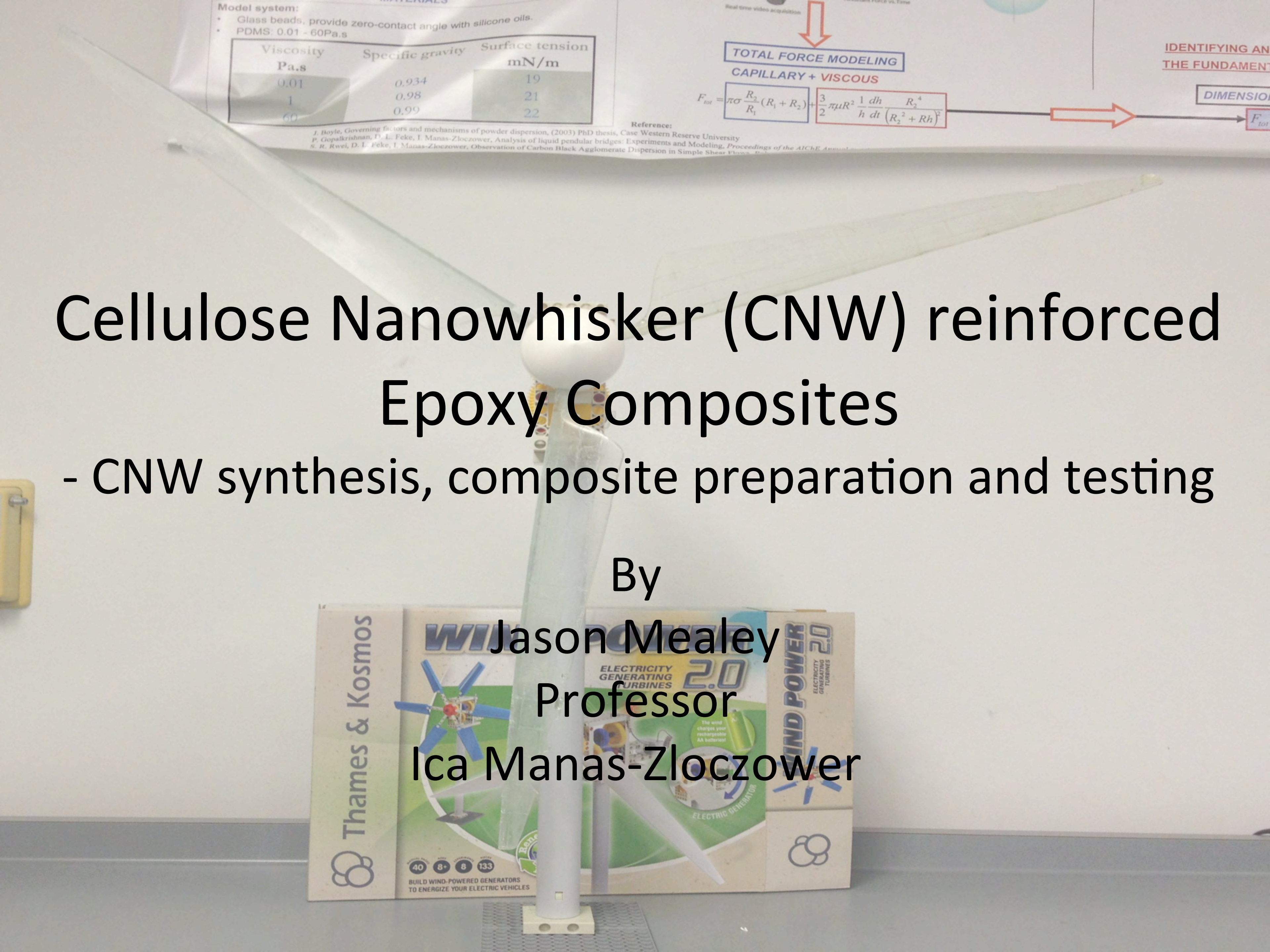

Cellulose Nanowhisker (CNW) reinforced Epoxy Composites

- CNW synthesis, composite preparation and testing

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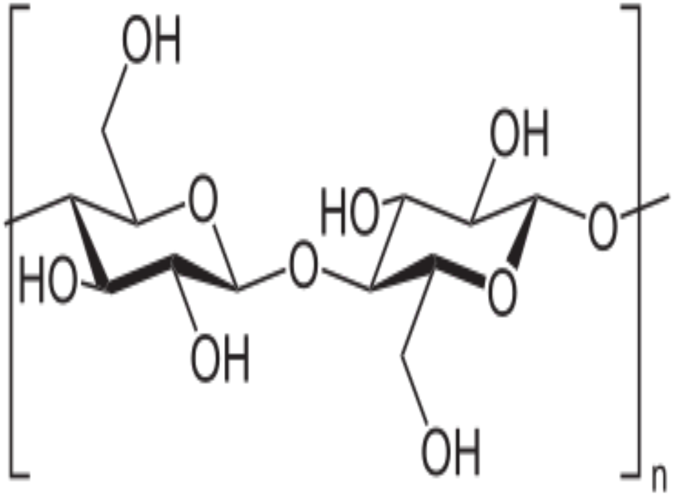
Objectives

- To learn and understand how to synthesize cellulose nanowhiskers (CNWs) by TEMPO-mediated oxidation
- To study how to disperse CNWs into epoxy uniformly
- Learn how to measure the mechanical properties of the nanocomposites
- To learn how to prepare wind turbine blades made from epoxy/CNWs composites by silicone mold casting

