2014

Phase behavior and application studies of cellulose nano-crystals synthesized by acetic acid

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Cellulose Nanocrystal Phase Behavior Studies and Spin-Coating Characterization Techniques

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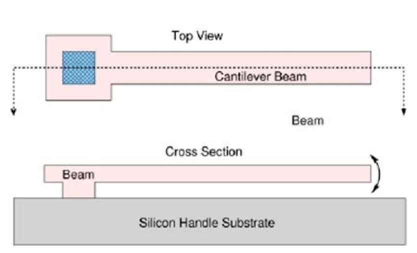
Motivation

- The objective of this research is to determine if cellulose nanocrystal (CNC) dispersions have potential for new bio-based miro-electro mechanical systems (MEMS).
- The MEMS industry is a multi-billion dollar industry that is currently dominated by the use of silicon to build the devices. Cellulose has the potential to be a more sustainable alternative to silicon.

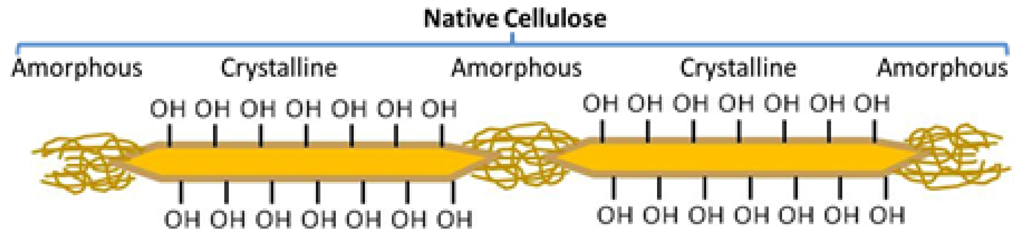
  CNC advantages:
  1. The most abundant biopolymer on the planet
  2. Analogous surface chemistry to hydrophilic silicon oxide, similar mechanical properties to silicon (axial modulus: 1.70 Gpa, bend strength: 10 GPA)[1] and can be fabricated using existing lithographic methods.
  3. Anisotropic property through liquid crystalline self-assembly
- CNC dispersions are processed into films (2-10μm) with tailored properties.
- Lithography will be applied to etch CNC films into MEMS devices as a drop-in alternative to silicon.

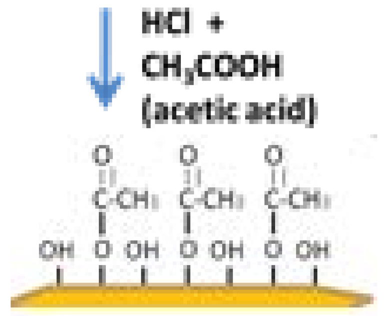


Introduction

Cellulose Nanocrystals (CNC)

- It's the most abundant renewable polymer
- High strength and light weight
- Good optical properties
- **It's hydrophilic** and surface modification is needed in order to make it compatible with organic media.





Synthesis of CNC and surface modification.
Method proposed by Dorgan and Braun 2010.

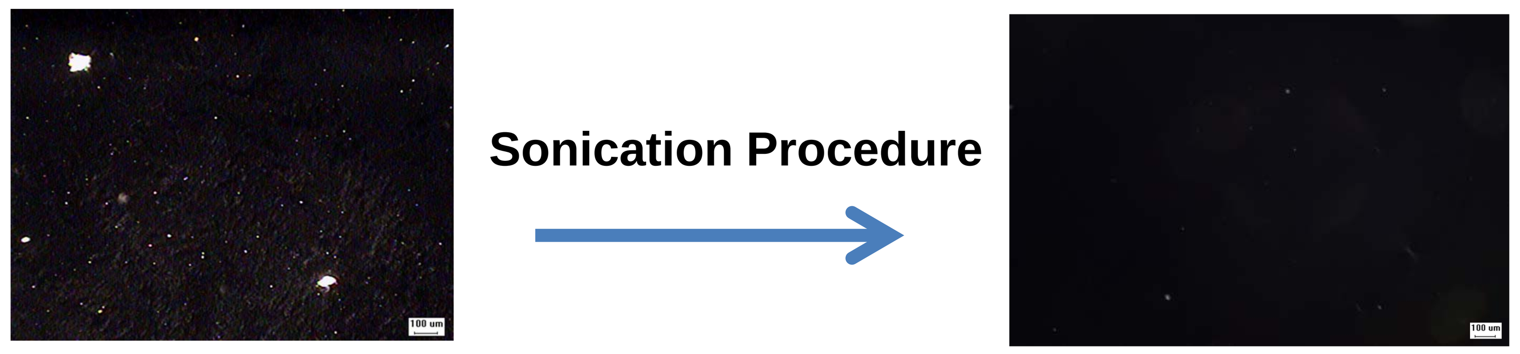
Characterization Methods

- Cross-Polarized Light Microscope was used to capture and record CNC aqueous suspension behavior
- Transmission Electron Microscopy was used to determine existence and structure of the CNC's
- Atomic Force Microscopy was used to characterize spin-coating film

