Sustainable Polymers

Great Pacific Garbage Patch (GPGP)



80,000 metric tons

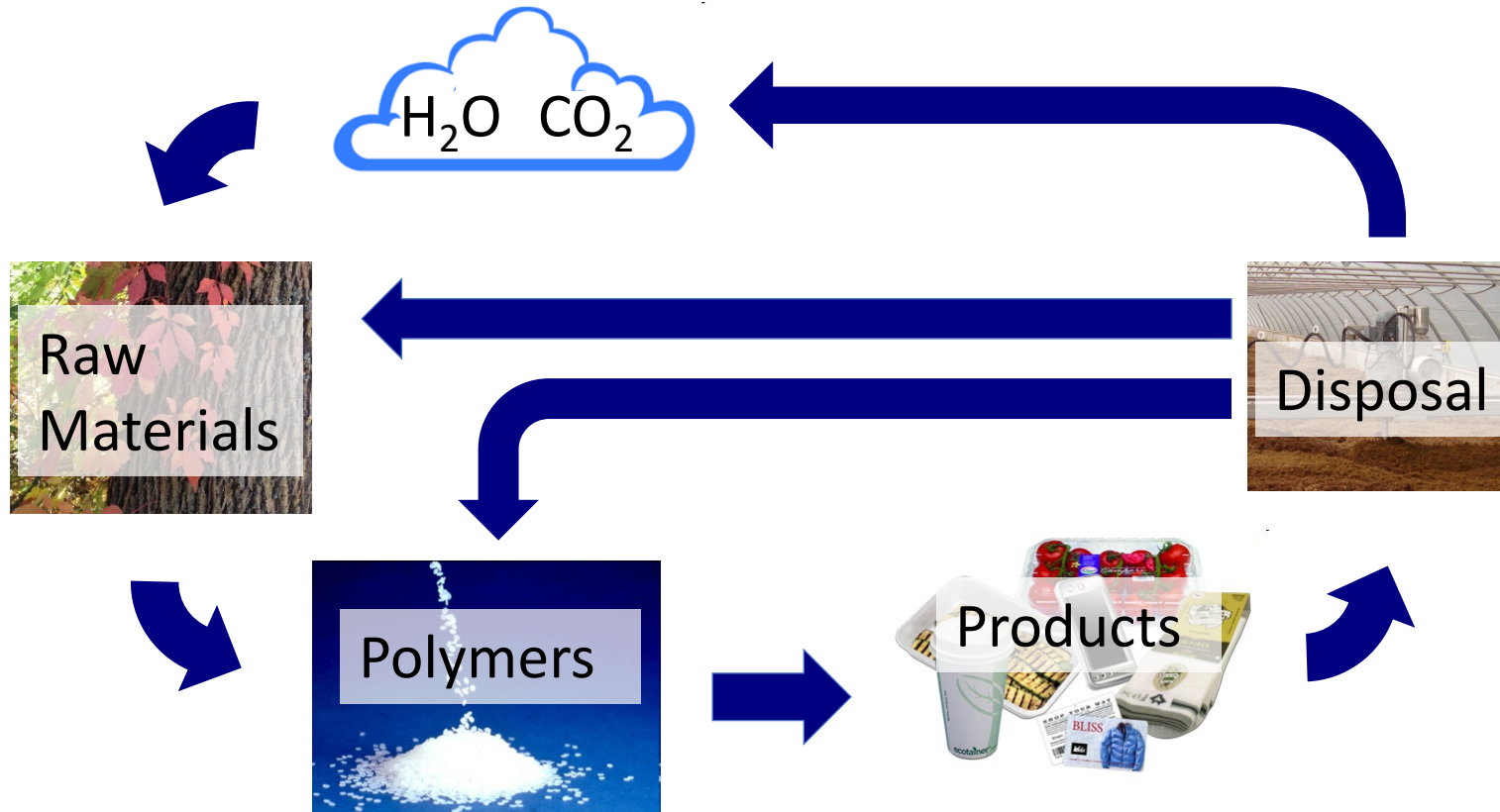
Fiber Deposition in National Parks



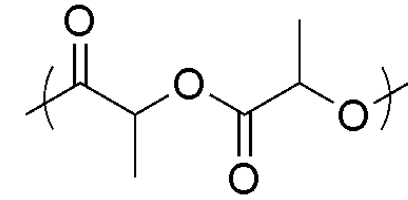
1,000 metric tons/year

- Accidental release into the environment is common
- Polymers do not readily degrade in the environment
- Unknown long-term effects

Replacing Petroleum Sourced Polymers



- Aiming to create sustainable polymers
- Poly(lactic acid) or polylactide (PLA) is renewably sourced
- Needs to be strengthened for durable goods applications

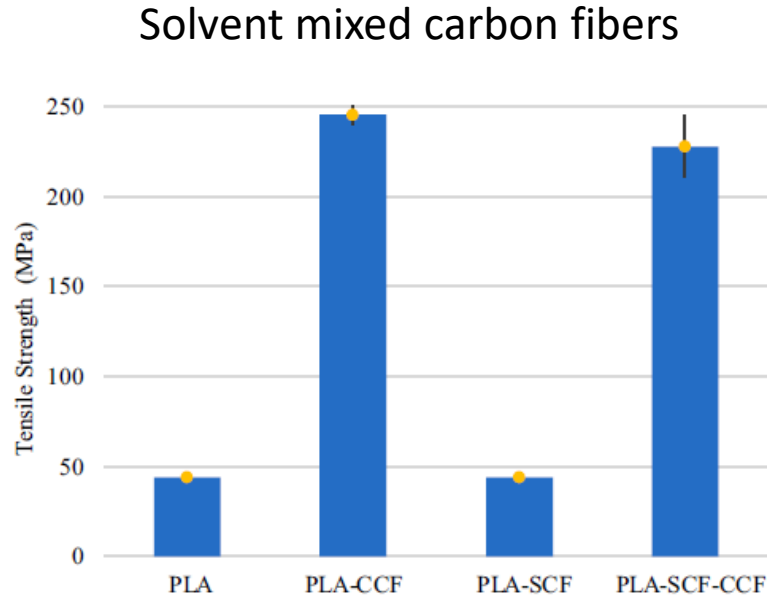


Polylactide



Disposable items

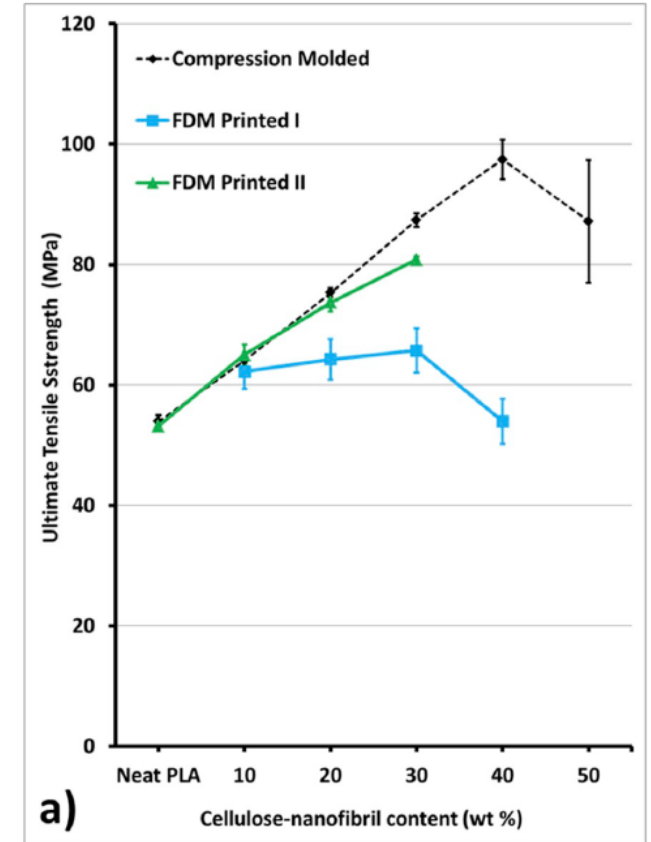
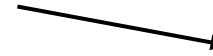
CNFs as reinforcement