Cellulose

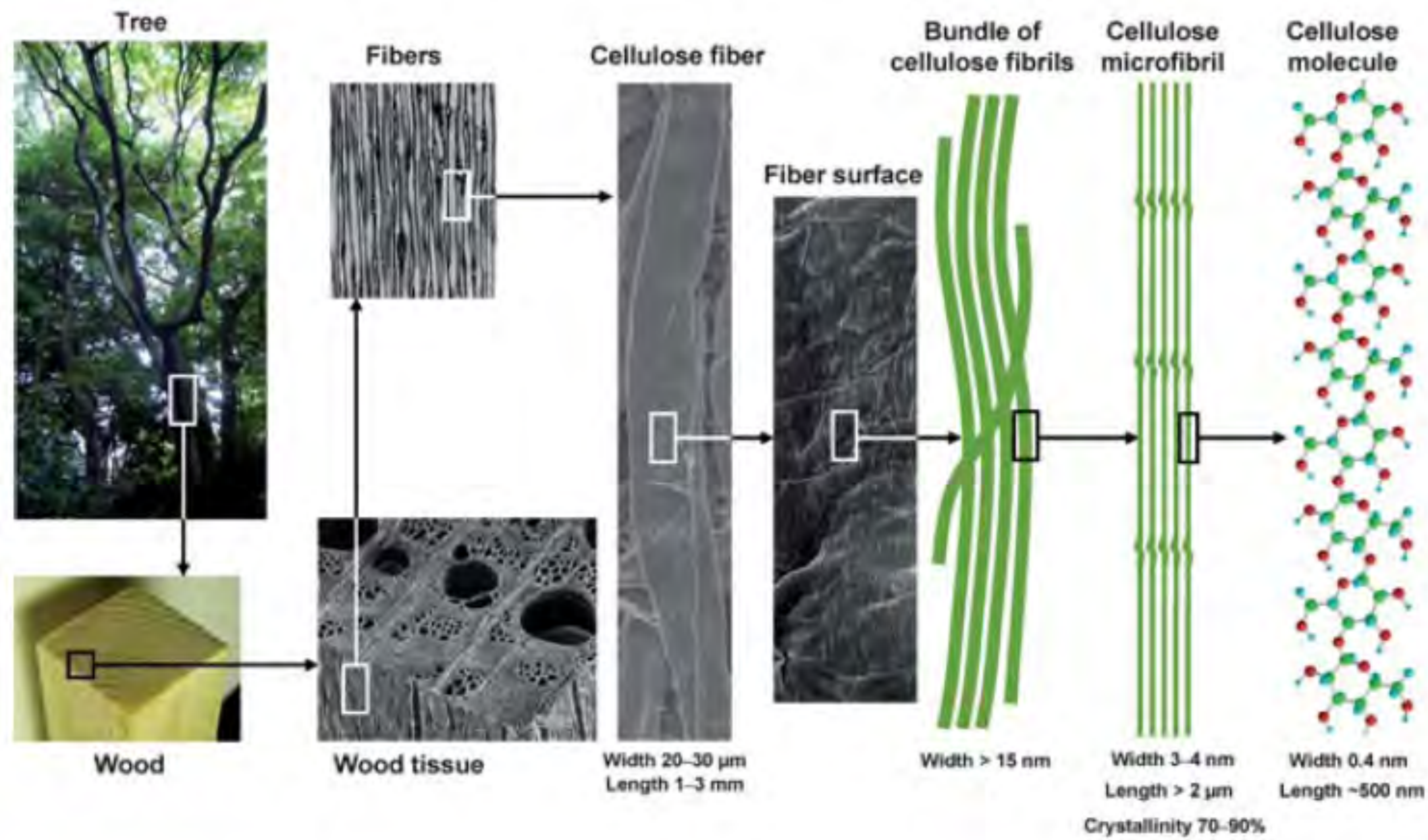
- Cellulose is an organic compound with the formula $(C_6H_{10}0_5)_{n,}$ a molecule consisting of a linear chain of several 100 to over 10,000 B-glycosidic bond linked D-glucose (sugar found in plant) units.
- Cellulose is the most abundant organic polymer on Earth.
- It makes up 40-45% of woods dry weight.
- Cellulose is mainly used to produce paperboard and paper.

Cellulose powder



Cellulose chemical structure

Cellulose Hierarchical Structure

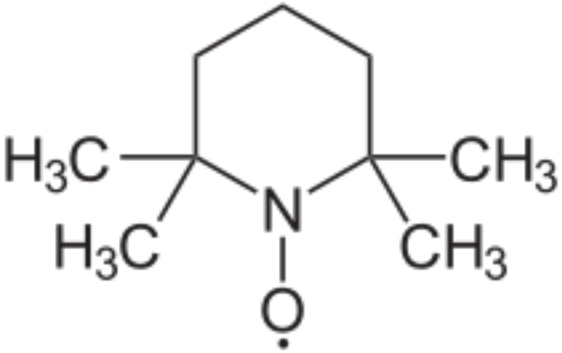


Isogai, Akira, Tsyguyski Saito, and Hayaka Fukuzumi. "Nanoscale." *TEMPO-oxidized cellulose nanofibers*. 3.71 (2011)

2,2,6,6,-Tetramethylpiperidine-1-oxyl radical (TEMPO)

- The TEMPO is a stable radical chemical compound and is the catalyst in the reaction.
- Without TEMPO the reaction can be very slow.

TEMPO pellets



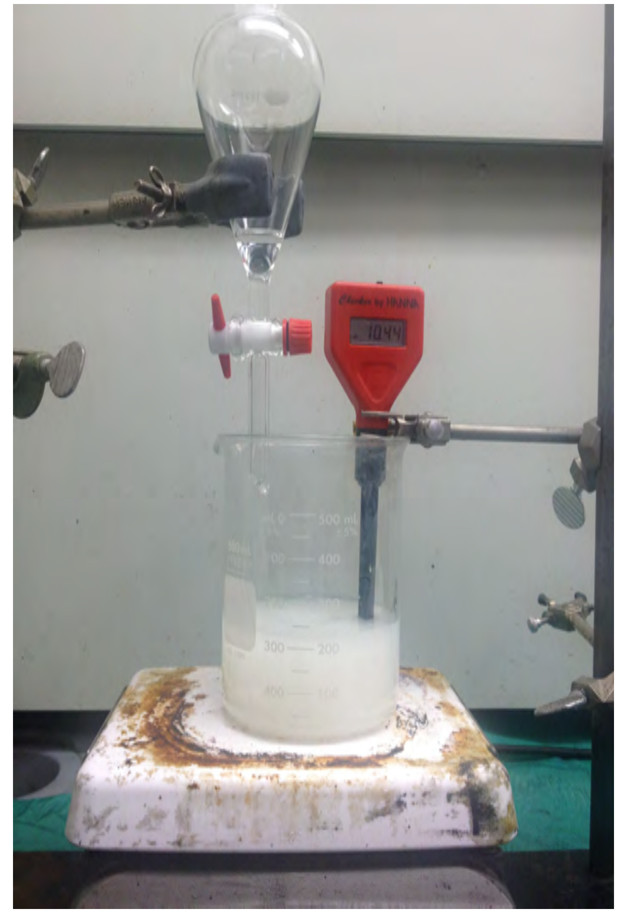
TEMPO chemical structure

Starting the TEMPO-mediated oxidation reaction

- Add 200 mg of Sodium Bromide and 32 mg of TEMPO in 200 mL of deionized water
- Once the TEMPO dissolved, add 2.07 g of microcrystalline cellulose (MCC) powder
- Disperse the powder with magnetic stirring until no large aggregates are showing
- Add 7.45 g of Sodium Hypochlorite solution (10 – 15 %) drop by drop to start the reaction
- Keep the pH level between 10 to 10.5 by adding Sodium Hydroxide solution

TEMPO-mediated oxidation reaction

- TEMPO-mediated oxidation reaction is the first stage of developing cellulose nanowhiskers from wood cellulose fibers.
- The reaction is going with using a magnetic stirring plate to mix the chemicals together for four hours.
- The main purpose of the reaction is to convert the hydroxyl ($-CH_2-OH$) groups on the surface of crystalline cellulose to carboxyl (-COOH) groups.
- During the reaction keeping the pH level between 10-10.5 using sodium hydroxide solution is important.
- Keeping the pH level between 10-10.5 is important to keep the reaction going and to produce well-defined nanowhiskers.
- If the pH level falls below 10 the reaction can take longer or not happen at all, and above 10.5 can damage the whiskers.



