

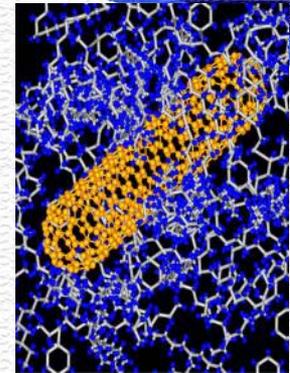
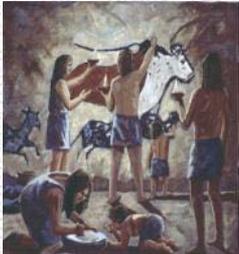
Progress on cellulose nanofiber-filled thermoplastic composites

Douglas J. Gardner, Yousoo Han,
Alper Kiziltas, and Yucheng Peng

**Session 5: The role of nanotechnology in
green materials and sustainable
construction.**

Overview

- Why cellulose nanofiber (CNF)-filled composites?
- UMaine's cellulose nanocomposites research program
- Engineering thermoplastics
- Thermoplastic starch carrier for CNF
- Drying CNF without agglomeration
- Challenges

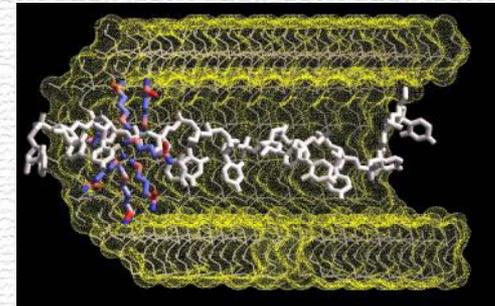


Stone Age Bronze Age Iron Age Nano Age?

- Nanotech is 3rd Industrial Revolution
- US Gov. R&D in Nanotech = \$1.5 billion/yr
- Surface of Nanos in 1 raindrop = 1 football field
- Cellulose: Maine's Niche to Compete in Nanotech

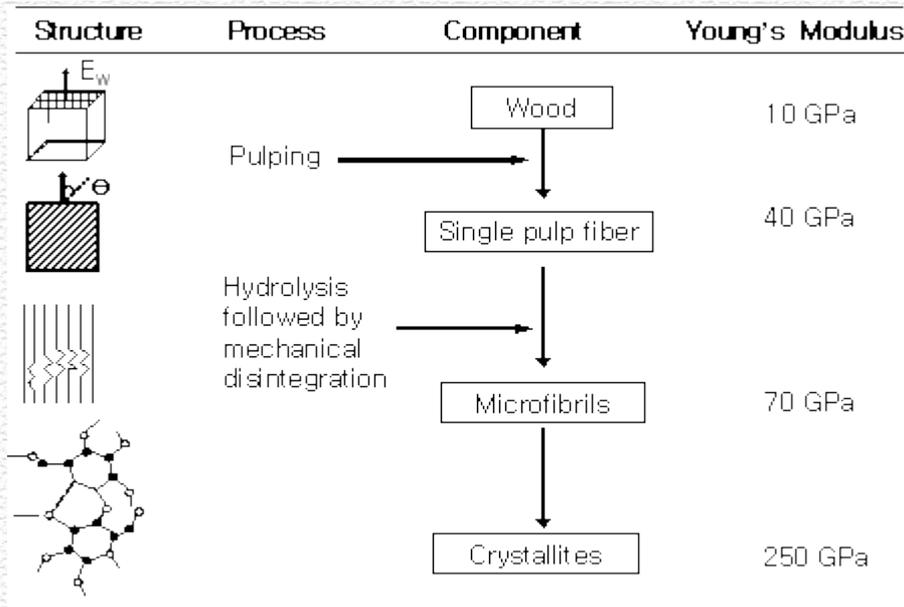


*“From the Sawmill
to the Nanomill?”*

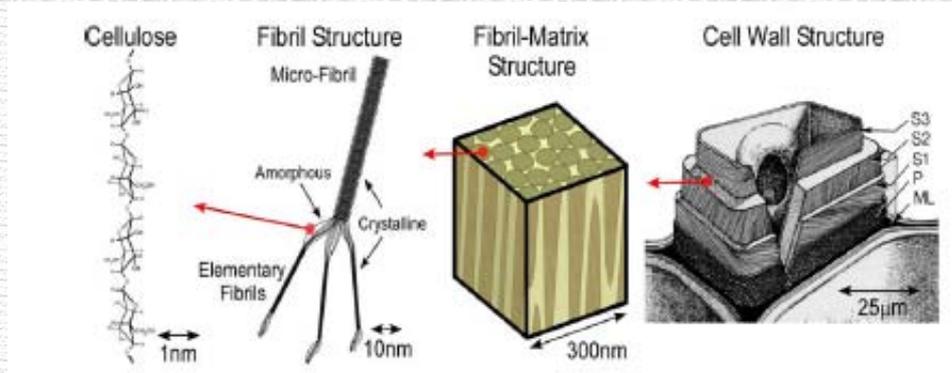


Why cellulose nanofibrils?

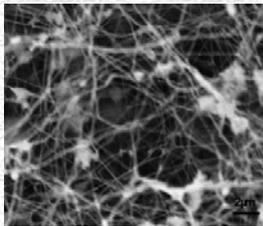
- Renewable resource and broad availability
- No impact of environmental pollution due to biodegradability
- No toxic by-products after combustion
- Low machine wear in processing
- Low density and high strength compared with inorganic fillers



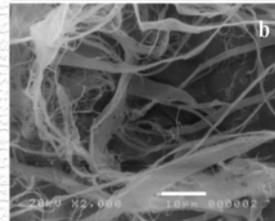
Lignocellulose is a Renewable Resource Abundant in Maine



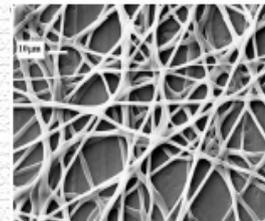
A Wealth of Cellulose Nanofibril (CNF) Architectures are Possible



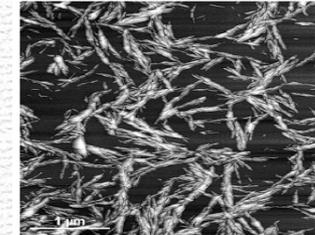
bacterial cellulose



nanofibrillated cellulose

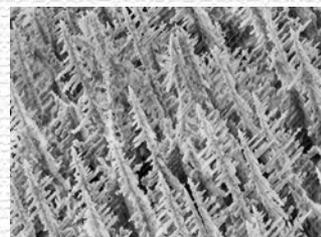
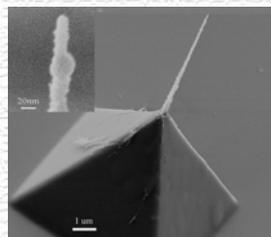
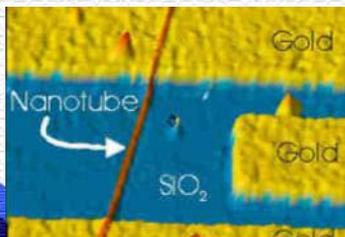


electrospun cellulose



cellulose whiskers

Applications Range from Nano to Macro Components

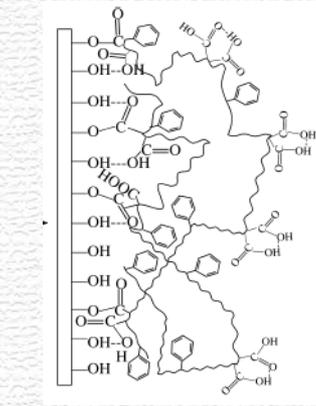


Research Theme #1
Synthesis of Nano-fibers
from Lignocellulose
Sources



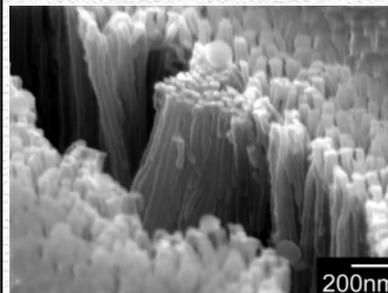
Objective: Produce inexpensive lignocellulosic-based nanofibers with known and consistent properties.

Research Theme #2
Functionalization of
Lignocellulose



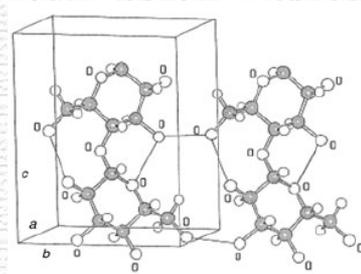
Objective: Achieve precise control of nanofiber surface and interfacial chemistry to obtain desired adhesion and dispersion.

Research Theme #3
Materials
Characterization



Objective: Characterize cellulose nanofibril-derived materials and determine structure/property relationships from nano- to macro- scales.

Research Theme #4
Modeling and Visualization



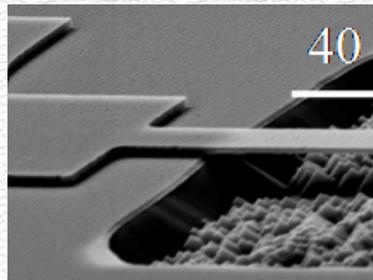
Objective: Develop multi-scale micro- and nano-simulation and visualization techniques to predict materials performance.

Research Theme #5
Structural Composites



Objective: Develop pilot-scale processes to utilize nanoscale lignocellulose derived fibers and CNFs in structural composites.

Research Theme #6
Smart Materials and Devices



Objective: Develop nanoscale devices, structures, and films for nanoelectronics, tissue engineering, sensing, actuation, and separation membrane applications.