Rimasauskas et al. Composites Part C 2021

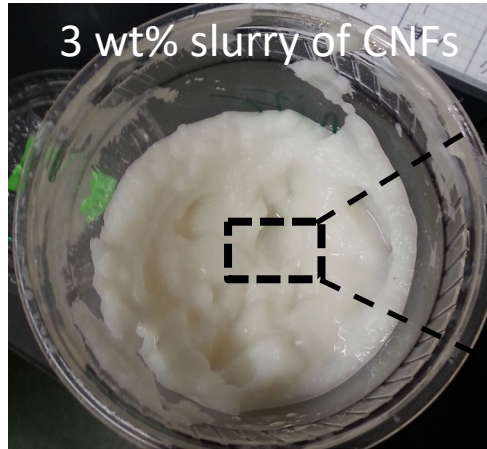
- Traditional reinforcements are non-degradable
- Cellulose nanofibrils (CNFs) can reinforce
- Need compatibilization for scalable melt blending

Solvent mixed CNFs

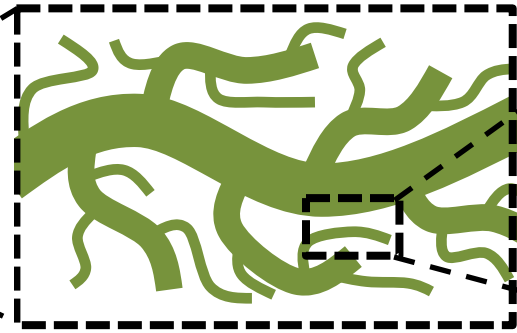


Tekinalp et al. Composites Part B 2019

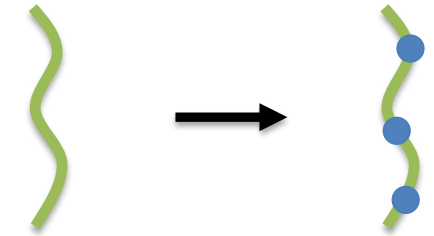
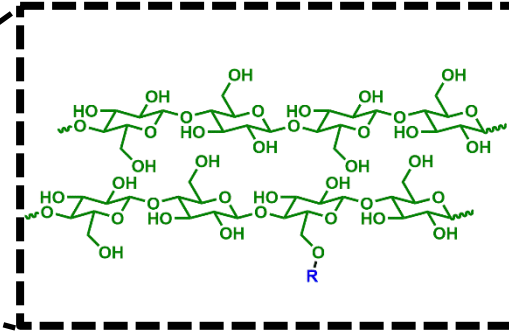
Modular modification of CNFs



3 wt% slurry of CNFs



Surface Modified CNF



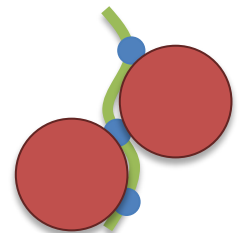
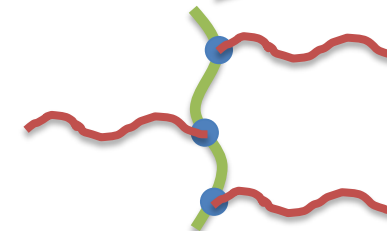
Native CNF

Reactive Handles

Small molecules

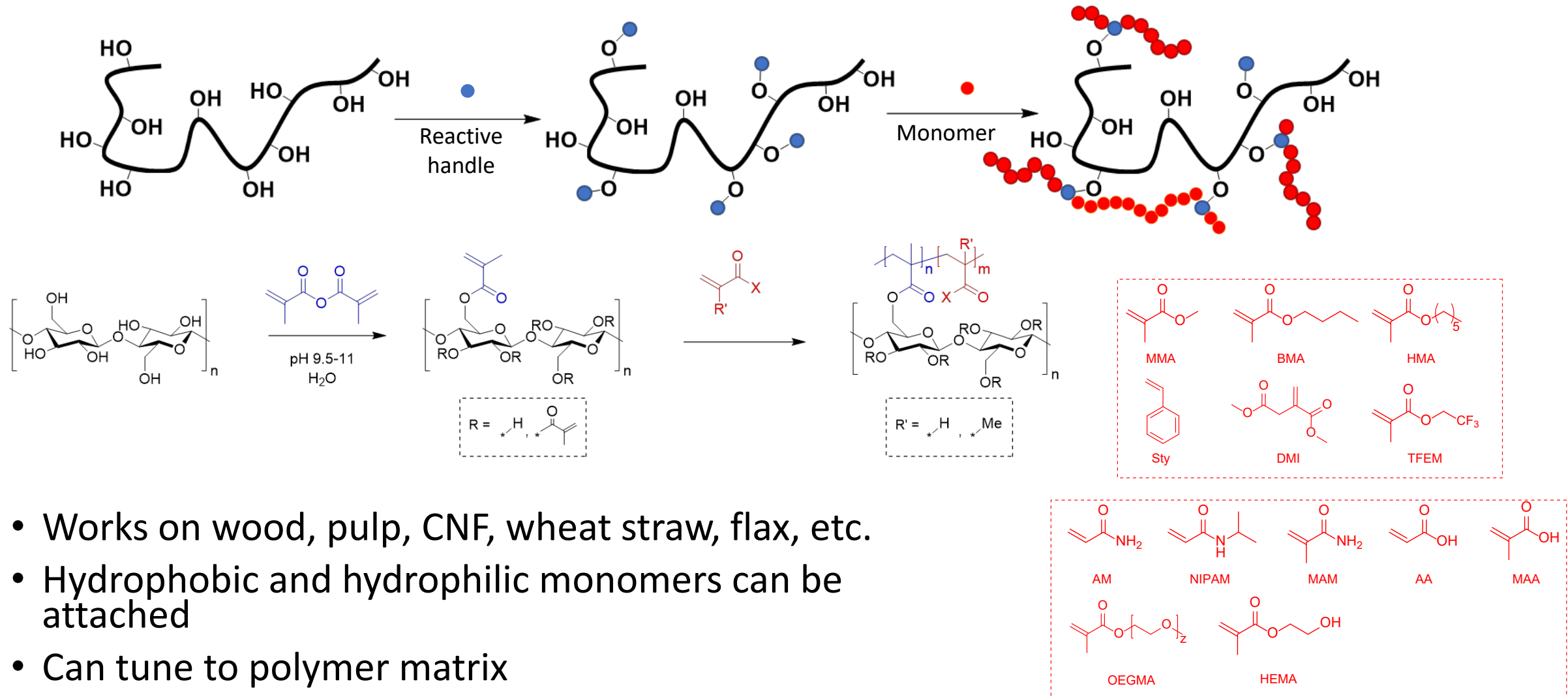
Polymers

Colloids



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

Grafting-through polymerization



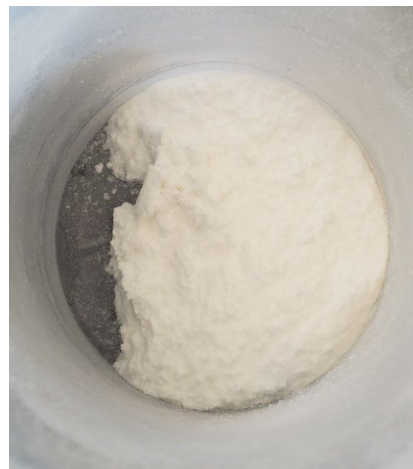
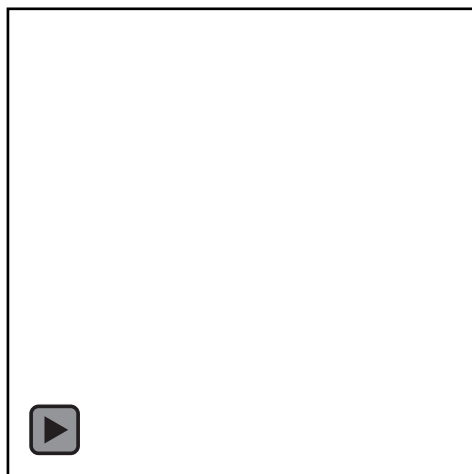
- Works on wood, pulp, CNF, wheat straw, flax, etc.
- Hydrophobic and hydrophilic monomers can be attached
- Can tune to polymer matrix