Reaction Setup

Washing

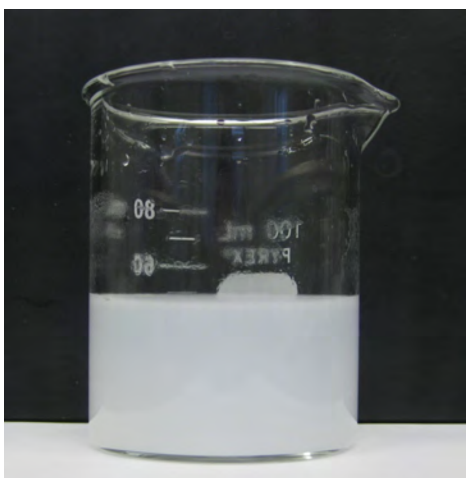
- Washing takes place after the reaction is over to separate the microcrystalline cellulose (MCC) from the water and the chemicals inside the water using a centrifuge.
- A centrifuge is a piece of equipment that spins an object in a rotation at a certain speed.
- Wash the MCC suspension three times with 15 minutes centrifugation each while replacing the DI water after each centrifugation.

Centrifuge

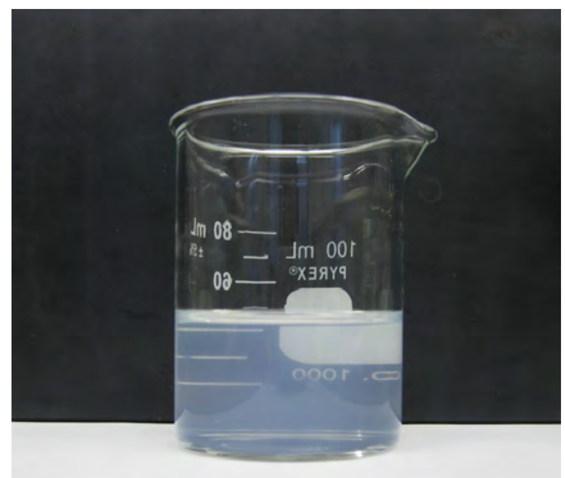
After centrifugation

Sonication

- After washing the MCC, a method called sonication is used to break down the disordered region of the MCC to form nano-sized crystalline structure by using sonic waves.
- This process will cause your MCC suspension to become transparent.



Before Sonication



After Sonication

Freeze Drying

- The first step to freeze drying is to place your CNW samples into a tube filled with dry ice for 15 minutes. You may add acetone to speed up the process. This causes your sample to become frozen.
- The next step is to use a lyophilizer to extract the frozen water out of the CNW for two days
- During these two days the water in the CNW suspension goes through sublimation that converts a substance directly from a solid to gas phase without going through a liquid stage.
- Advantage of freeze drying is to keep the original packing structure of the CNWs in water

After freeze drying

Dispersing CNWs into Epoxy

- Dispersion happens when you mixed CNWs with epoxy resin.
- For epoxy to be greatly reinforced you have to get a good dispersion of CNWs throughout every aspect of the epoxy resin.
- The better the dispersion the stronger the CNWs epoxy composite will be.
- High shear rate mixing and sonication are used to disperse CNWs in epoxy.
- Surfactants were tested for CNW dispersion.

Degassing

- Before curing, it is important to get rid of any bubbles in the CNW-epoxy composite that were caused from high shear rate mixing.
- A large amount of bubbles in your sample will cause your cured samples to be weaker.
- A vacuum degasser was used to remove bubbles by creating pressure to suck out the bubbles in the CNWs epoxy composi

Vacuum Degasser

Preparing for Mechanical Testing

- Once the bubbles are removed you can begin to prepare the dog bone and flexural samples for mechanical testing.
- Hardener has to be added to the CNWs/epoxy mixture and gently mix together for three to five minutes until unify.
- Carefully pour and fill each dog bone and flexural mold with the CNW- epoxy-hardener mixture.
- When finish it has to sit in room temperature for 24 hours and then put in an oven (60 C) for 12 hours for curing.

Mechanical Testing

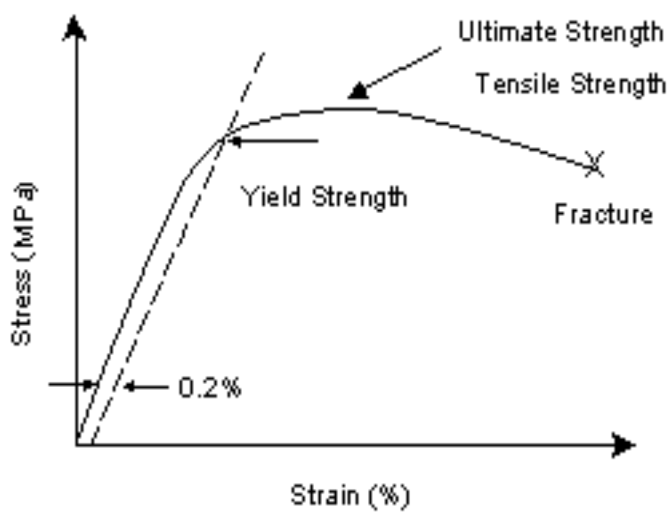
- Mechanical testing involves measuring the width and thickness of your cured CNW-epoxy dog bone and flexural samples using a caliper and using a MTS Insight to measure the tensile properties for the dog bone samples, and flexural properties for the flexural samples.