Physical Infrastructure for Cellulose Nanotechnology



Cellulose Nanofiber Production and Functionalization Laboratory - FBRI



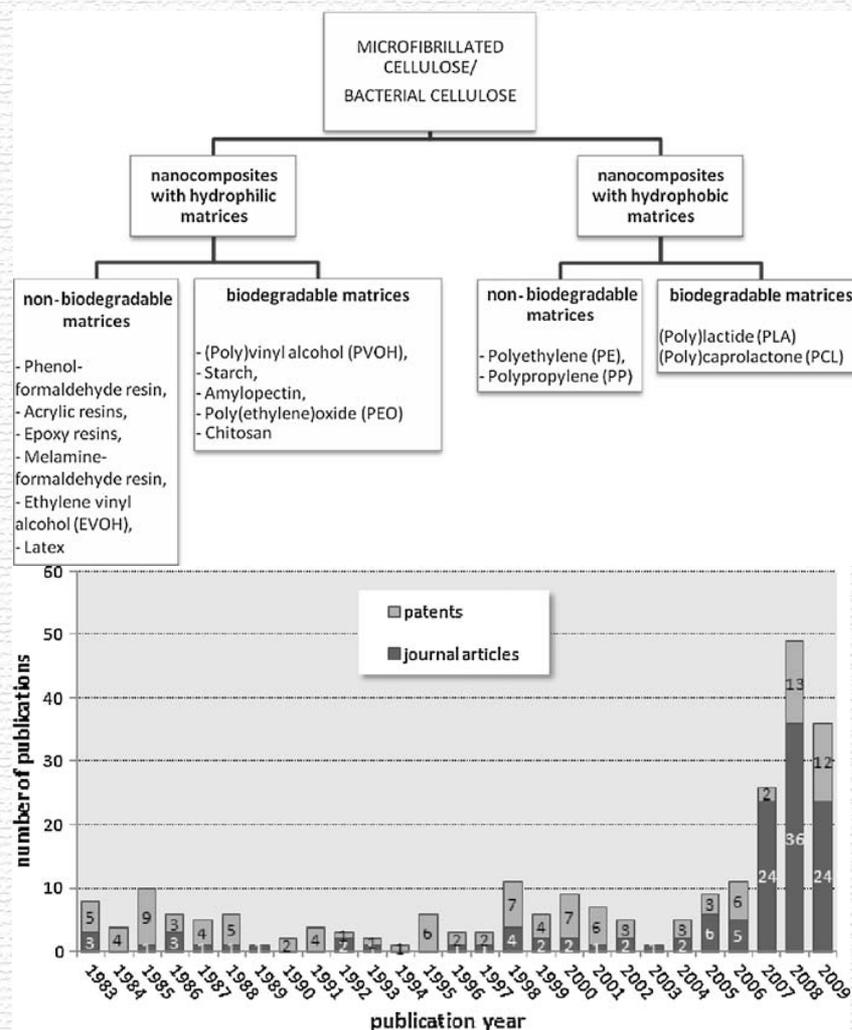
Processing Lab for Cellulose Nanocomposites in Structural/Off Shore Wind Applications - AEWC



Nanoscale Imaging & Characterization Laboratory - LASST

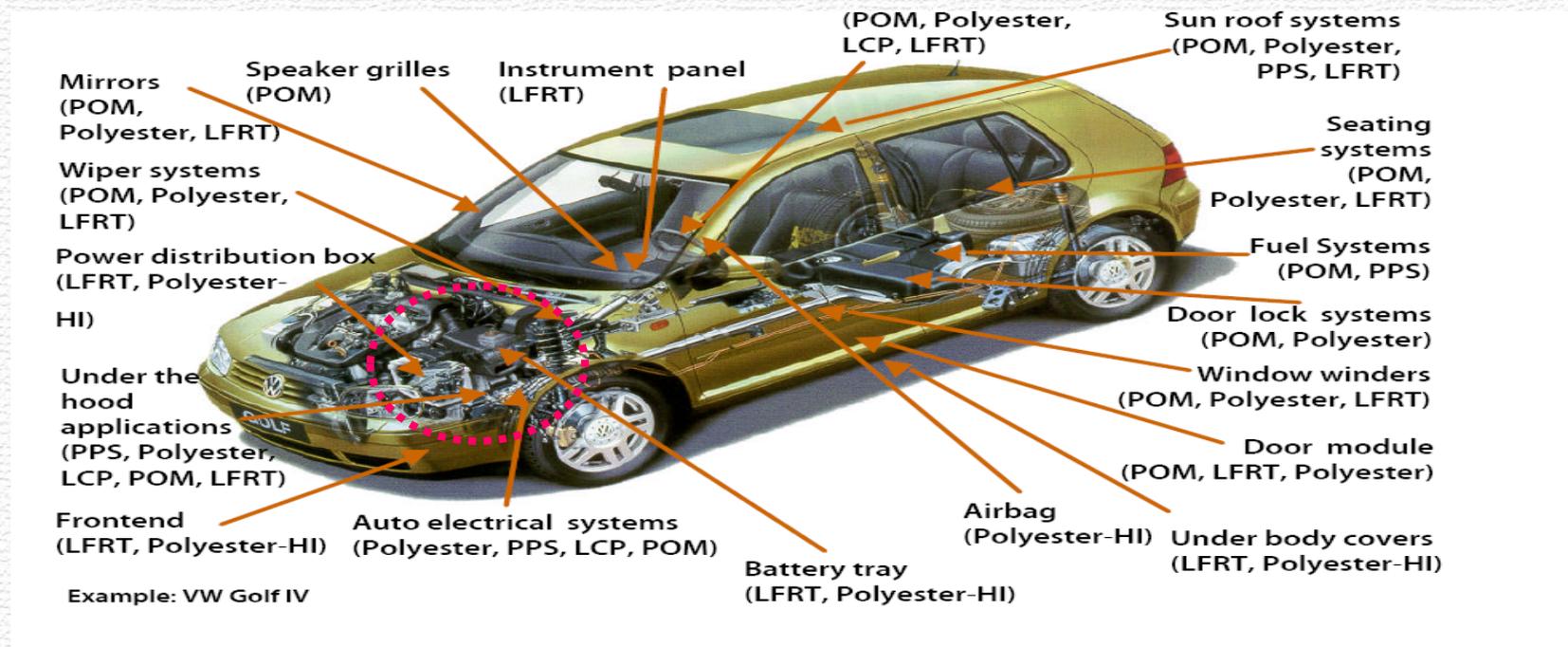
Challenges using CNF in Hydrophobic Polymers

- Because of the hydrophilic nature of cellulose nanofibrils many studies have focused on nanocomposites based on hydrophilic polymer matrices.
- There have been very few research studies focusing on CNF in hydrophobic polymers such as PE and PP.



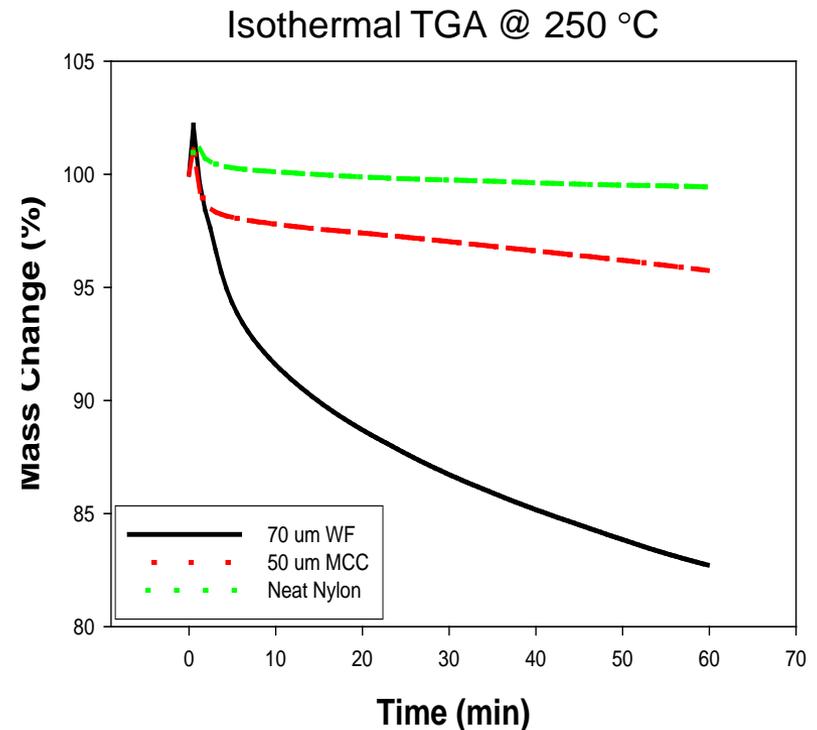
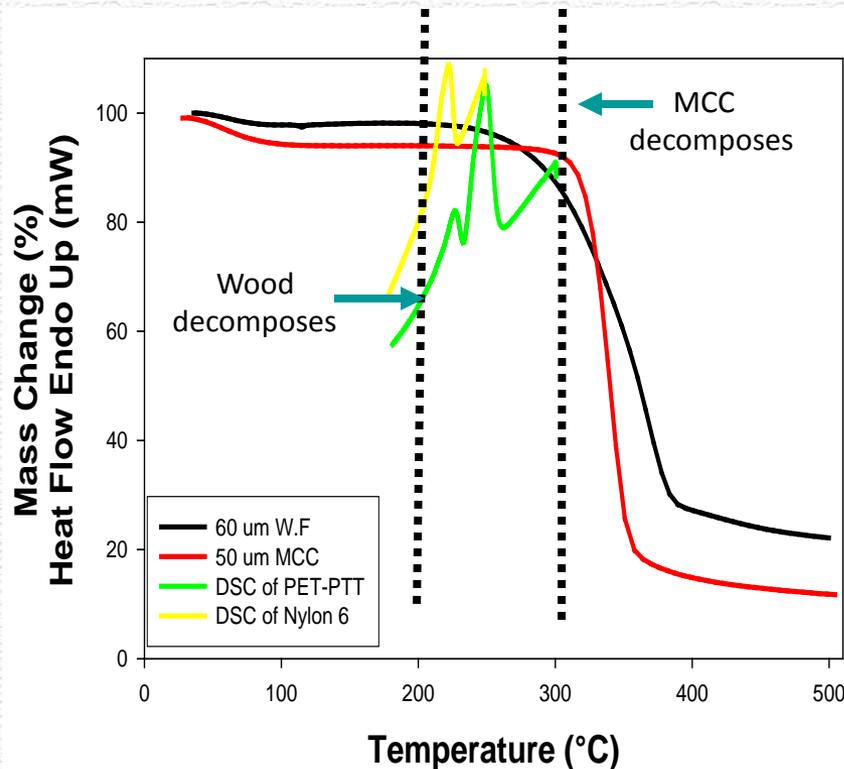
Why engineering thermoplastics (ETP)?