Creating and testing PLA reinforcements



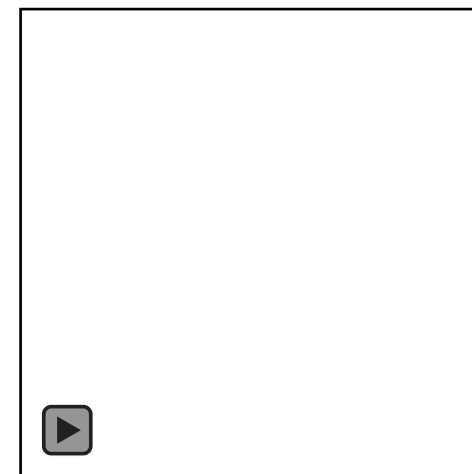
Aqueous Modification

Drying



Dried Powder

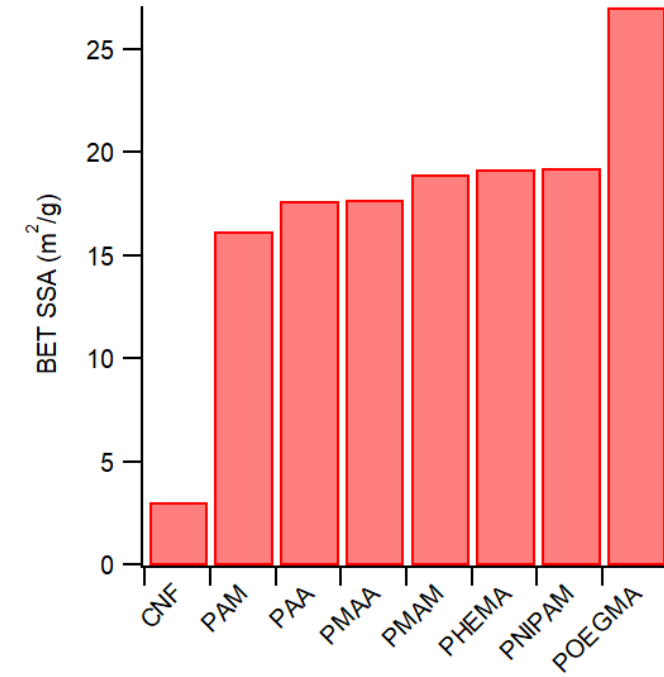
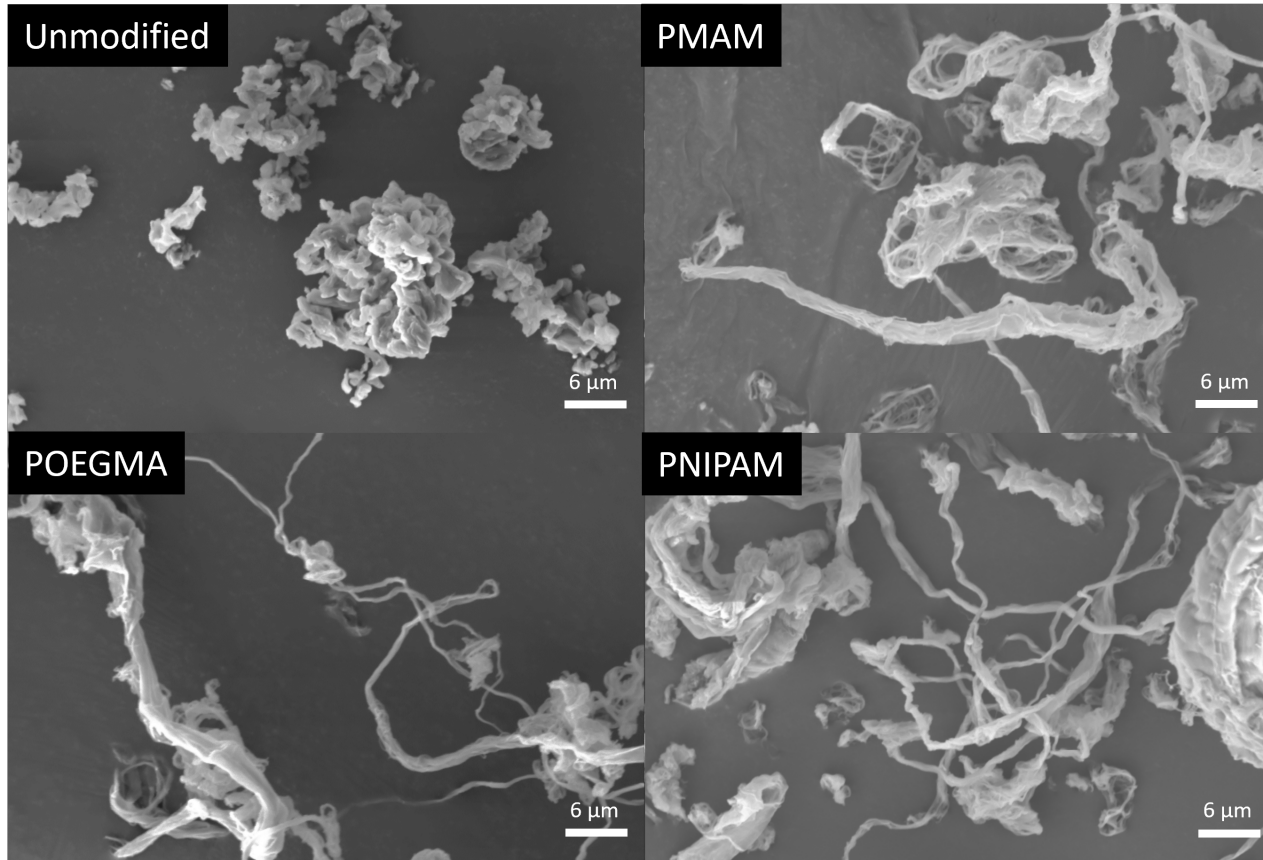
Melt Mixing



Composite

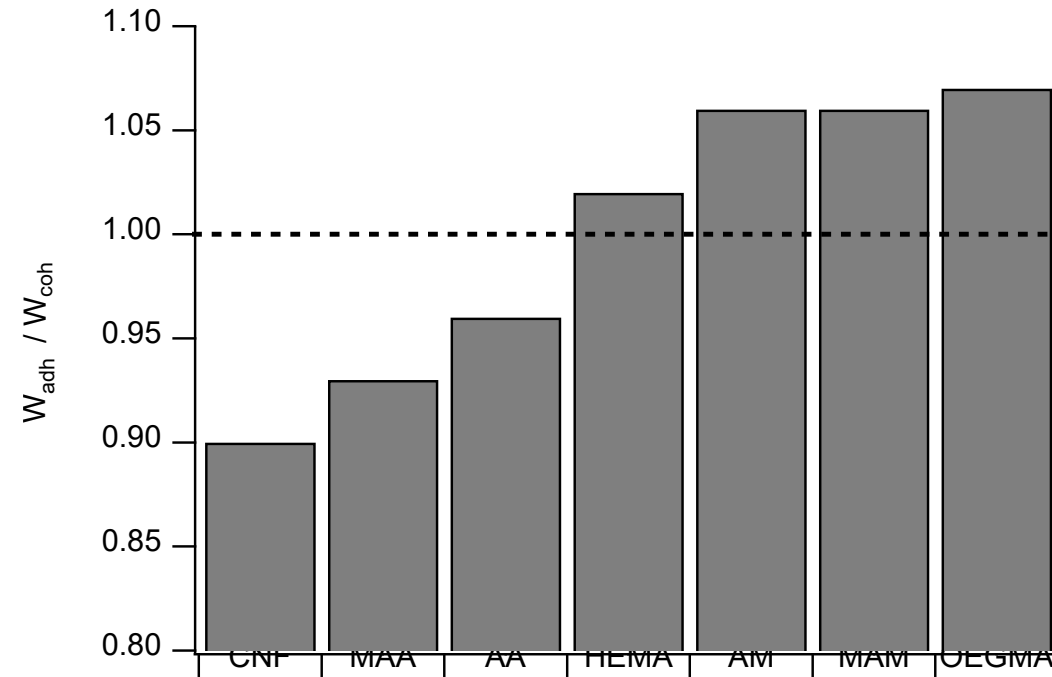
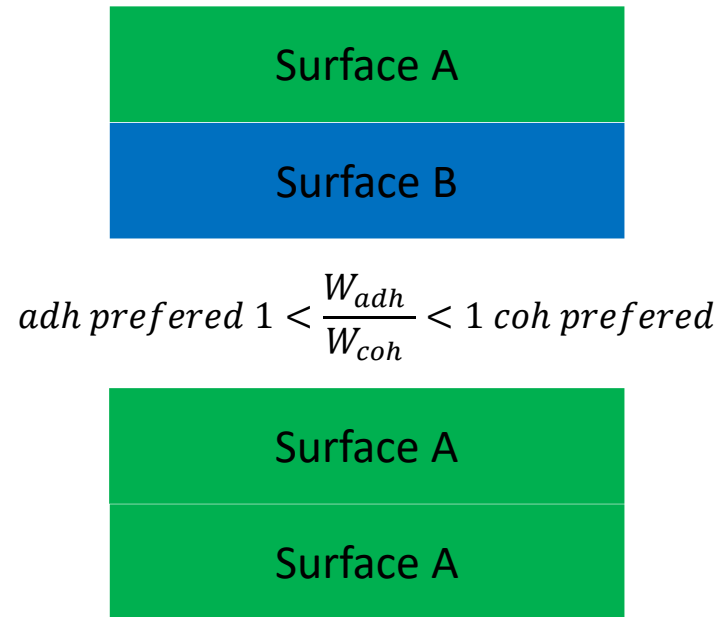
- Understand how polymer coating affects spray drying process
- Understand how polymer coating affects composite properties

