Transparent composite films of all-cellulose and cellulose-polyvinyl alcohol nanocomposites: Effect of relative humidity and temperature on mechanical performance

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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

All-cellulose nanocomposites

In-situ polymerization of Nylon 66
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
CNC / PVA example: RH study

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
- Study the mechanical properties of all-cellulose nanocomposites
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>
</tr>
</thead>
<tbody>
<tr>
<td>CNC</td>
<td>2  4  6  8</td>
</tr>
<tr>
<td>CNF</td>
<td>2  4  6  8</td>
</tr>
<tr>
<td>PVA</td>
<td>0  -  -  -</td>
</tr>
</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

![Graph showing stress vs. strain for different concentrations of CNF and PVA at 0% R.H.](image-url)
CNF – 60% R.H. in Static Tension
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
Bar graph for E% reduction in E when RH goes from 0% to 60% of 100%
do this for both CNF and PVA

-40%
-16%

Young’s Modulus (E)

GPa

0.38
0.63

5.62
-16%

6.69
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

E' (MPa)

0% RH
20% RH
40% RH
60% RH
80% RH

Increased RH

Frequency (Hz)

1 10 100
Modulus Retention Term

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

100% PVA

Storage Modulus $E'$
8% CNC

Storage Modulus $E'$
8% CNF

Storage Modulus
E'
All Cellulose nanocomposites
Mechanical properties of all cellulose nanocomposites

![Graph showing mechanical properties](214x208)

**Tensile Modulus (MPa)**

**Tensile Strength (MPa)**

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**CNC CONTENT (%)**

- 0%
- 10%
- 20%
- 30%

**TENSILE STRENGTH (MPa)**

- 0 to 160

**TENSILE MODULUS (MPa)**

- 0 to 12,000
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
- Mechanical properties of CNF films can be significantly improved by the addition of CNC
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Thank you!

Questions?