- ETP defined as materials which can be used structurally, typically replacing metals, wood, glass, or ceramics.
- These high-performance polymers provide innovative solutions that save weight and reduce costs.

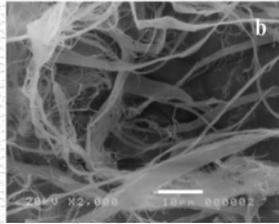


Thermal stability

- The processing temperature of wood/natural fiber composites are typically restricted to around 200 C.
- The earliest experiments to reinforce engineering thermoplastics exhibited severe discoloration and pronounced pyrolytic degradation.



Methods-Production



nanofibrillated cellulose



ETPs
MCC
Lubricant

High Speed
Mixer

Melt Blend
Brabender

Dry Ground
Mixture



Injection
Molding

ASTM Test
Samples

Comparison of ETPC's and Commodity Plastics

Mechanical Properties

Mechanical Properties of PP, PA6 and PET-PTT Blend Composites

Groups	Properties			
	T.S. (MPa)	T.M. (GPa)	F.M. (GPa)	N.I.S. (J/m)
Polypropylene	27.6	1.39	1.39	16.1
PP+33% WoodFlour	33.1	3.38	3.19	18.7
Nylon 6(PA6)	37.6	2.89	2.65	64.5
PA6+20% MCC	52.5	3.21	3.76	29.1
PA6+20% MCC+1%NC	59.2	3.67	3.75	31.3
PET-PTT Blend	24.8	1.11	2.10	47.0
PET-PTT+20%MCC	36.3	1.68	2.96	24.7

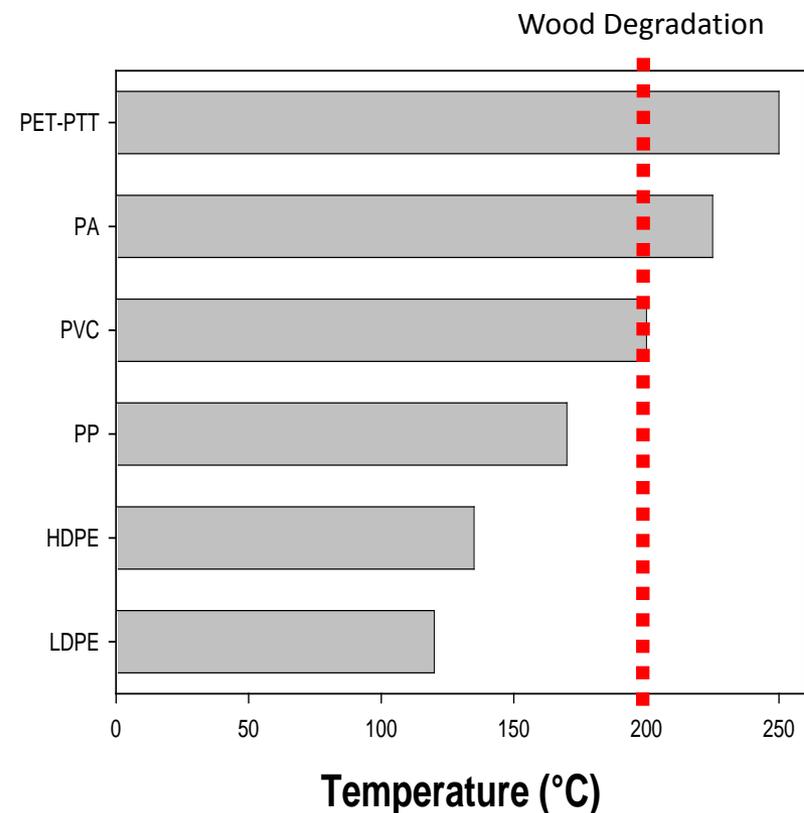
T.S.=Tensile strength, T.M.=Tensile modulus of elasticity, F.M.= Flexural modulus of elasticity and N.I.S.=Notched Izod impact strength

Jacobson et al. Sixth Inter. Conf. on Woodfiber-Plastic Composites

Kiziltas A. et al. Wood and Fiber Science, 2010: 42 (2): 165-176

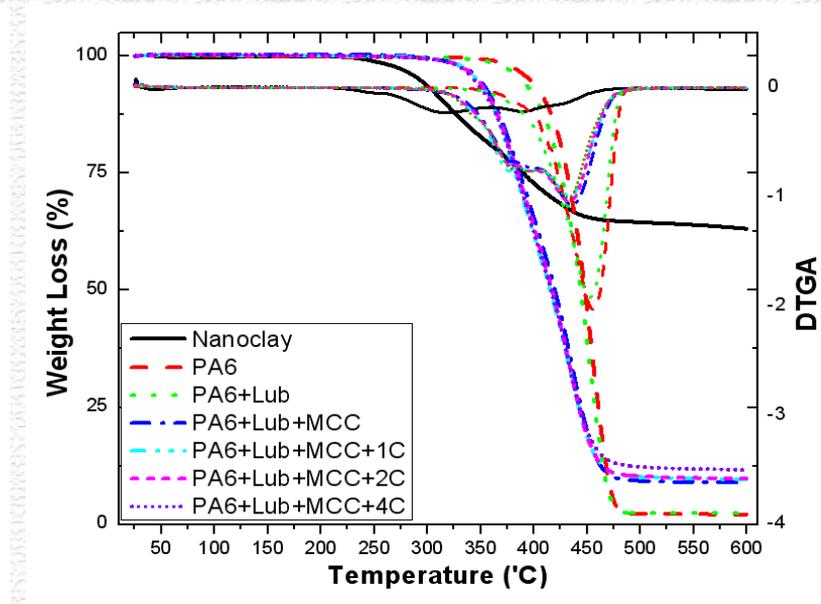
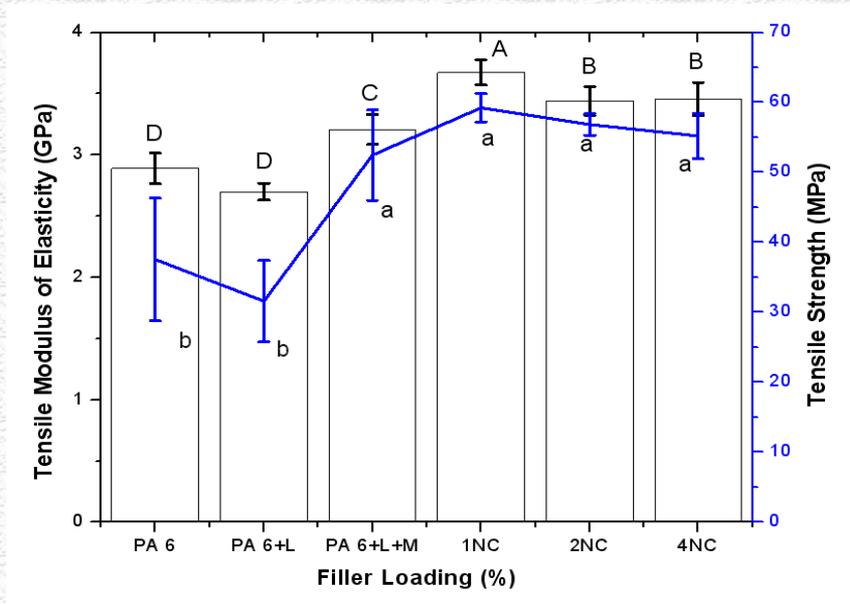
Kiziltas A. et al. submitted to Polymer Testing, POTE-D-10-00383.