Polymer modification prevents fibrillar aggregation



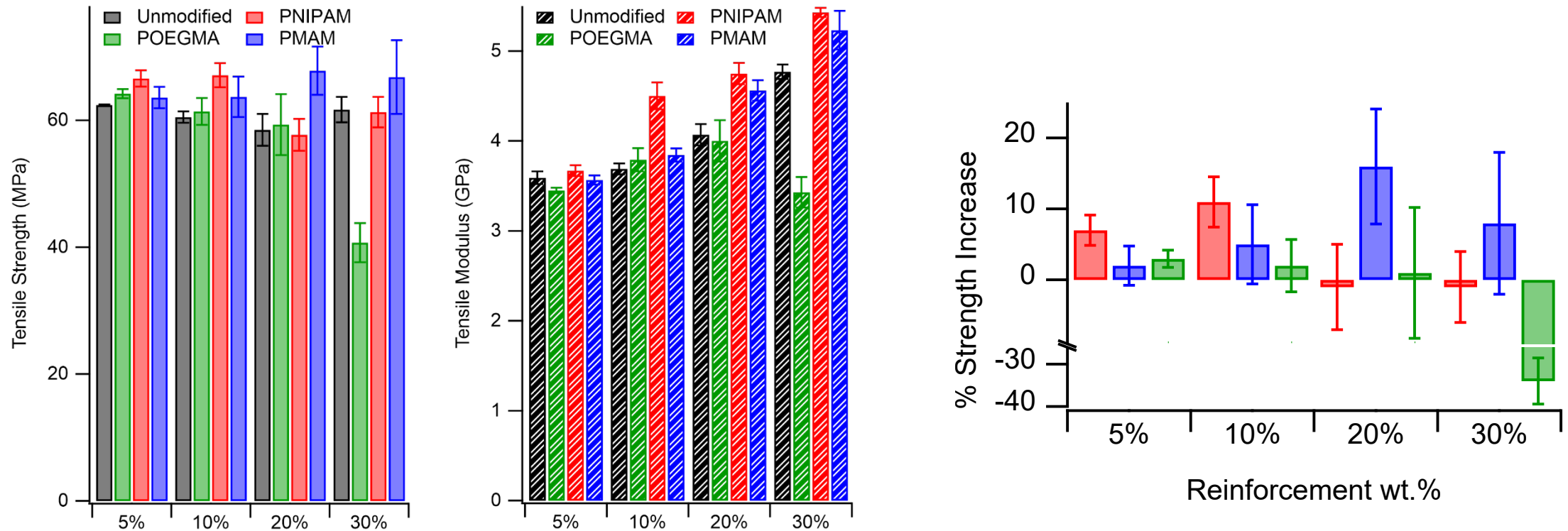
- Polymer coating blocks hydrogen bonding
- Increased surface area

Surface energy analysis suggests target modifications



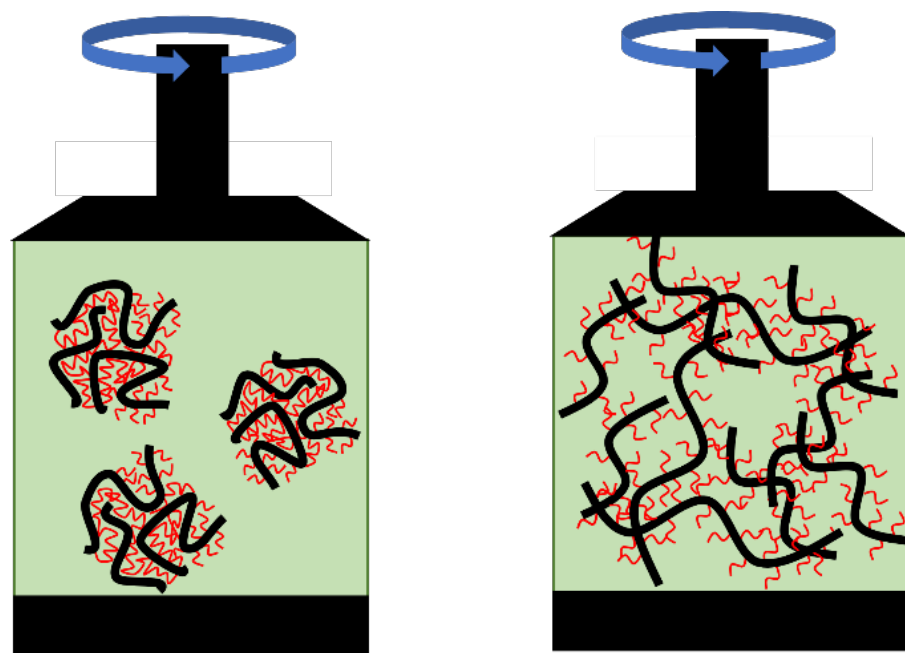
- Work of cohesion reduced after modification
- NIPAM could not be measured
- Targeted three modifications for compounding

Improved composite properties



- PNIPAM and PMAM improved strength
- POEGMA plasticized the PLA and reduced strength