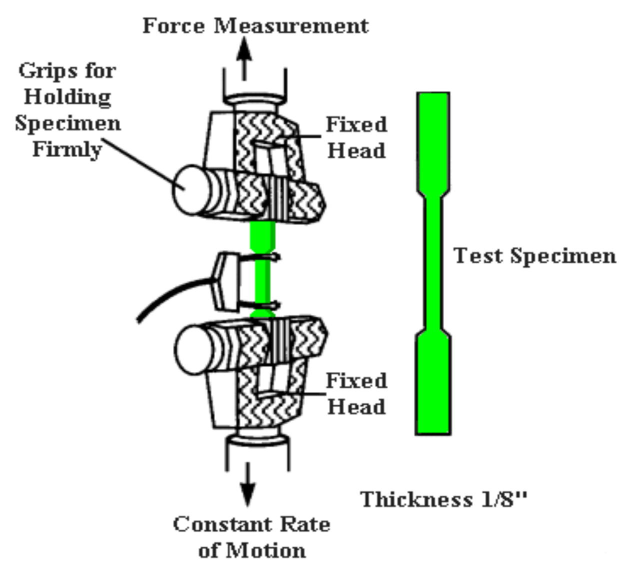
Digital Calipers

MTS Insight

Tensile properties

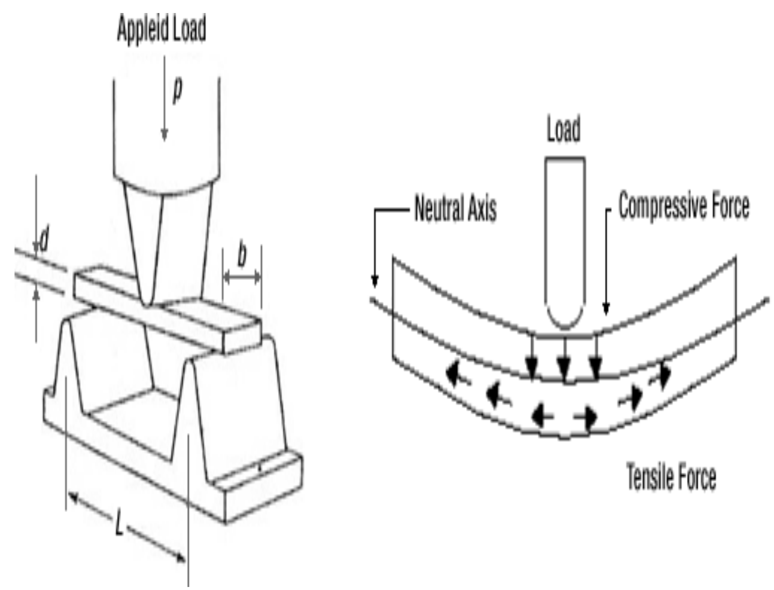
- Ultimate tensile strength measures the maximum stress that a material can stand while being stretched before breaking.
- The ultimate tensile strength is found by recording the stress versus the strain and the highest point of the stress strain curve.
- Tensile modulus measures the stiffness of a material by the ratio of the stress along an axis over the strain of an axis





Flexural properties (3-point bending)

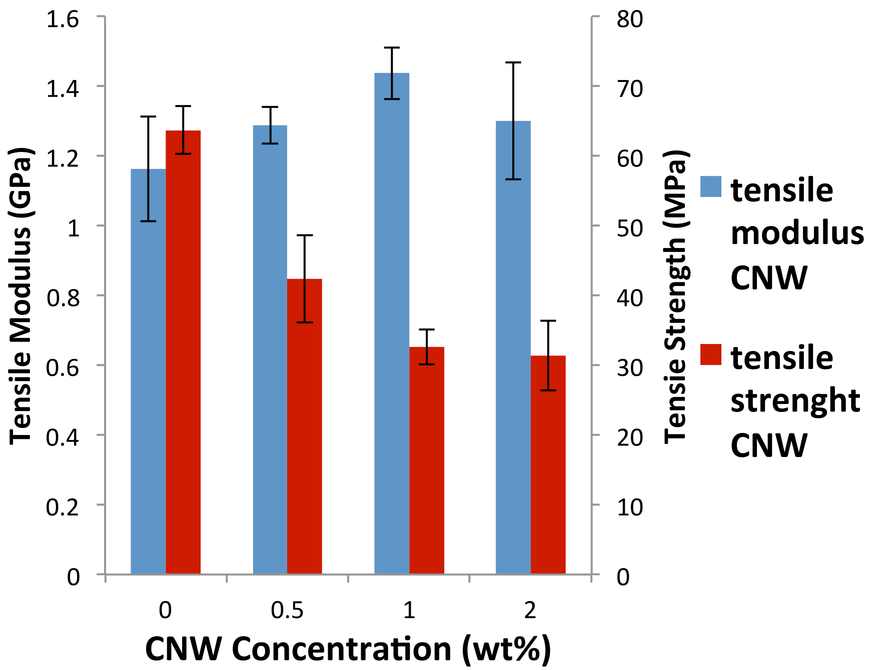
- Flexural strength is measured by how much a material can resist deformation under a load.
- Flexural modulus measures the ratio between stress and strain in the deformation of the flexural sample.