Melting Temperature



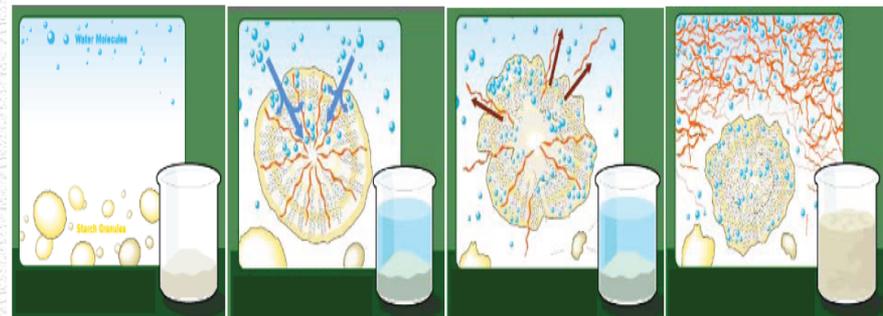
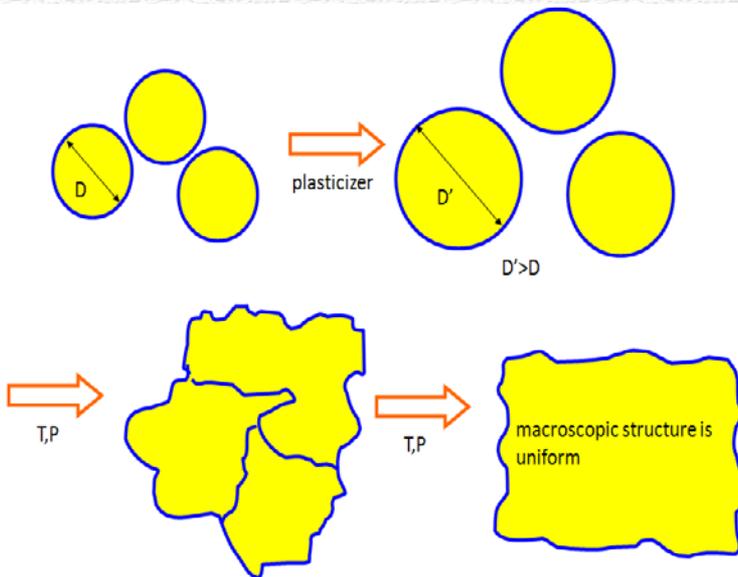
Stiffness Enhancement of MCC-Filled ETPC's Using Nanoclay

- To investigate the reinforcement effects of Nanoclay on the stiffness of 20% MCC- filled engineering thermoplastic composites.
- To also investigate the effect of Nanoclay on the MCC/Nanoclay/PA 6 composites thermal properties.



Thermoplastic Starch

- The literature is confusing and describes thermoplastic, destructured, gelatinized and plasticized starch.
- Structure is overcome with a combination of plasticizer, heat and pressure to process the starch.
- Plasticization is the easiest and cheapest way to put technological materials in a processable state.



The water penetrates the starch, hydrating it from the outside to the inside. Hydrogen bonds between the molecules force the granule to hold its shape.

As more water enters the granule, it starts to swell.

The hydrogen bonds weaken. Amylose strands work their way out of the granule and into the water. Amylopectin strands stay inside the granule. Some granules collapse.

The freed amylose thickens and stabilizes the water around it. The mixture becomes thick and viscous.

Our Approach

Base Polymer
(Hydrophobic Matrix)

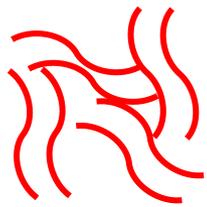


Nanoscale Additive
(Filler, Dispersed Phase NC)

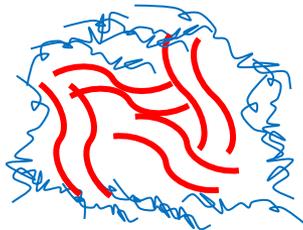


Carrier System
(Thermoplastic Starch)

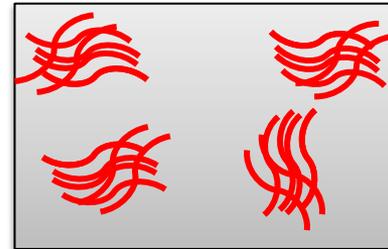
Hydrophobic Thermoplastic Composites
with better dispersion and improved properties



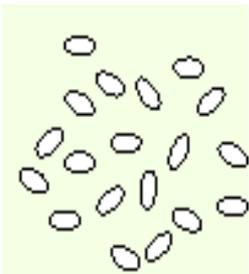
NC



NC in Hydrophobic Matrix



Conventional Composite



Native Starch

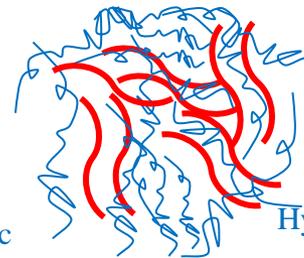
Water
Glycerol
Heat
Pressure



Thermoplastic Starch (TPS)

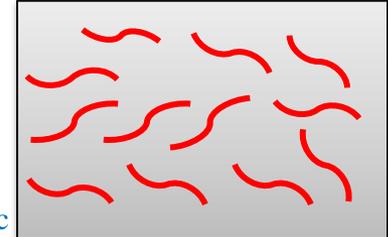


NC
Hydrophilic



NC filled TPS

Polymer
Hydrophobic



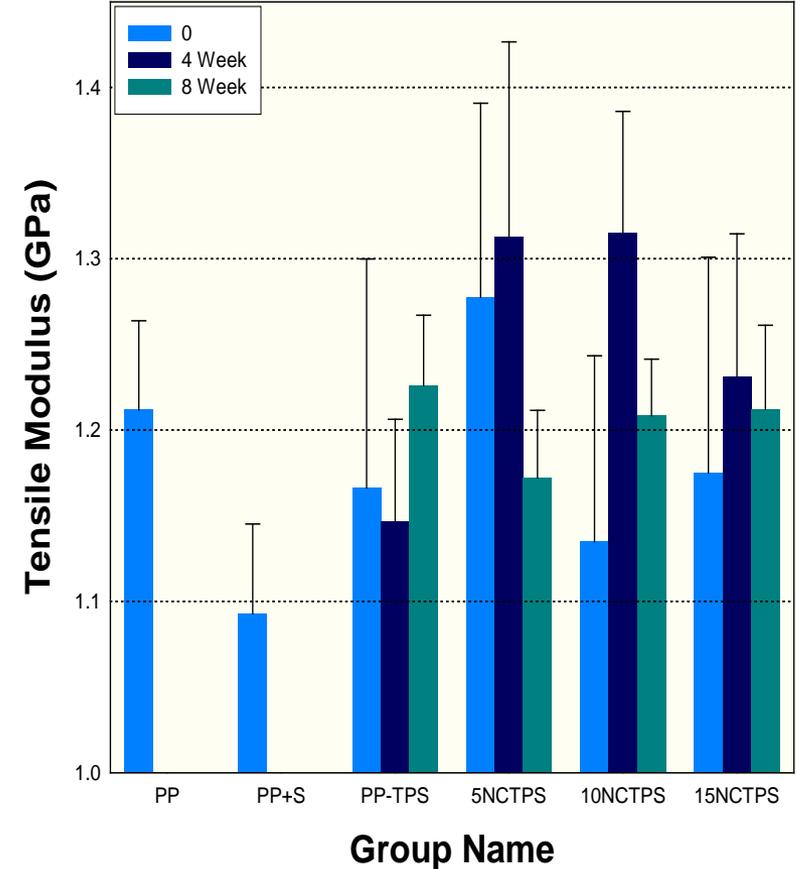
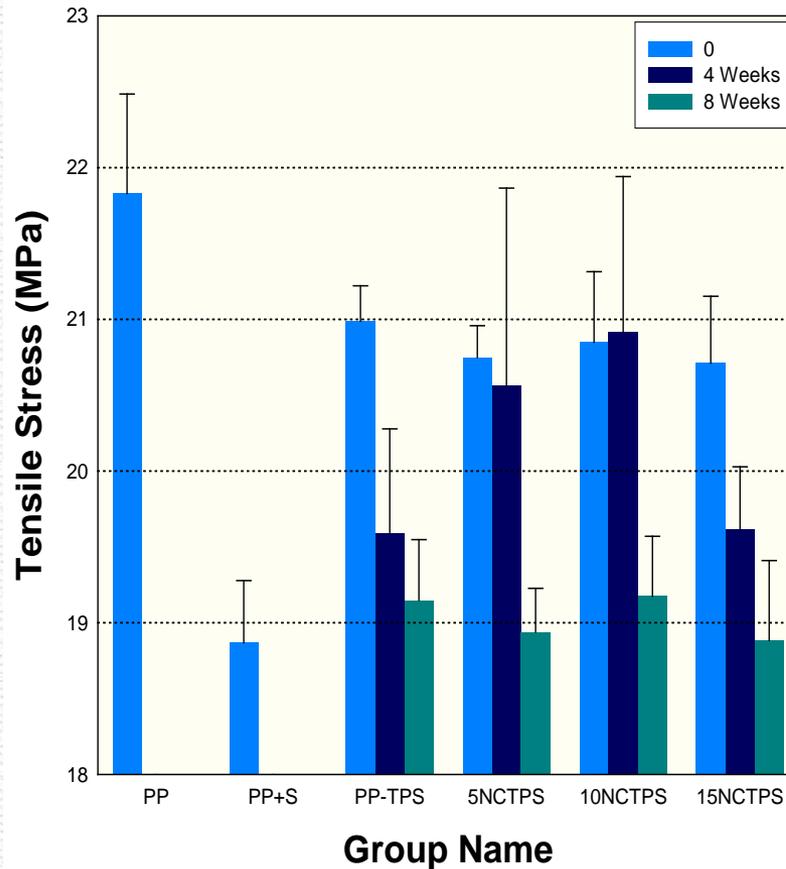
Dispersed NC in
Hydrophobic Matrix

Formulations

TPS Composition							
Sample Code	Starch	Glycerol	Water	CN	Glycerol/Water	Plasticizer/Starch	Total
TPS	50	15	35	-	0.43	1	100
5NCTPS	47.5	14.25	24.25	14	0.43	1	100
10NCTPS	45	13.5	12.5	29	0.43	1	100
15NCTPS	42.5	12.75	1.75	43	0.43	1	100