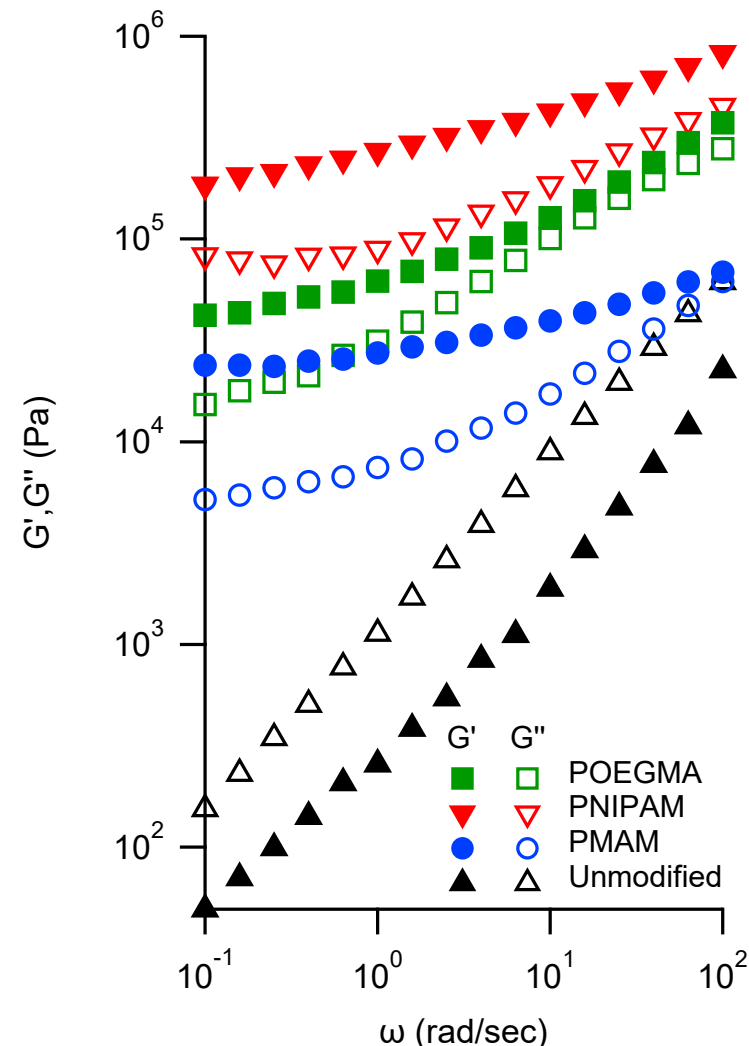
Rheology indicates improved dispersion



Poor dispersion

Good dispersion

- Modified materials give an elastic response in the melt

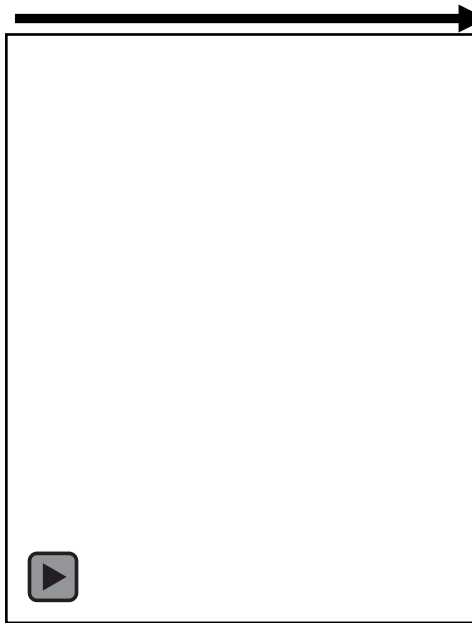


Scaling up to pilot scale



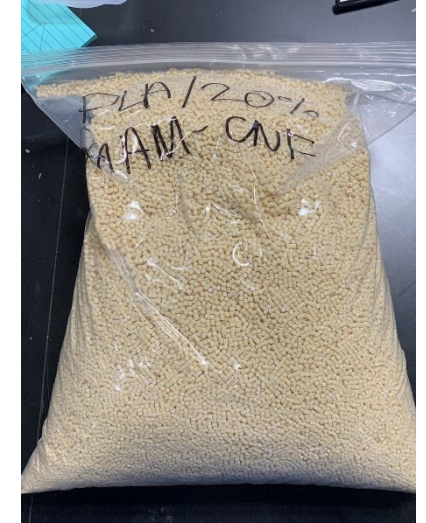
Aqueous Modification

Drying



Dried Powder

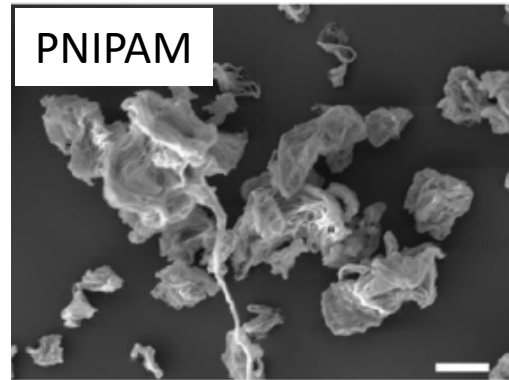
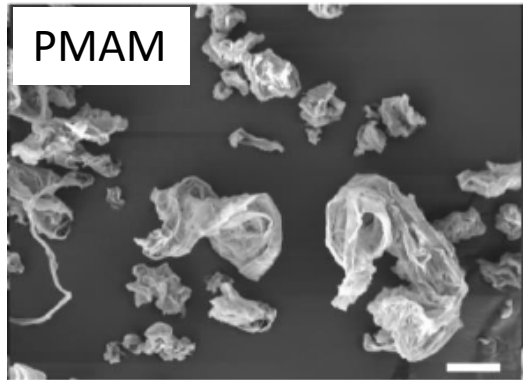
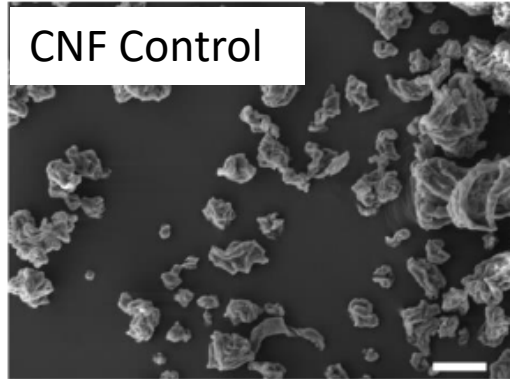
Melt Mixing



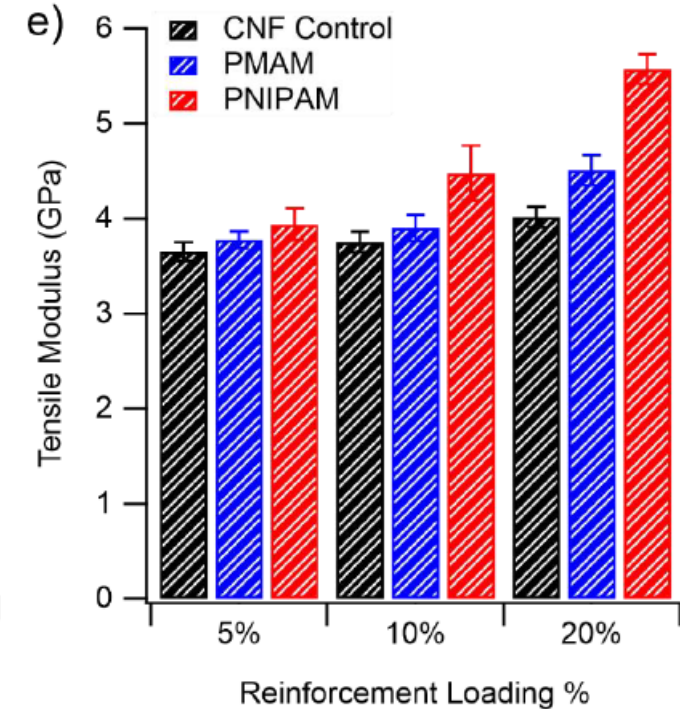
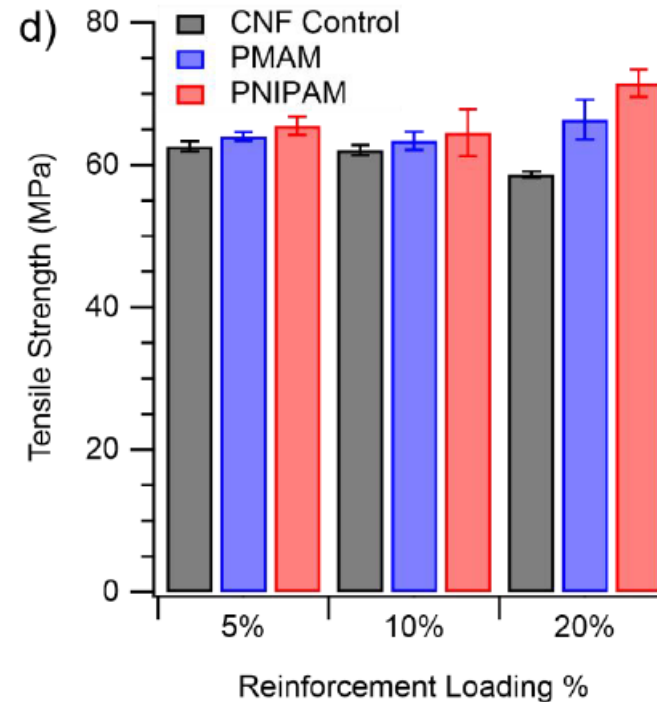
Composite

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

Pilot scale products give similar trends

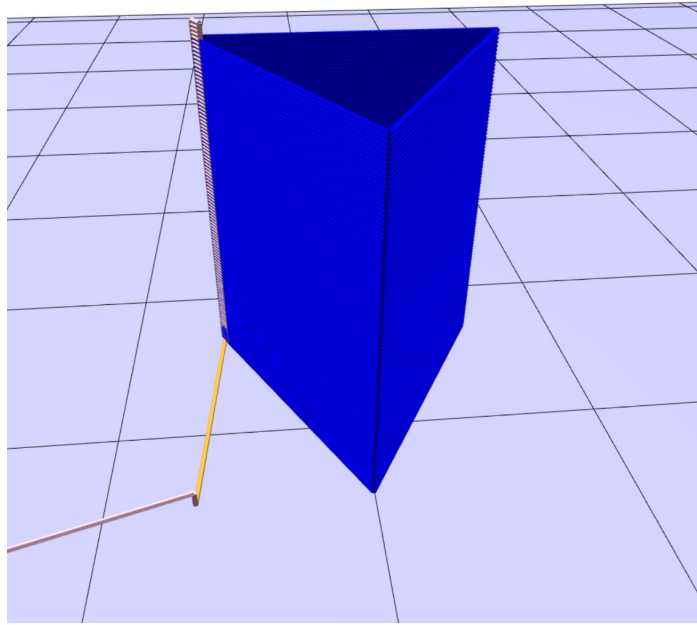


Scale bar = 6 μm



- Different spray drying gives different morphology
- Increase in mechanical properties over CNFs