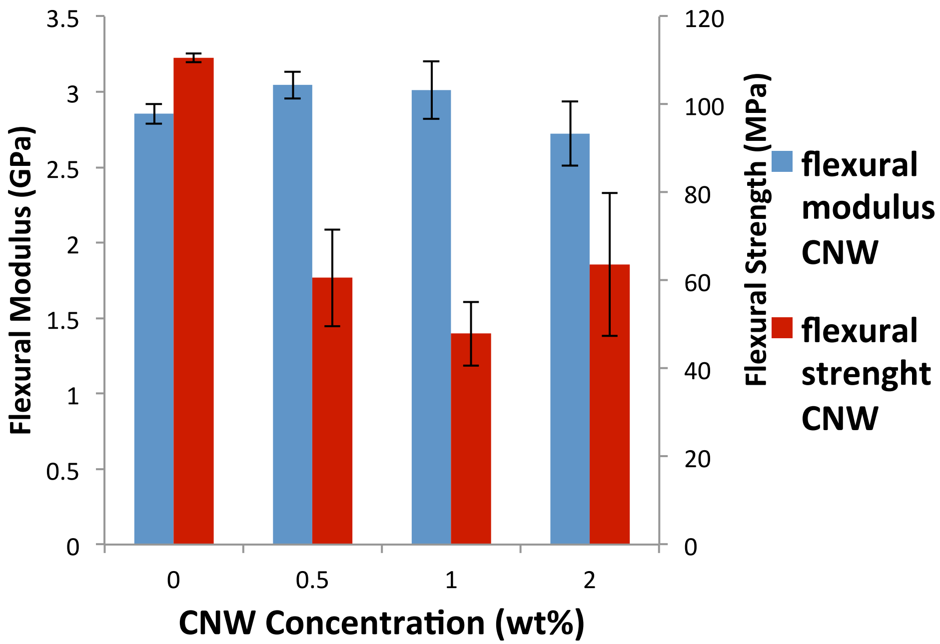


CNW/epoxy composites prepared

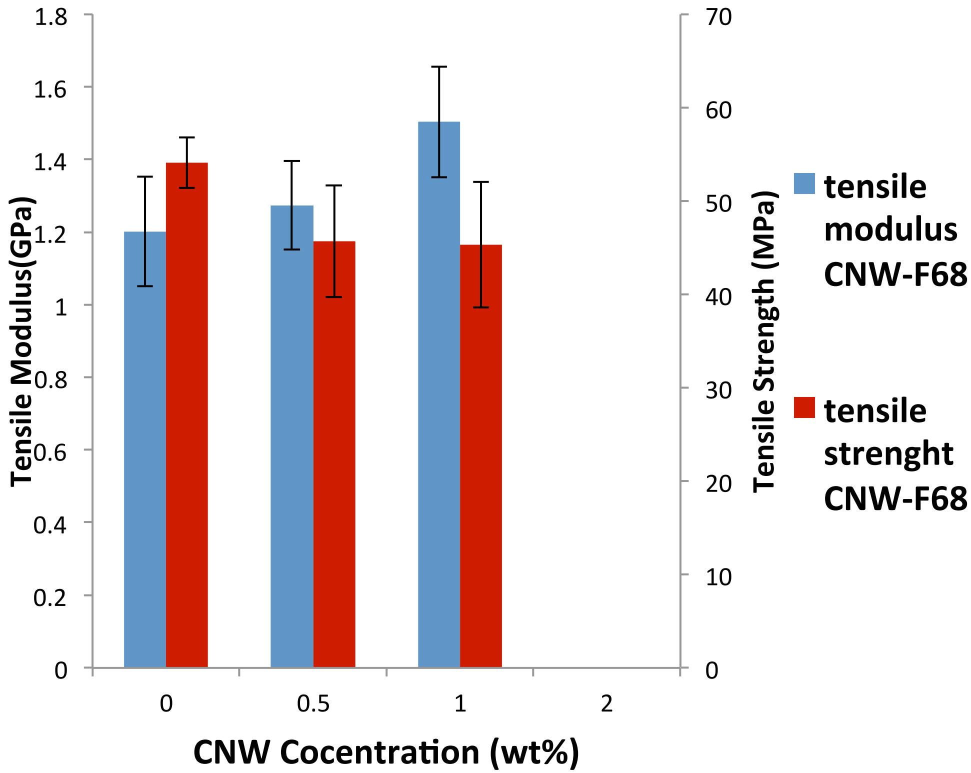
Samples	CNWs	Surfactants	Processing
Control(neat epoxy)	0%	0%	High Shear mixing 2hr, sonication for 30min
0.5wt%CNW	0.5wt%	0%	
1wt%CNW	1wt%	0%	
2wt%CNW	2wt%	0%	
Control (epoxy+F68)	0%	0.5%	
0.5wt%CNW+0.5wt%F68	0.5wt%	0.5wt%	
1wt%CNW+1wt%F68	1wt%	1wt%	
Control (epoxy+F108)	0%	1%	
0.5wt%CNW+0.5wt%F108	0.5wt%	0.5wt%	
1wt%CNW+1wt%F108	1wt%	1wt%	
Control (epoxy+L121)	0%	1%	
0.5wt%CNW+0.5wt%L-121	0.5wt%	0.5wt%	
1wt%CNW+1wt%L-121	1wt%	1wt%	
2wt%CNW+2wt%L-121	2wt%	2wt%	