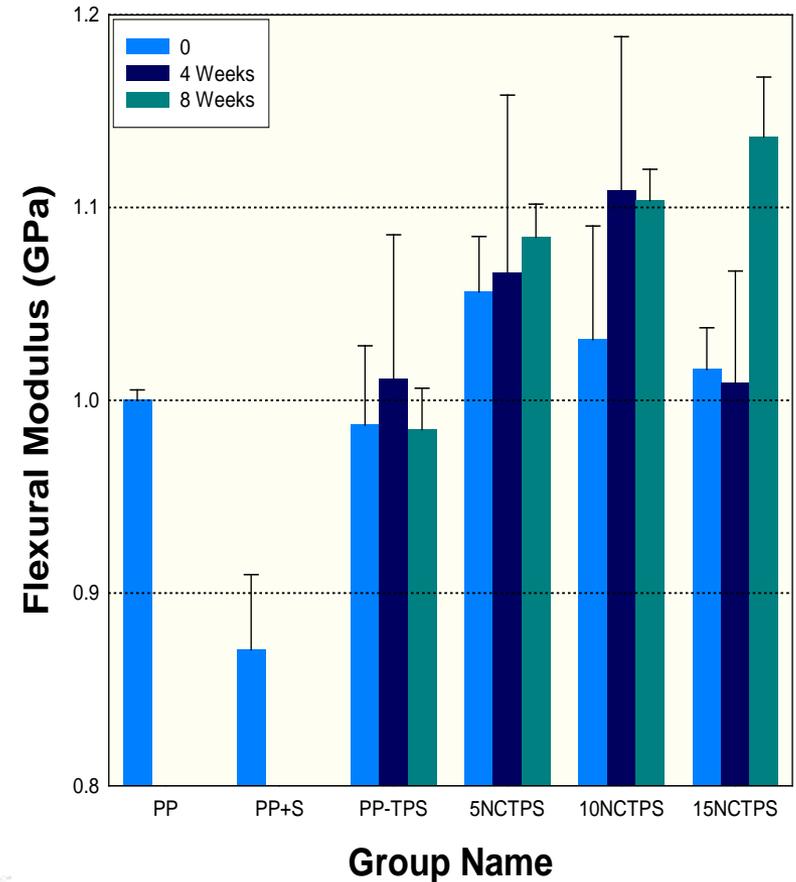
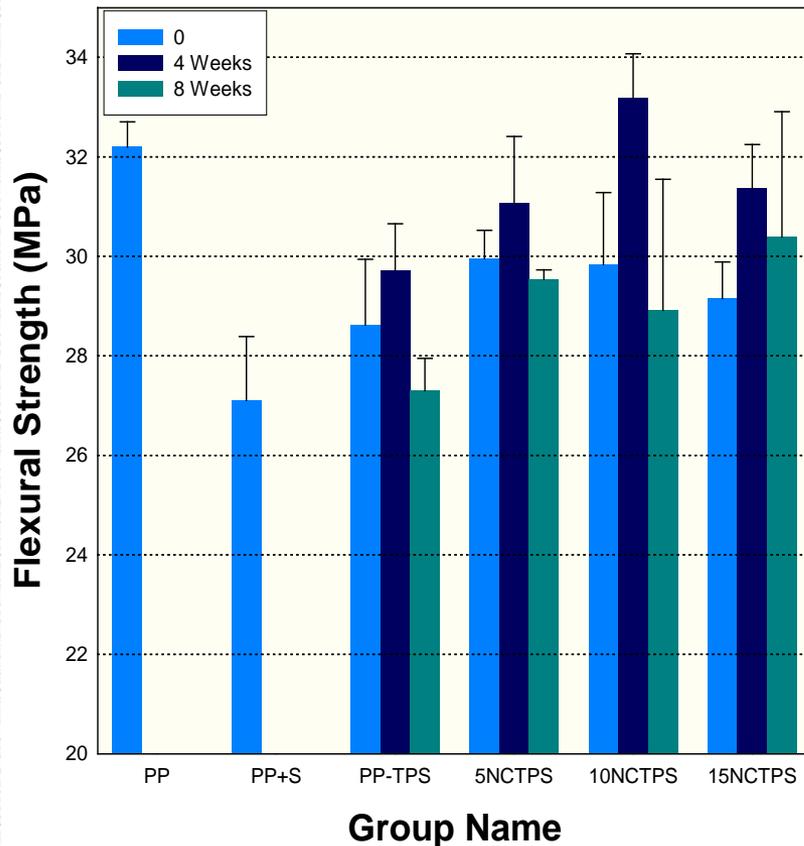
Composition of Composites						
Sample Code	PP	TPS	5NCTPS	10NCTPS	15NCTPS	Total
Neat PP	100	-	-	-	-	100
PP+TPS	90	10	-	-	-	100
PP+5NCTPS	90	-	10	-	-	100
PP+10NCTPS	90	-	-	10	-	100
PP+15NCTPS	90	-	-	-	10	100

Tensile Properties of the Composites



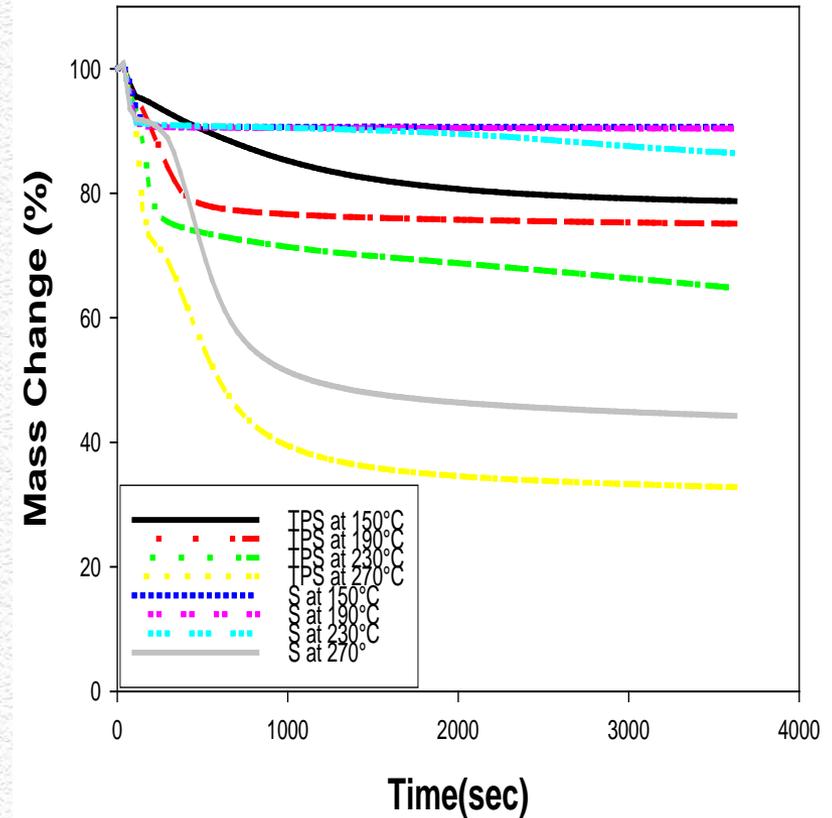
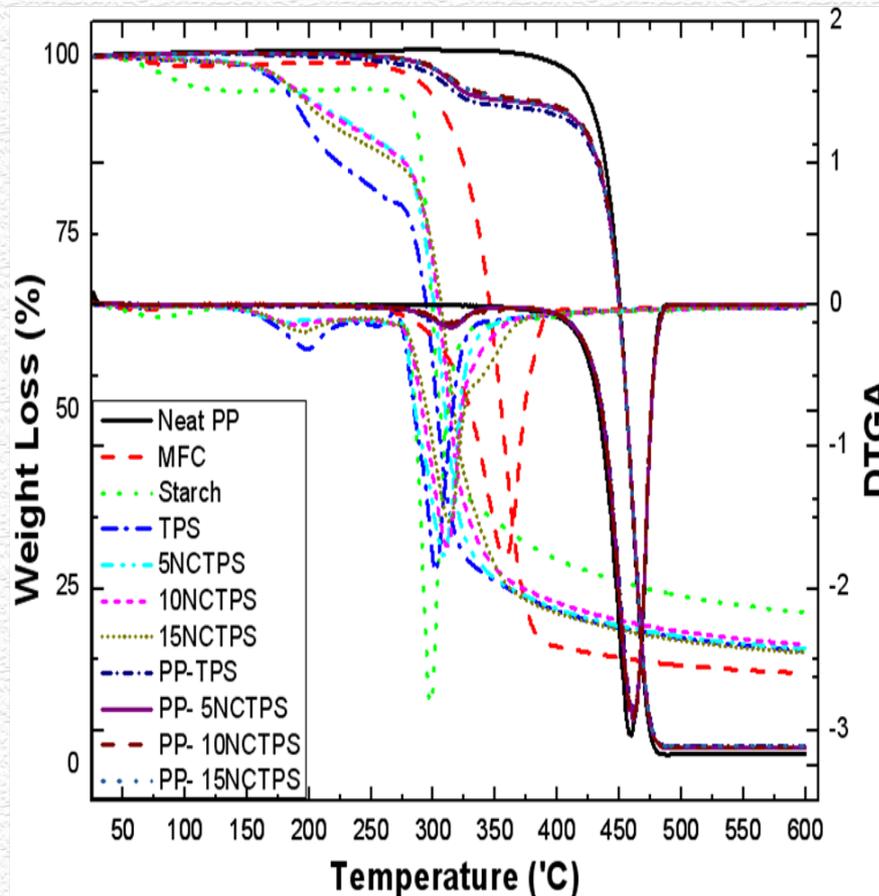
TPS and NCTPS filled PP composites showed comparable or lower tensile strength and modulus compared to control samples.