3D Printing composites

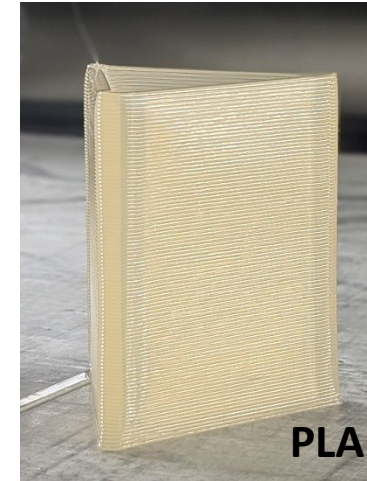


CAD



Print

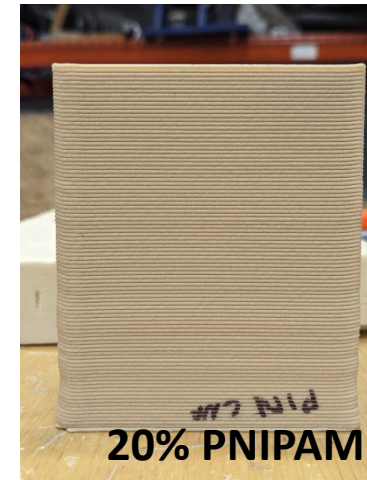
- Optimized parameters to yield consistent bead height



PLA



20% PMAM



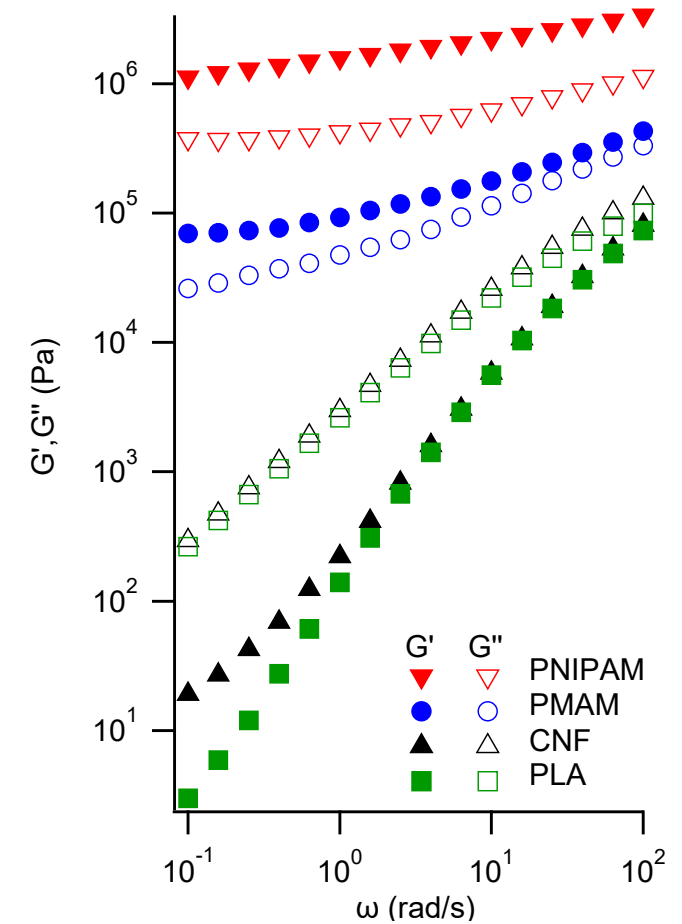
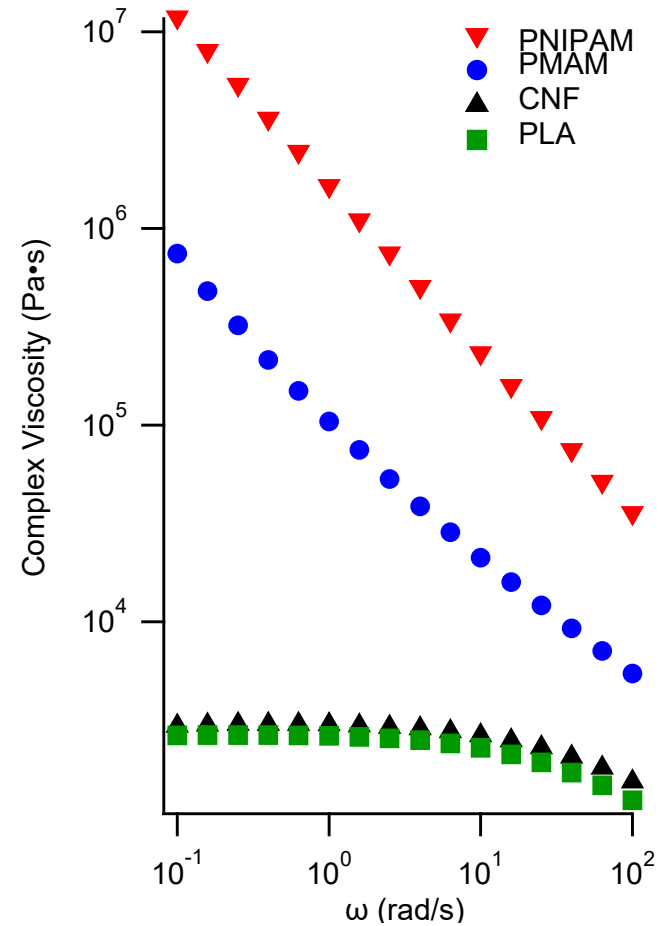
20% PNIPAM



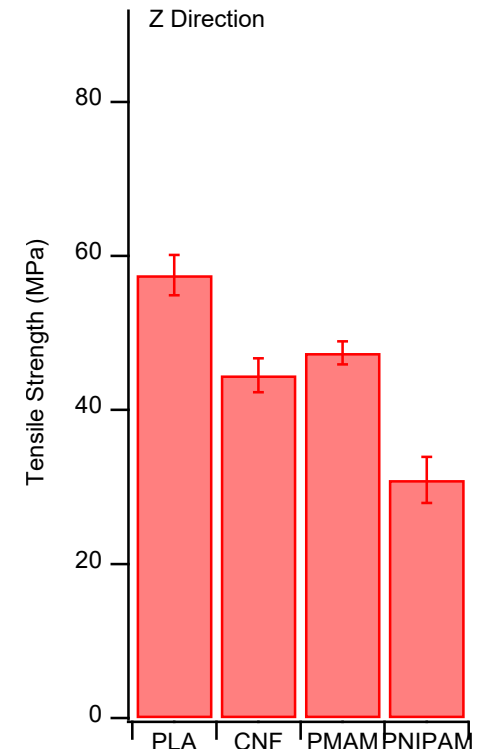
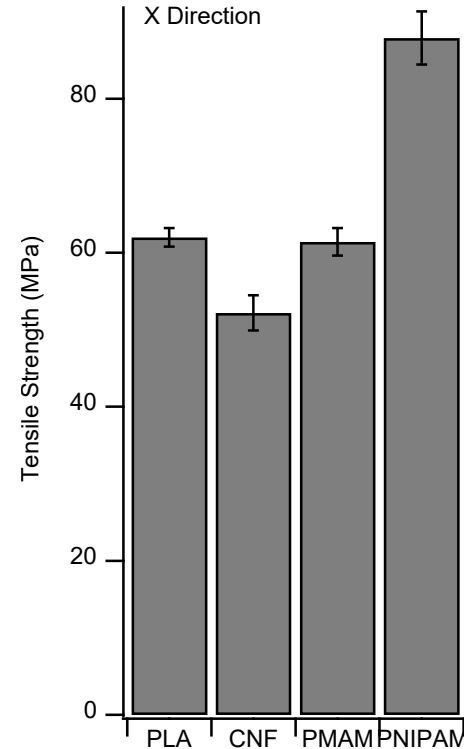
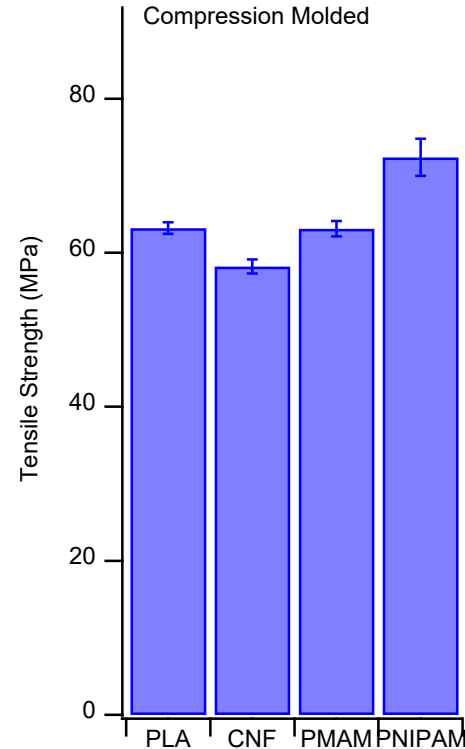
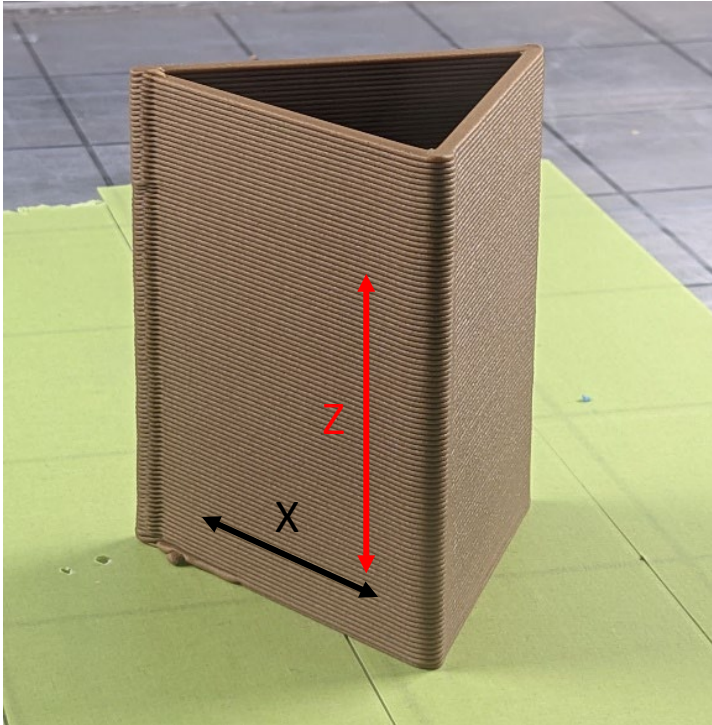
20% SD CNF