Results

Agglomeration Studies

- The de-agglomeration of the cellulose nano-crystals is essential to its performance and applicability. We discovered an ideal procedure to deagglomerate the cellulose was sonication for 25 minutes (post-synthesis) followed by 3 minute centrifugation. This was determined to best deagglomerate the cellulose "nano-whiskers" without damaging its structural integrity.



a. Agglomerated suspension
b. De-agglomerated suspension

Figure 1.Cross-Polarized Light Microscope Images

CNC-AA Phase Behavior

Figure 4. Cross-polarized film images of CNC-AA after sitting 2 months
a. Low concentrations in 20mL glass vials
b. Higher concentrations in glass cuvettes

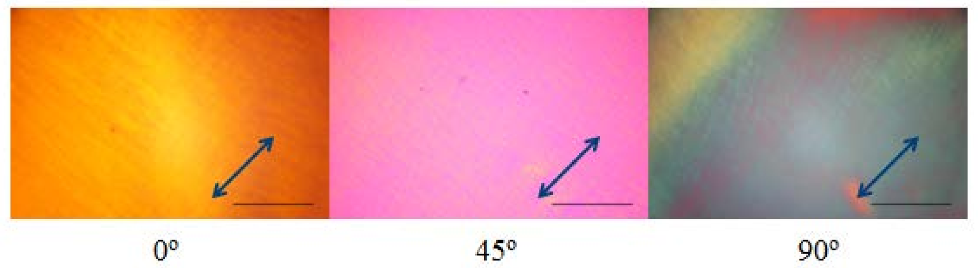
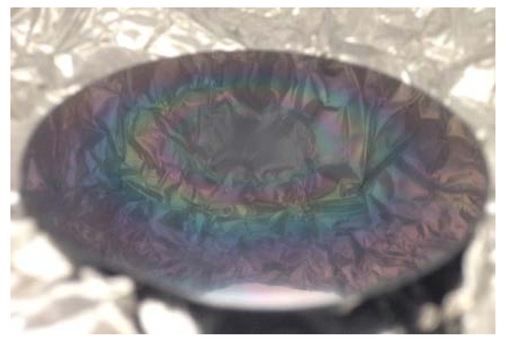


Figure 5. CNC-AA suspension (9.1 % g/ml) liquid crystal pattern rotated from 0 to 90° under the cross-polarized microscope

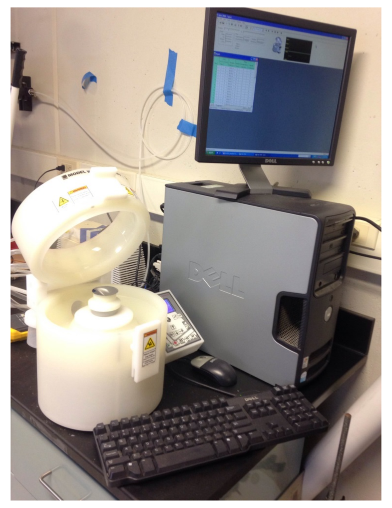
- As seen in Fig. 1a, two months passed before phase separation was observed in the glass vials, and phase separation was seen in CNC-AA concentrations ranging from 0.005-0.3% g/mL. At 0.4% g/mL, total liquid crystal behavior was observed.
- Birefringence was seen in lower concentrations up to 2% g/mL as seen in Fig 1b, but it was more difficult to observe at higher concentrations.
- As seen in Fig. 2, when rotated from 0°- 90° under the cross polarized microscope, the 9.1% g/mL CNC-AA image changed from yellow to blue.
- Measurements taken from a Transmission Electron Microscope image of our cellulose indicated that the average dimensions of the cellulose are 179nm by 40nm.