Flexural Properties of the Composites



TPS and NCTPS filled PP composites showed comparable or lower flexural strength and modulus compared to control samples like tensile properties.

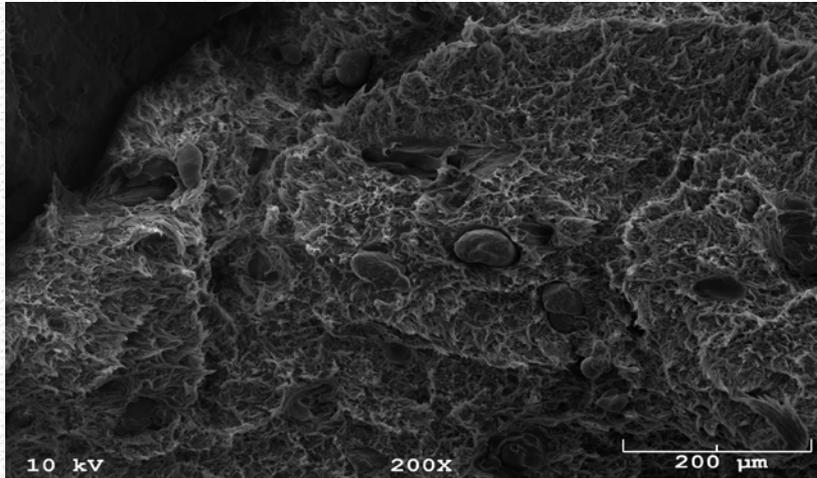
TGA and DTGA of Composites



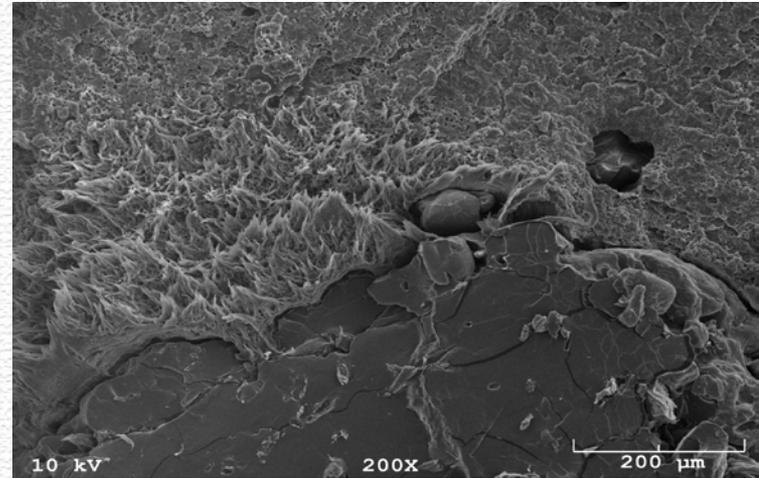
TGA and DTGA results showed that thermal stability of composites decreased marginally with the addition of TPS and NCTPS.

SEM Micrographs of TPS-Based Comp.

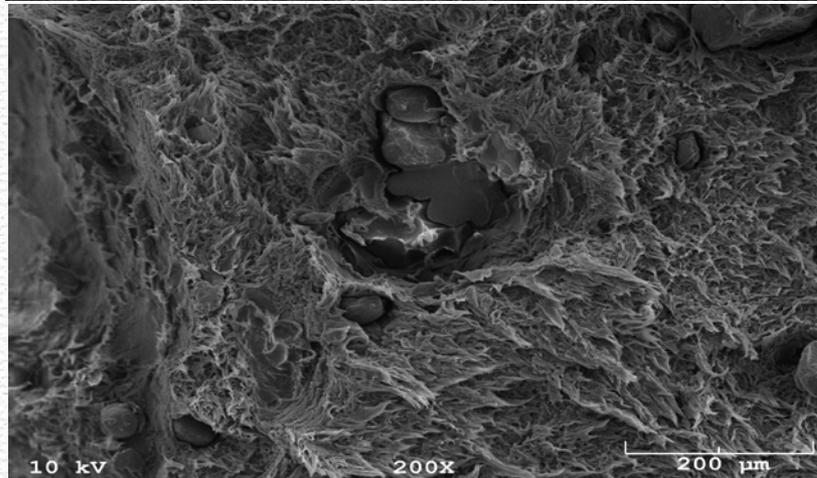
PP-TPS



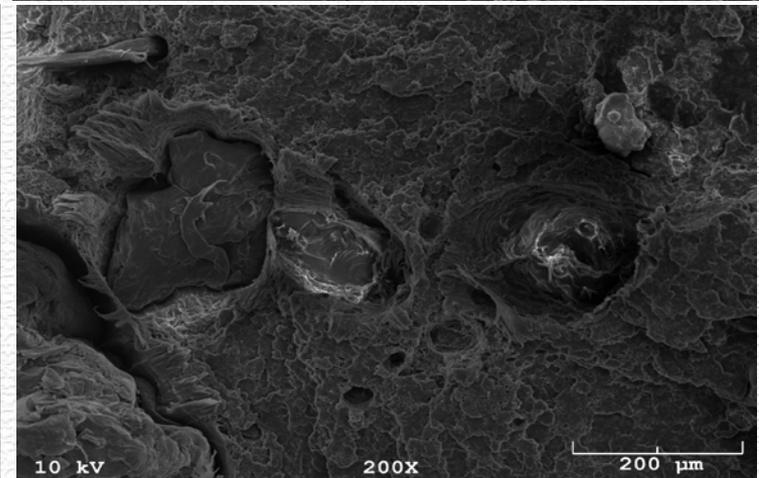
PP-5NCTPS



PP-10NCTPS



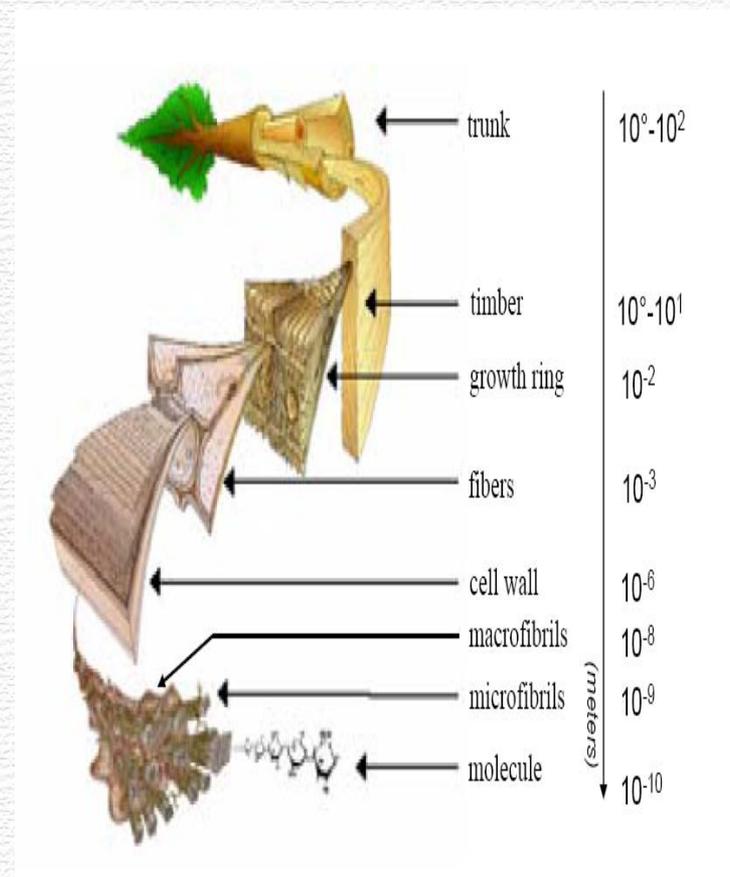
PP-15NCTPS



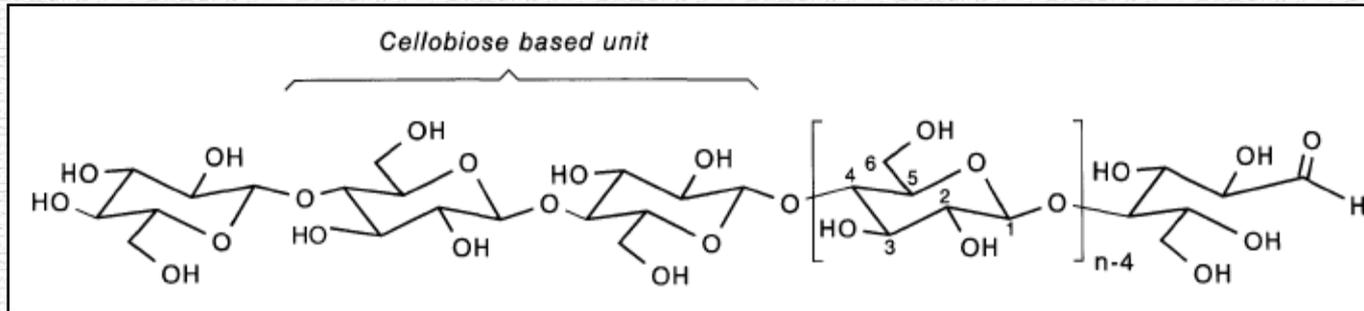
The PP matrix was inert, we had no TPS–matrix interactions. From SEM observation, we can visualize that the fibrils were embedded in TPS. This is due to strong interactions between the cellulose fibrils and the plasticized starch matrix.