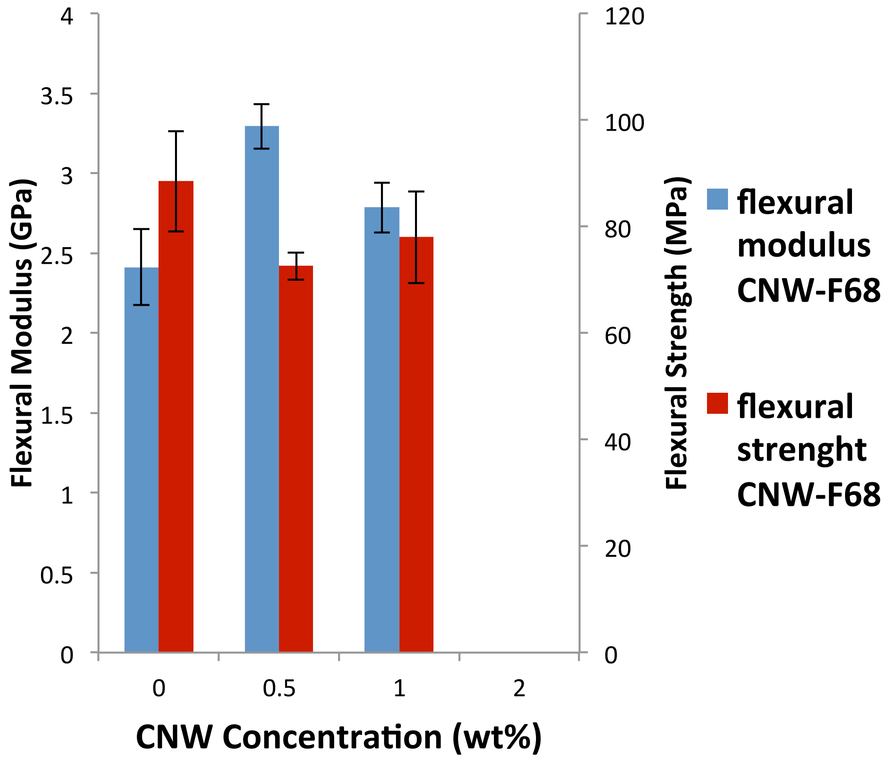
CNW Composites without surfactant



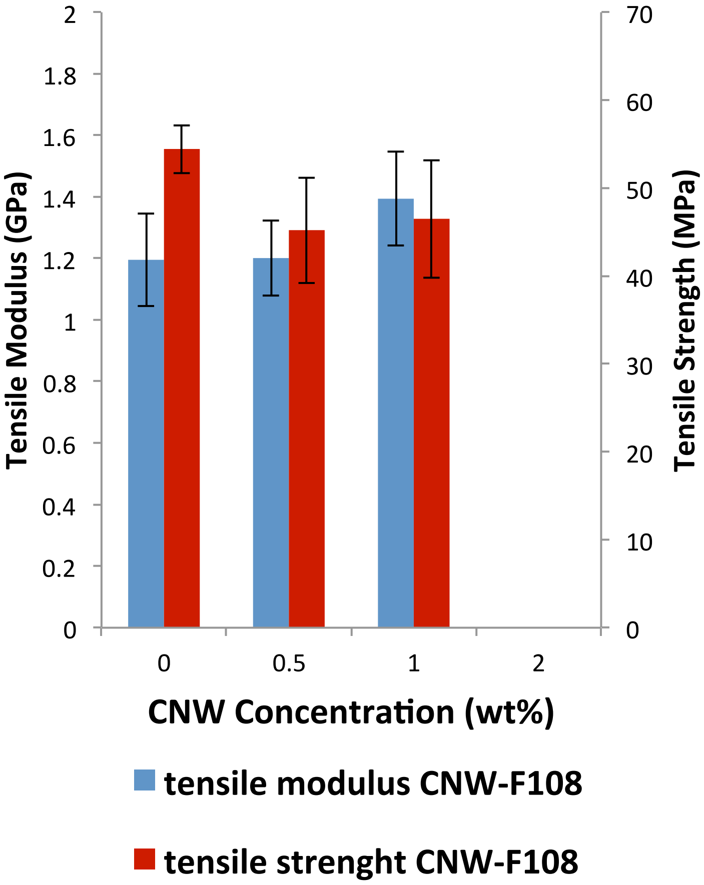


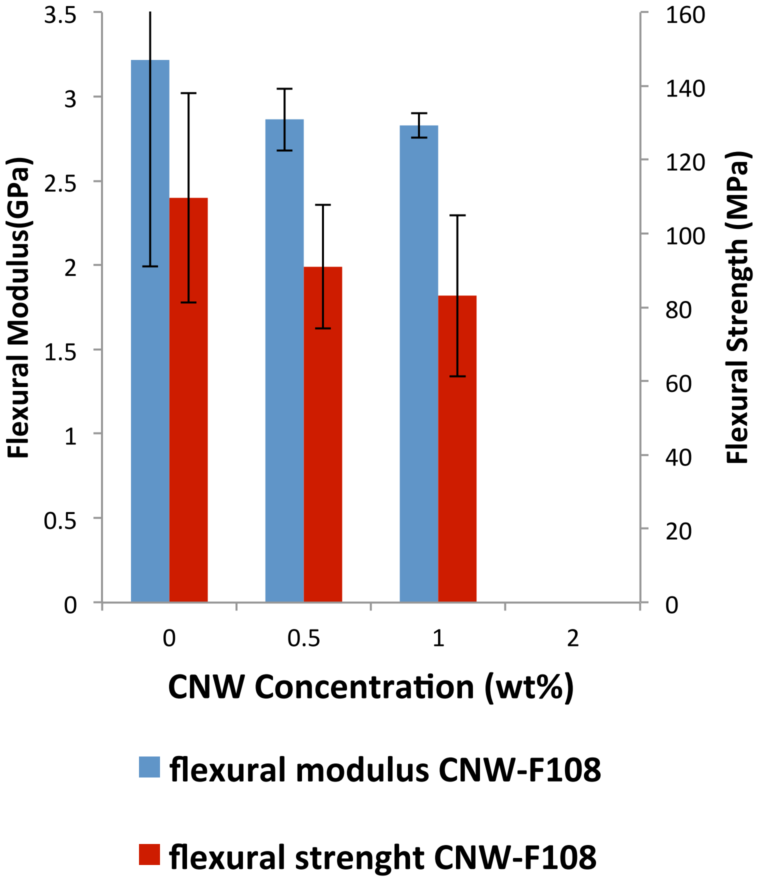
CNW Composites with F68 Surfactant



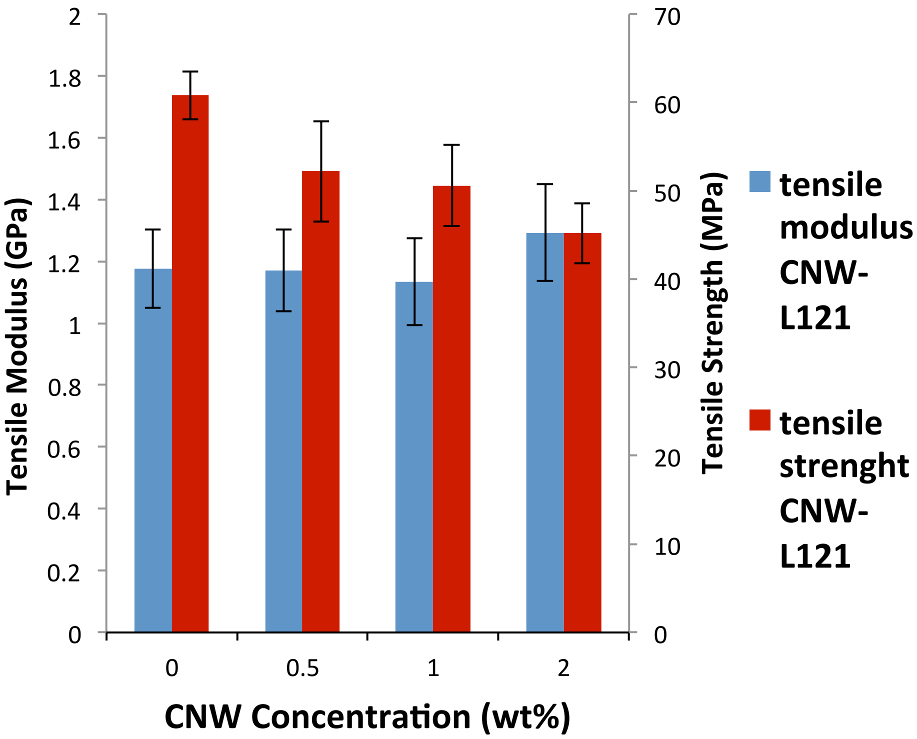


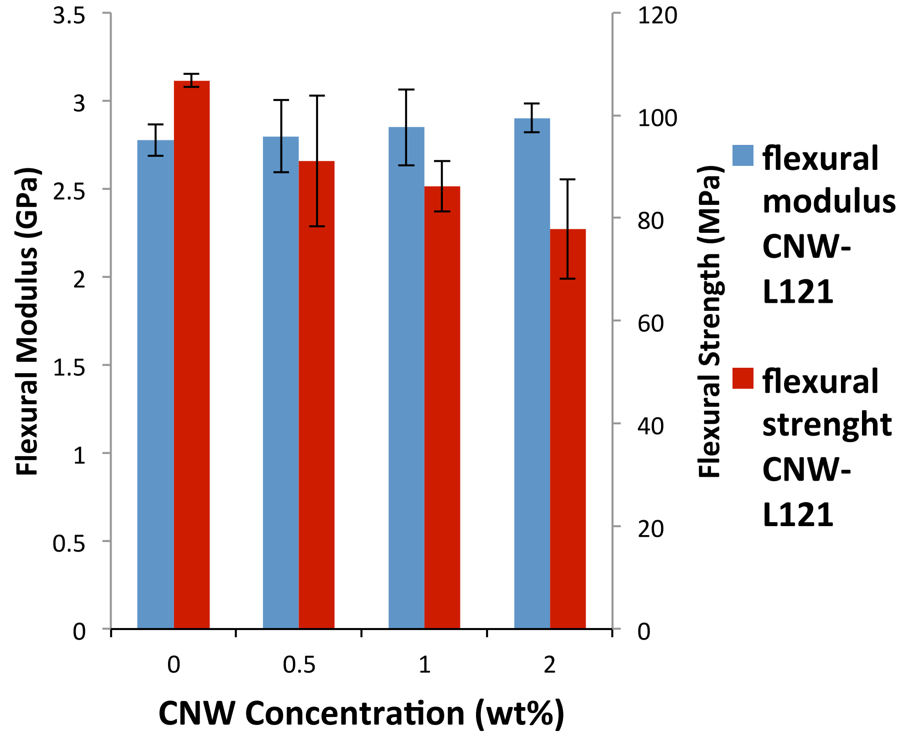
CNW Composites with F-108 surfactant



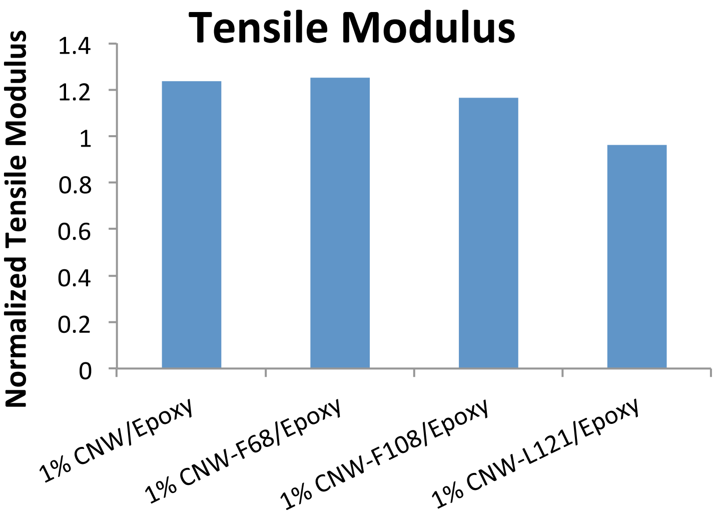


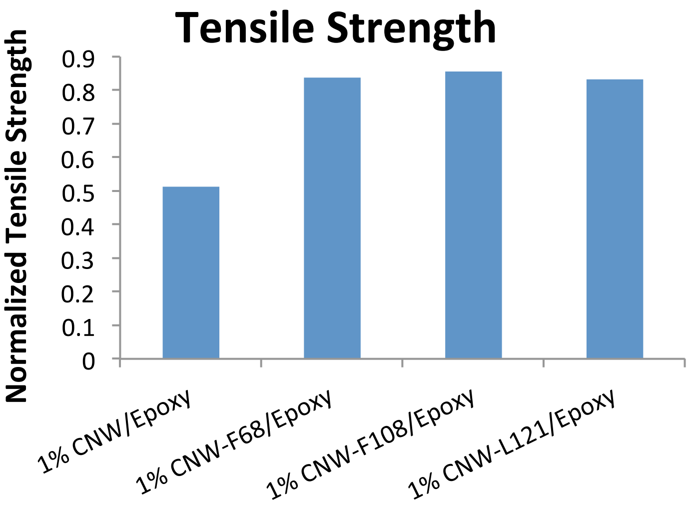
CNW composites with L-121 surfactant

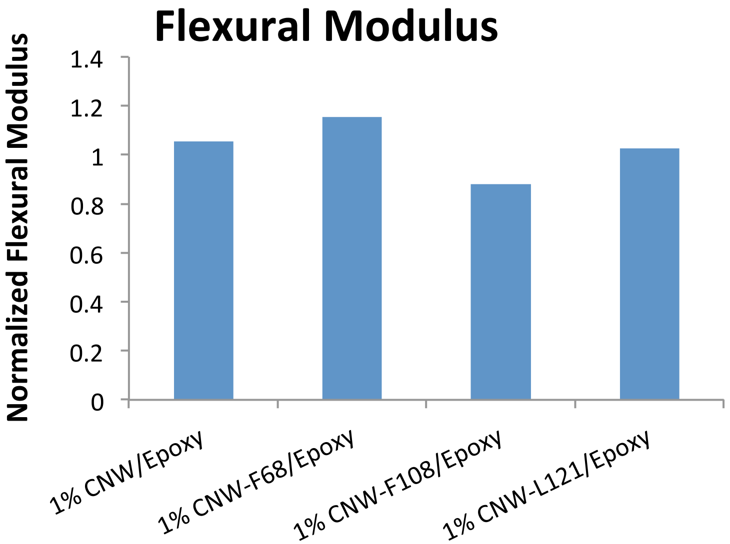


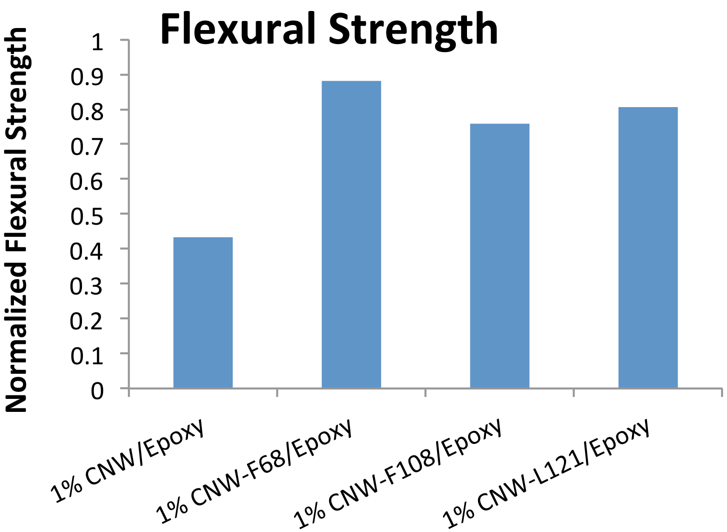


Compare surfactants

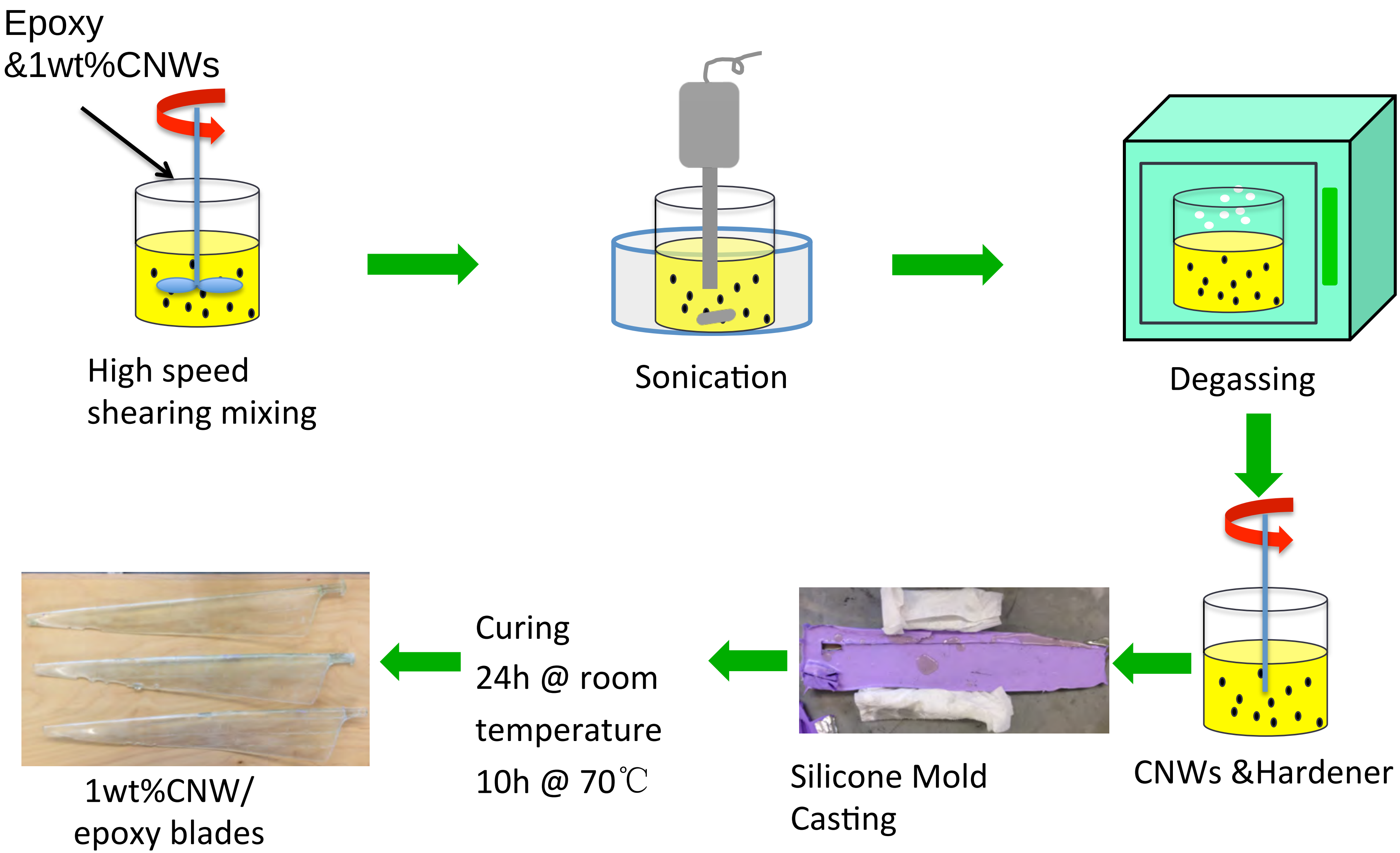








Processing Wind Blades



Conclusions

- The tensile modulus and flexural moduli of CNW/epoxy composites increase when adding a higher concentration of CNWs.