Spin-coating optimization

- To better synthesize films to create cantilever MEMS devices, the optimum procedure for spin-coating CNC-AA onto silicon wafers has been studied.
- Three Different Procedures were performed
  - Awesome #1
    - 500 rpm/s for 5 seconds, 1500 rpm for 20 seconds
  - Awesome #2
    - 500 rpm/s for 5 seconds, 2500 rpm for 20 seconds
  - Awesome #3
    - 1000 rpm/s for 5 seconds, 2500 rpm for 20 seconds
- Results were analyzed using CLIF interferometer (Clemson Light Imaging Facility)



a. Coated wafer (9.1%)



b. Spin-coater and analysis programs

Figure 6. Spin Coating Equipment

Table 1. Spin Coating Analysis

a. Surface Roughness (μm)

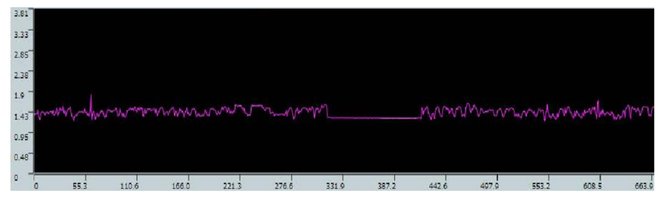
	Awesome #1	Awesome #2	Awesome #3
1.08%	0.022	0.024	0.087
4.5%	0.451	0.438	0.079
9.1%	0.389	0.391	0.043

b. Center Thickness (nm)

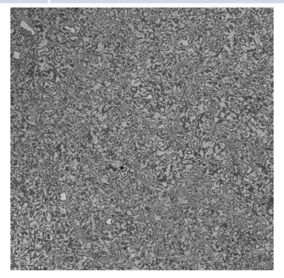
	Awesome #1	Awesome #2	Awesome #3
1.08%	Below 100	Below 100	Below 50
4.5%	400	600	600
9.1%	200	200	150

c. Edge Thickness (nm)

	Awesome #1	Awesome #2	Awesome #3
1.08%	NA	NA	Below 50
4.5%	300	NA	600
9.1%	150	Below 100	200



a. Surface thickness analysis



b. Film Surface Image

Figure 7. CLIFF Interferometer Data

CNC Nano-rods dimensional characterization

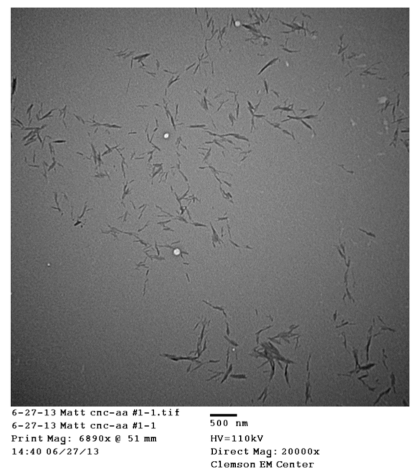


Figure 2. TEM Microscopy proving structural integrity of nano-rods

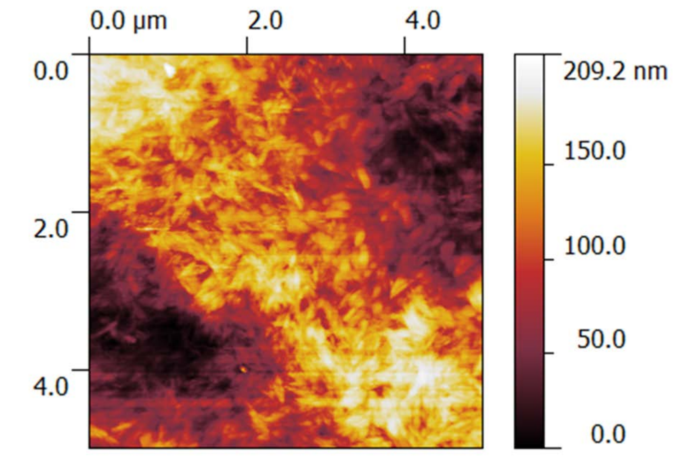


Figure 3. AFM Microscopy of silicon water CNC film

Conclusions

- CNC suspensions were successfully de-agglomerated, which is essential to preserving the mechanical strength and inherent properties of the nano-crystals. Also, micron-sized agglomerates would be detrimental to a MEMS Device.
- The Phase behavior of synthesized CNC's was examined and the optical properties of the suspensions were documented to better understand the CNC phase behavior, which will allow more informed research on its application.
- Research concerning Spin-coating procedures of CNC-AA are on-going, but conclusive evidence shows scarcity of cohesion with single layer low concentrations. Thus multiple layered higher concentration spin-coats will next be studied and analyzed using with Atomic Force Microscopy and CLIF interferometer.

Acknowledgments

National Science Foundation, Award #130825; Devante Horne, Clemson Light Imaging Facility (CLIF); Clemson Creative Inquiry Program

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