Challenges for scale-up of producing CNF

- Major issue : Processing by classical method (extrusion, injection) using cellulose micro-nanofibrils in dry state without any chemical modification.
- Scaling-up of homogenization technologies.
- Energy and enzymes consumption.
- Reduction of clogging problems.
- Controlling cellulose micro-nanofibrils agglomeration.
- Reduction of production costs.



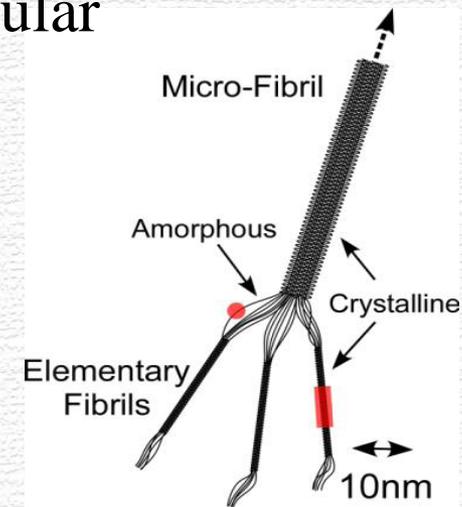
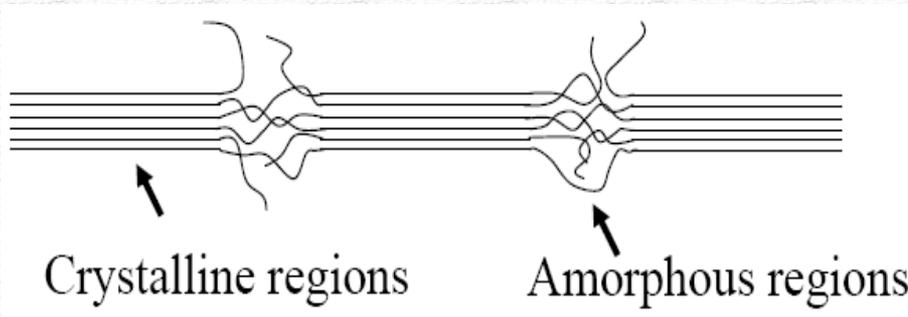
Cellulose and Hydrogen Bonding



(Klemm et al. 1998)

Aggregation

- 1) Inter and intra-molecular hydrogen bonds
- 2) van der Waals forces



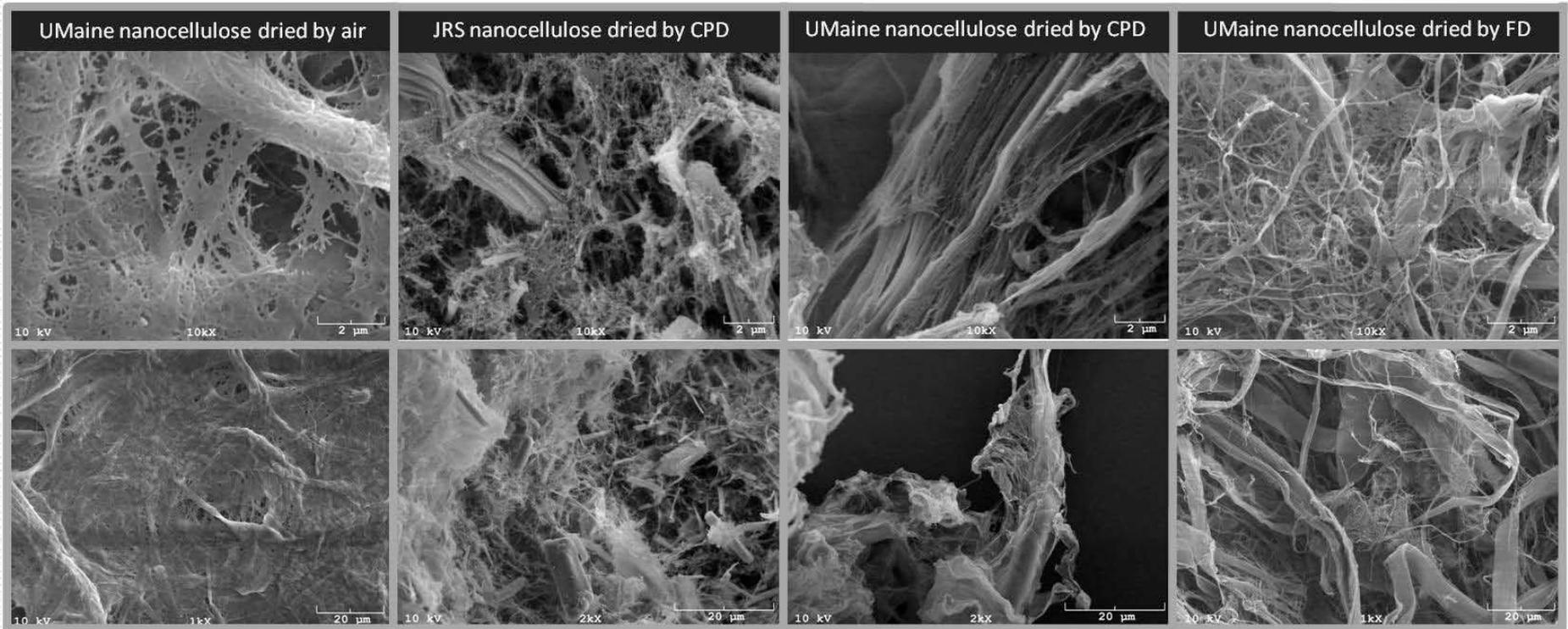
(Wegner 2009)

Challenges

- Aqueous nature of cellulose nanofibrils because of the rich hydroxyl groups on the surface
 - Agglomeration
 - Absorption of atmospheric moisture
 - Poor compatibility between polar cellulose nanofibril and apolar polymer matrix

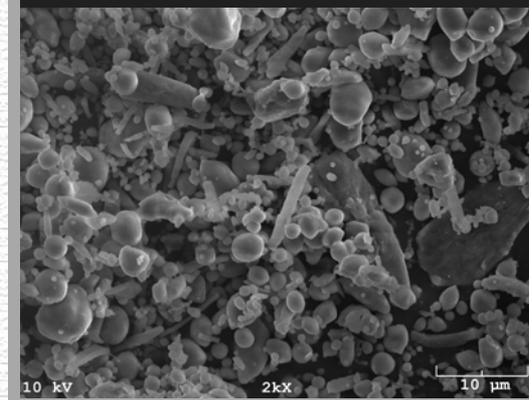


Different morphologies of nanocellulose by different drying processes



Ideal dry form of cellulose nanofibrils for polymer processing with thermoplastics

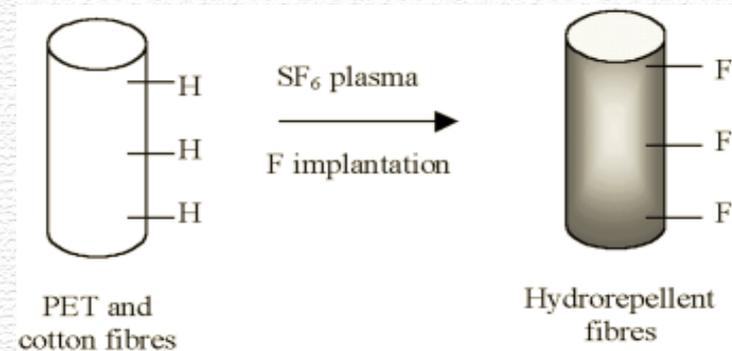
Something like this?



Planned Surface Modification

- Methods

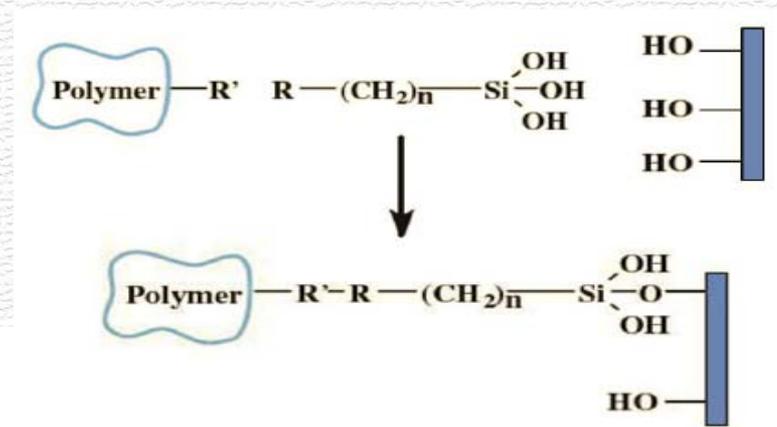
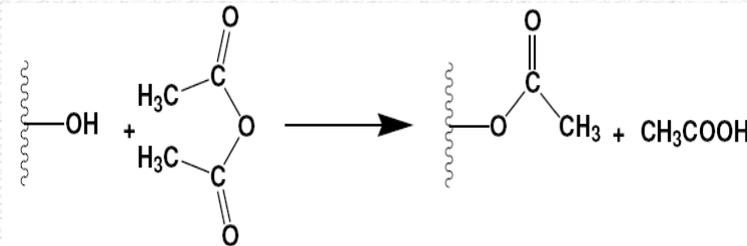
- Physical
 - Plasma



(Selli et al. 2001)

- Chemical

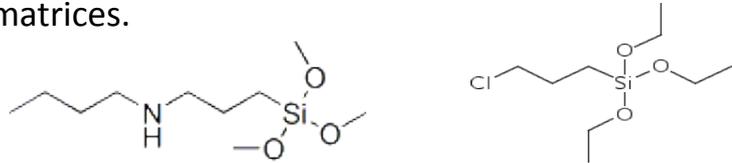
- Esterification
- Coupling agent treatment



