Temperature and humidity dependent mechanical performance of nanocellulose and its composites

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University of Maine Nanocellulose

• Pilot plant can produce 1 ton per day of CNF at 3% solids

• Distribution of CNC at 12% solids from Forest Product Laboratory in Madison, WI.

• UMaine research scales from nanocellulose study to full-scale wind blade testing.

• UMaine Process Development: umaine.edu/pdc/nanofiber-r-d/

• UMaine Advanced Structures and Composites: composites.umaine.edu
Wet applications

- Particleboard
- Cellubound
- Barrier film
Nano Nano...

The term “nano” is used to describe any particle, or composite thereof, which measures less than 100 nanometers in any one dimension.

SEM 50.38 kX CNC film
CNF vs. CNC

TAPPI (WI3021) is standardizing the terminology

Cellulose Nanocrystal (CNC): A type of cellulose nanofiber with pure crystalline structure, with dimensions of 3 - 10 nm in width, and aspect ratio of greater than 5.

Cellulose Nanofibril (CNF): A type of cellulose nanofiber that contains both crystalline regions and amorphous regions, with dimensions of 5 - 30 nm in width, and aspect ratio usually greater than 50.
Why use CNC and CNF in composites?

• Increased tensile strength properties
• Added dimensional stability in extreme heat and moisture conditions
• Renewable
• Biodegradable
• Broad application
  medical devices
  3D printing
  structural composites
  packaging films
  paper coatings
• Advantage to using nanomaterials in an aqueous system:
  preserves nanoscale by avoiding drying and reducing agglomeration
Why this research is being done

• CNC and CNF have good mechanical properties at 20° C and 50% RH

• What about other environments? These composites will see a broad spectrum of conditions.

...food packaging, for example. Stacks of warehoused cardboard will see creep effects at various environments. This research is based on the assumption that a simple formulation with a common polymer will be predictive. Moisture resistance and therefore strength properties may be improved by adding nanocellulose particles to polyvinyl alcohol (PVA).

• PVA is water soluble and widely utilized → Ideal for aqueous suspensions of CNC and CNF
Figure 1. FE-SEMs of electrospun neat PVA fibers (left) and loaded with 15% of cellulose nanocrystals (right) after equilibration at two different conditions of relative humidity, 0 and 98%, as indicated.

From Peresin et al., Biomacromolecules, 2010
OBJECTIVE

Evaluate the effects of RH and temperature on the mechanical properties of nanocellulose and its composite with PVA
DMA -- Dynamic Mechanical Analyzer

- **Temperature range:**
  - -145 to 600 °C (up to 20°C / min.)

- **Variables:** temperature, time, frequency, stress, force, displacement, strain

- **Sample states:** bulk solid, film, fiber, gel, viscous liquid

- **Interchangeable clamps measure:**
  - modulus (storage, loss, tanδ)
  - damping
  - creep
  - stress relaxation
  - glass transitions
DMA-RH accessory
Preparation of PVA + (CNC or CNF) cast films

5% PVA solubilized in H₂O (90°C, stir 3+ hrs.)
Add suspensions of:
  ● 11.8% CNC – FPL, Madison WI
  ● 3% CNF - UMaine PDC
Ultrasonication - 2 minutes to break up agglomerated bundles of CNC and CNF

Casting
Concentrations of cellulose suspensions in films

<table>
<thead>
<tr>
<th>Material</th>
<th>Cellulose material in dry casting (wt%)</th>
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<tbody>
<tr>
<td>CNC</td>
<td>2</td>
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<tr>
<td></td>
<td>4</td>
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<tr>
<td></td>
<td>6</td>
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<td>8</td>
</tr>
<tr>
<td>CNF</td>
<td>2</td>
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<tr>
<td>PVA</td>
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<td>-</td>
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</tbody>
</table>
Casts dried overnight in fume hood

8% CNC

8% CNF

100% PVA
Static Tension Testing

All treatments at 30°C and either 0%RH or 60%RH:

• 8% CNF, 8% CNC
• 2% CNF, 2% CNC
• 100% CNF
• 100% PVA

= 12 TREATMENTS

Each specimen was equilibrated before testing at a tensile load rate of 20 N / minute (18 N maximum)
CNF – 0% R.H. in Static Tension
CNF – 60% R.H. in Static Tension

![Graph showing stress-strain relationship for CNF and PVA under static tension at 60% R.H.]

- 100% CNF – 60% RH
- 20% CNF – 60% RH
- 8% CNF – 60% RH
- 100% PVA – 60% RH
CNC – 0% R.H. in Static Tension

- 8% CNC – 0% R.H.
- 2% CNC – 0% R.H.
- 100% PVA – 0% R.H.
CNC – 60% R.H. in Static Tension

- 8%CNC – 60%RH
- 100%PVA – 60%RH
- 2%CNC – 60%RH

Stress (MPa) vs. % strain graph.
Bar graph for % reduction in E when RH goes from 0% to 60% of 100%

- For both CNF and PVA:
  - 6.69 GPa
  - 5.62 GPa
  - -16%
  - -40%
Dynamic Tension Testing – Frequency Sweeps and Temperature sweeps

Frequency Sweeps
– Hz from 1 to 100
– strain fixed at 0.05%
– Temp fixed at 30°C
– 5 different RH values from 0% to 80%

Temperature sweeps
– Hz set at 1
– 30°C to 150°C
– temperature ramp at 2°C per min
– strain 0.1%
– No humidity control
Frequency Sweep – 4% CNC

Storage Modulus

- Frequency (Hz)
- $E'\ (\text{MPa})$
  - 3000
  - 3500
  - 4000
  - 4500
  - 5000
  - 5500
  - 6000
- Increased RH
- 0% RH
- 20% RH
- 40% RH
- 60% RH
- 80% RH
Modulus Retention Term

\[ \frac{(E' \text{ at } 30^\circ \text{C}) - (E' \text{ at } X^\circ \text{C})}{(E' \text{ at } 30^\circ \text{C})} \times 100\% \]
AFM in AMFM mode

AMFM = Amplitude Modulation / Frequency Modulation

Utilizes Viscoelastic Mapping tool with the Atomic Force Microscope
100% PVA

Storage Modulus

E’
8% CNC

Storage Modulus

\( E' \)
8% CNF

Storage Modulus
E’
Conclusions

- Both cellulose nanomaterials and the PVA are temperature and humidity sensitive.
- CNF and CNC improve mechanical properties of PVA at any RH and temperature.
- They also improve humidity resistance of the composite formulations.
- Cellulose nanomaterials are far less temperature dependent than PVA as shown by the MRT values.
- AMFM viscoelastic mapping tool can be used to map surface mechanical properties.
Next Steps.....

Continue with:

- Isothermal humidity sweeps of all material manufactured so far
- Isohume temperature sweeps
- Frequency scans at all temperature points and relative humidity points
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Thank you!

Questions?