Rheology suggests improved dispersion

- High viscosity in the melt
- Modified materials behave differently than PLA

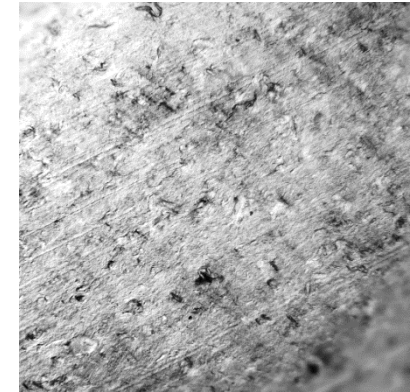
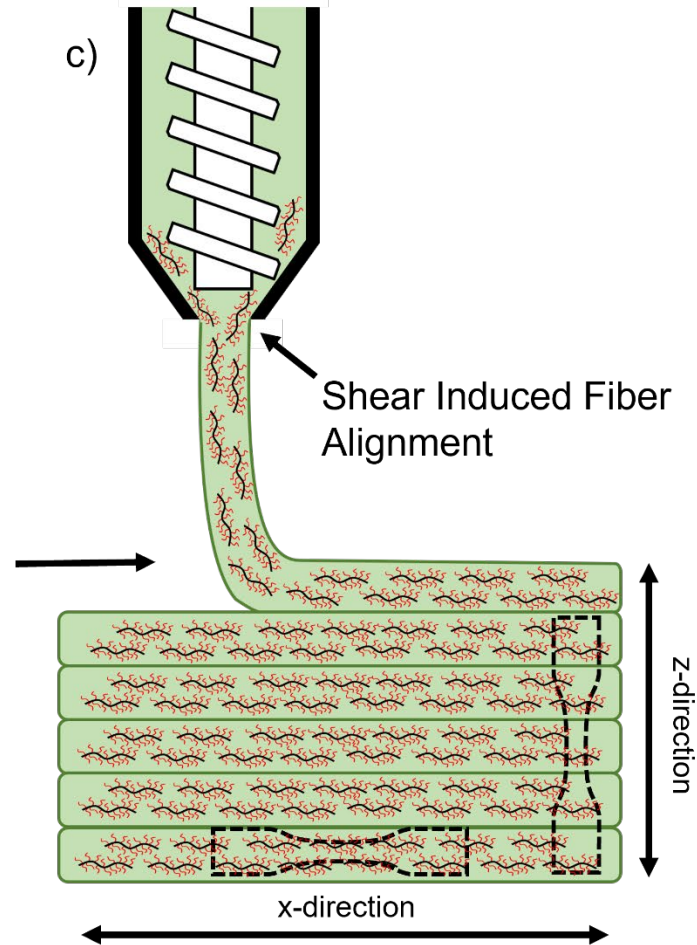
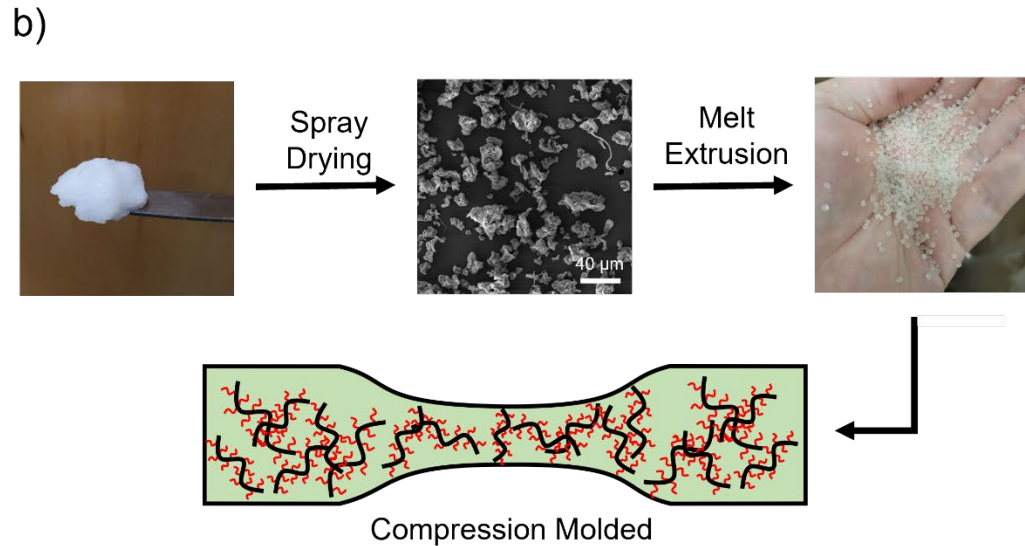
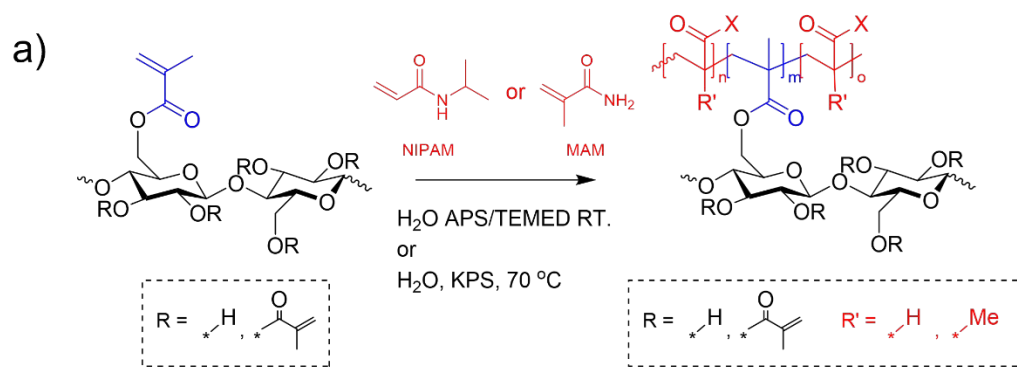