Silane treated wood fibers for reinforcing fillers in thermoplastic composites

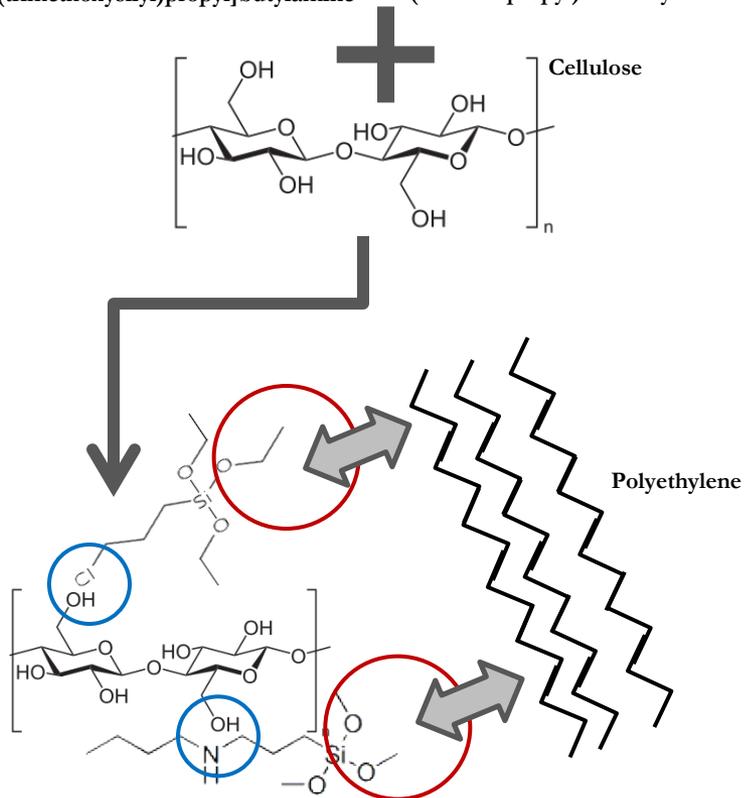
Experimental Concept

Surface of cellulose or wood fiber treated with organic silanes which have two or more domains for fillers and matrices.

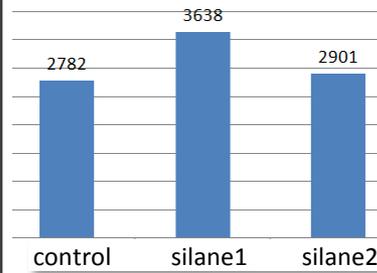


Silane 1:
N-[3-(trimethoxysilyl)propyl]butylamine

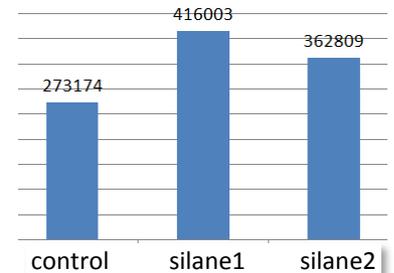
Silane 2:
(3-Chloropropyl)triethoxysilane



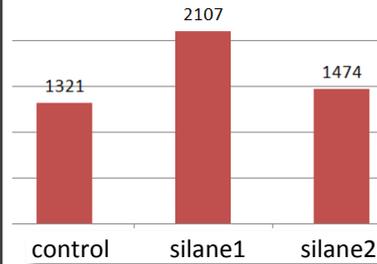
Experimental Results



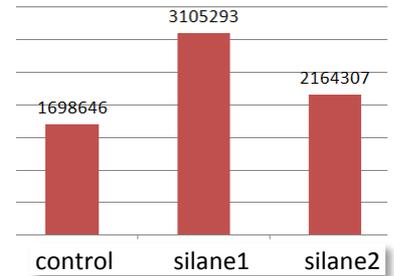
Flexural MOR, psi



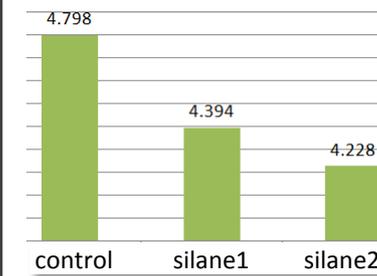
Flexural MOE, psi



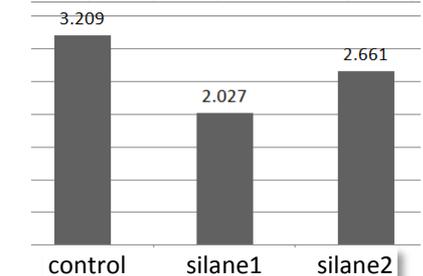
Tensile strength, psi



Tensile modulus, psi



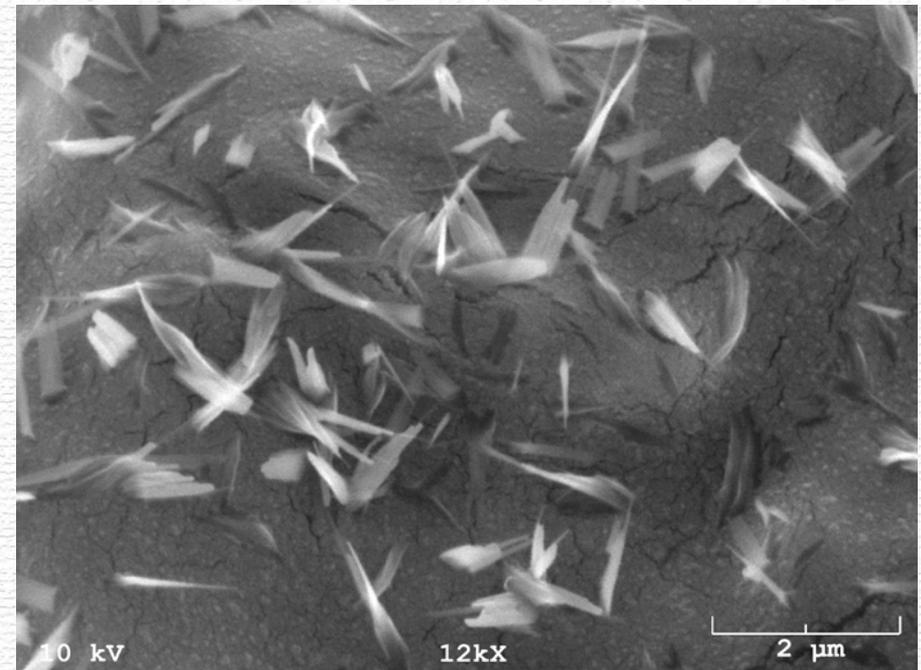
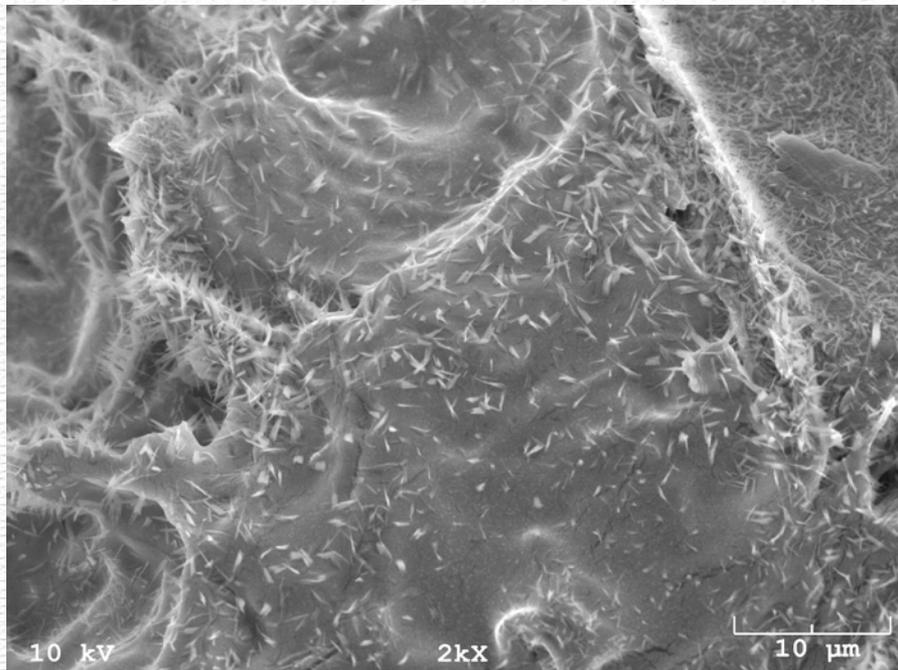
CTE, 10⁻²



Water weight percent gain, %

Dispersion of CNF in composites

Cellulose nanofibrils were dispersed in the wood-inorganic composite through a sodium silicate solution.



Fracture surface of wood-inorganic composite (5 wt. % of cellulose nanofibrils)

Conclusions

- Thermoplastic-CNF composites with enhanced material properties are possible.
- Ongoing challenges for scale-up of utilizing cellulose nanofibrils in hydrophobic thermoplastics will be the need for obtaining large quantities of CNF in the dry state.
- For the process of producing nano-fibrillated cellulose on the commercial scale, scale up of adequate homogenization technologies is still needed.
- Control of CNF agglomeration and scalable drying technologies is also a big challenge.
- Surface treatment of CNF via physical and/or chemical modification methods will be important to tailor CNF surfaces for application in specific polymer matrices.

Acknowledgements: The authors thank the Army Corp of Engineers ERDC, USDA Wood Utilization Research Special Grant, and McIntire Stennis for funding support.