- By adding CNWs the tensile and flexural strength decrease due to uneven dispersion of CNW throughout the epoxy resin.
- The same trend in increasing and then decreasing of the moduli has been observed in the samples containing CNWs in presence of surfactants.
- The extent of modulus reduction in the presence of surfactant is decreased due to improved state of dispersion and better interaction between CNWs and epoxy.
- Composite samples prepared in the presence of Pluronic F-68 as a surfactant show better mechanical properties than other samples.

Future Work

- Continue to work with different concentrations of CNWs with different surfactants (F68, F108, L-61, L-121)
- Continue preparing CNW/epoxy composites with different surfactant-wrapped CNWs and do mechanical testing
- Develop a better silicone mold casting to make better blades

Acknowledgements

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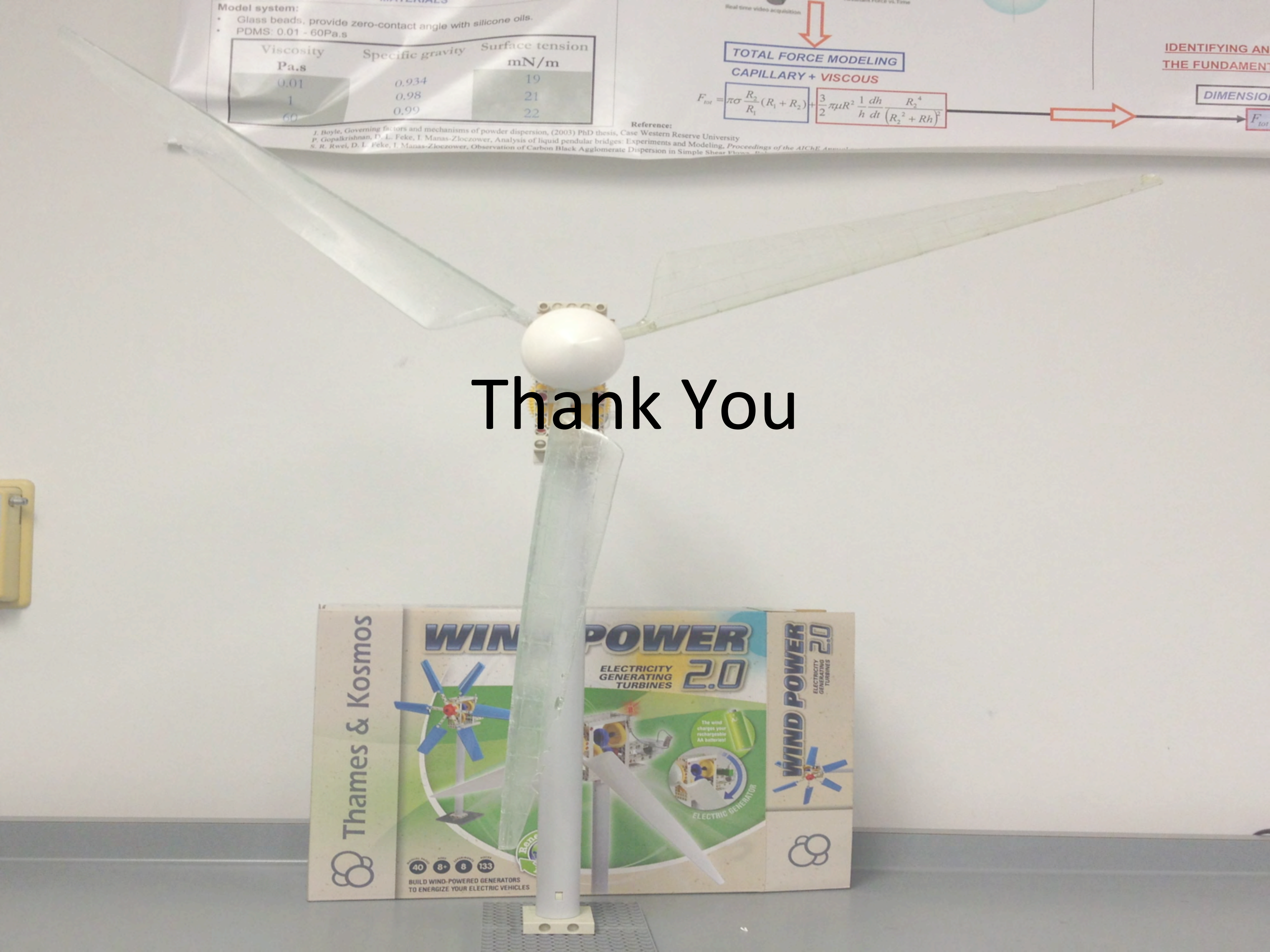
Thank You


Model system:
Glass beads, provide zero-contact angle with silicone oils.
PDMS: 0.01 - 60Pa.s
Viscosity Pa.s
Specific gravity
Surface tension mN/m
0.01
0.934
19
1
0.98
21
60
0.99
22
Reference:
TOTAL FORCE MODELING
CAPILLARY + VISCOUS
Thames & Kosmos
POWER
ELECTRICITY GENERATING TURBINES
2.0
WIND POWER 2.0
ELECTRIC GENERATOR
BUILD WIND-POWERED GENERATORS TO ENERGIZE YOUR ELECTRIC VEHICLES