Significant improvements in print direction

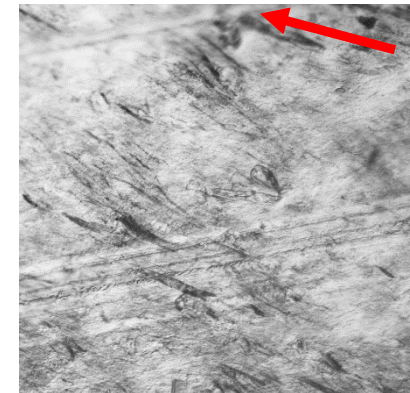


- Potential alignment of fibers or fibrils in print direction

Printing aligns fibers



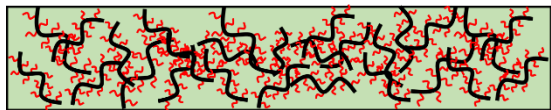
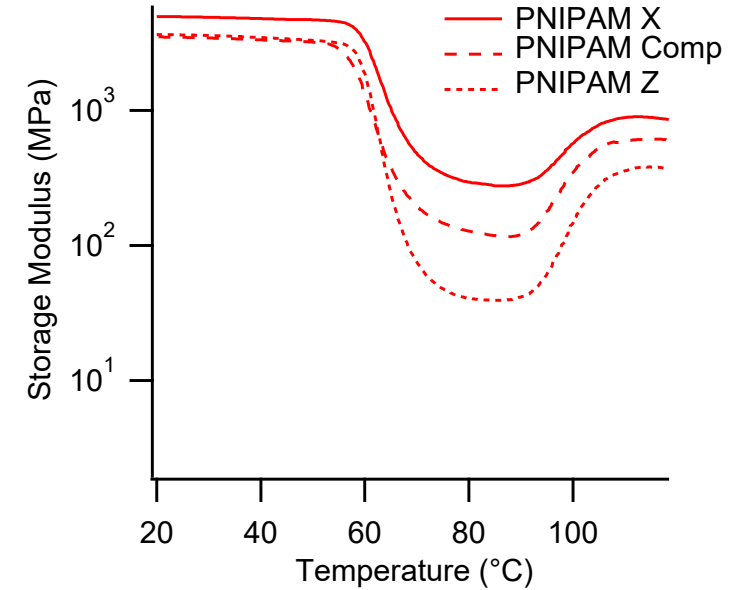
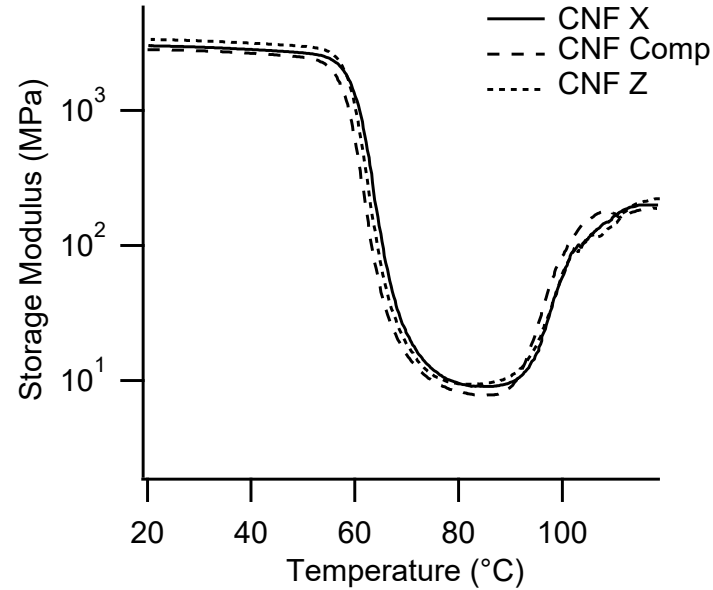
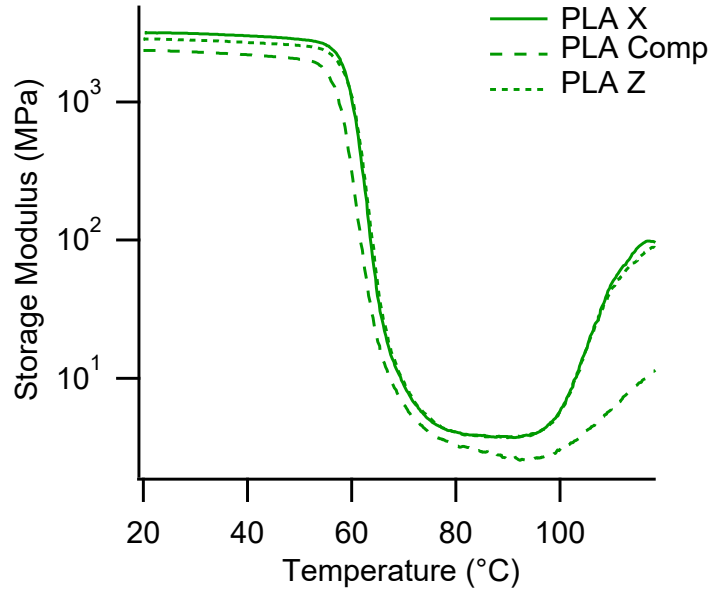
Compression Molded



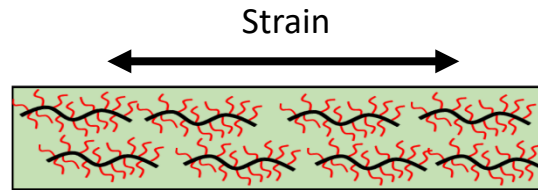
Printed

- Microscopic fiber alignment observed in print direction

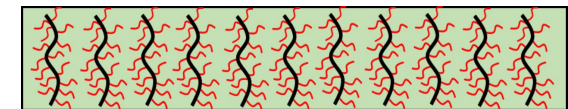
Directionality observed in dynamic mechanical analysis



Compression



X Direction

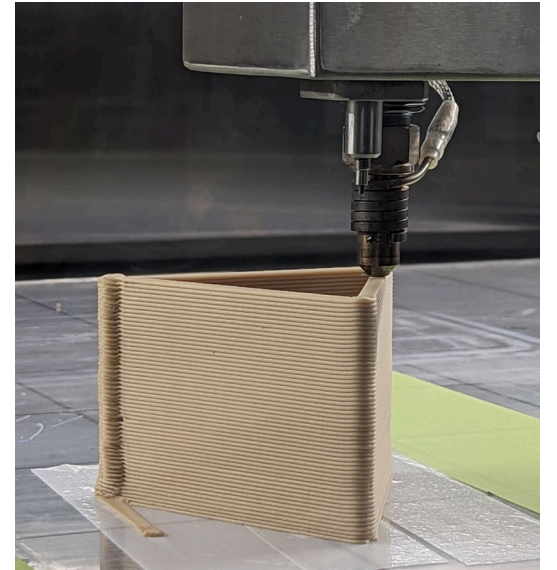
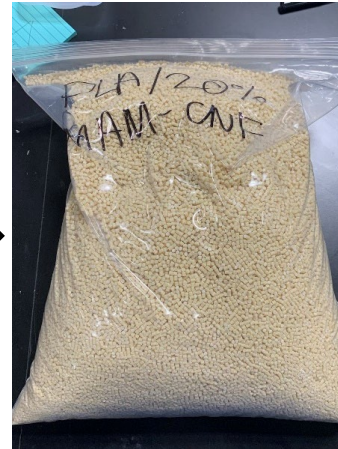
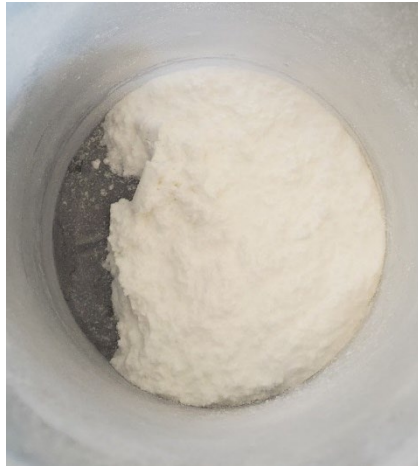
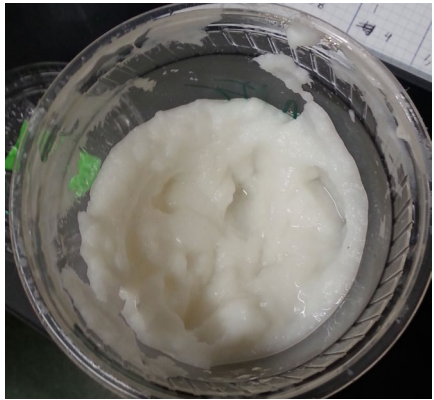


Z Direction

- PNIPAM has different storage modulus for different directions

Conclusions

- Modular system that can produce bio-based reinforcements
- Compatible with current and future melt processing
- Enables high strength PLA composites



Acknowledgements



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Dr. Meghan
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Questions?