West Coast – East Coast: Research in Cellulose Nanotechnology

CELLULOSE NANOCRYSTAL RESEARCH AT OREGON STATE UNIVERSITY

Oregon Wood Innovation Center

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TEM image of a CNXL.
Courtesy of A. Pakzad, R. S. Yassar, Michigan Technological University

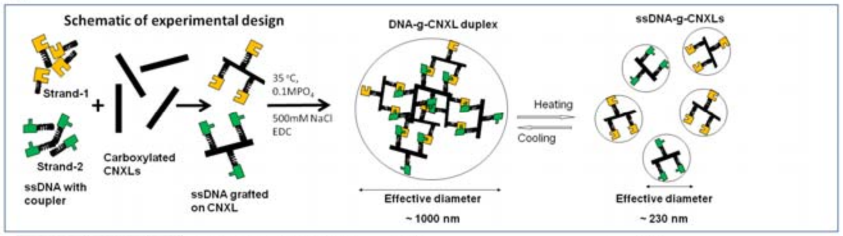
- Cellulose nanocrystals (CNXLs) can be extracted from many sources
- Typical sizes range from 5-20 nm in cross section X 50-2000 nm in length
- Typical modulus values are "stiffer than aluminum" (~150 Gpa)
- Estimated strength values are "stronger than steel" (5-10 Gpa)
- This poster presents two examples of research ongoing at OSU

SEM image of a CNXL aerogel.
Image courtesy of B. Arey, PNNL.

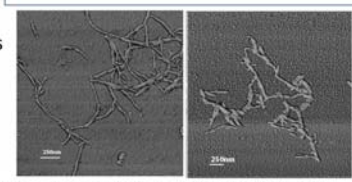
DNA/CELLULOSE HYBRID NANOMATERIALS

A. Mangalam, J. Simonsen and A.S. Benight. Biomacromolecules 10 (2009) 497-504

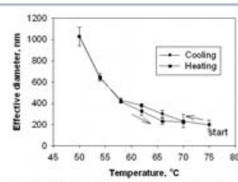
This proof of concept experiment demonstrated that CNXLs could be self-assembled using DNA recognition technology. Both 20-mer and 72-mer DNA oligomers were grafted to carboxylated CNXLs (DNA-g-CNXLs) using the standard carbodiimide reaction. The DNA-g-CNXLs were observed to duplex, i.e. the DNA bonded the CNXLs together at low temperatures, but "melted," or dissociated, at higher temperatures similar to the ungrafted DNA.



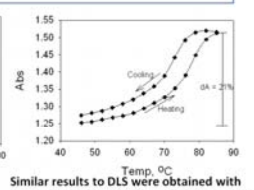
RESULTS



AFM phase images of self assembled duplexed DNA-g-CNXLs on modified silicon wafers. Note varying magnifications in the different images.



Dynamic light scattering thermal scan showing the change in effective size of the DNA-g-CNXL with temperature.



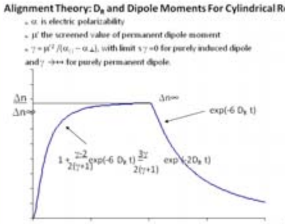
Similar results to DLS were obtained with hyperchromicity UV-VIS thermal scans which showed the DNA "melting" while grafted to the CNXL.

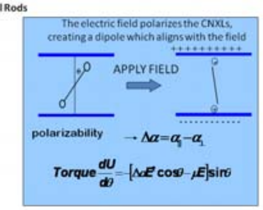
CELLULOSE NANOCRYSTAL SIZE DISTRIBUTION FROM TRANSIENT ELECTRIC BIREFRINGENCE MEASUREMENTS

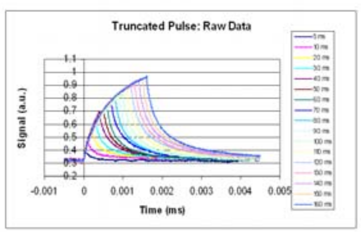
Melissa Taylor[1], John Simonsen[2] and Wei Kong[3]
[1]Materials Science Program, OSU; 2. Dept. of Wood Science and Engineering, OSU; 3. Dept. of Chemistry, OSU

Transient electric birefringence (TEB) results from the alignment in an electric field (E) of an optically anisotropic material. CNXLs are especially birefringent and give a strong TEB response. By recording the alignment due to a series of different pulse lengths (truncated pulses) of constant E, the size distribution of the high aspect ratio CNXLs can be estimated using a least squares regression of the observed rotational diffusion coefficients (D_R).

Alignment Theory: D_R and Dipole Moments For Cylindrical Rods

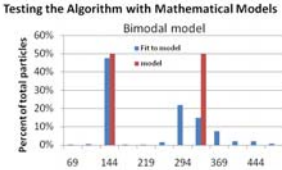




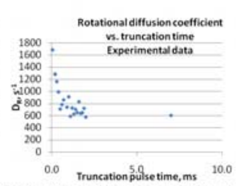


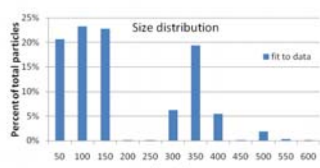
EXPERIMENTAL RESULTS

Testing the Algorithm with Mathematical Models



Carboxylated CNXL experimental sample





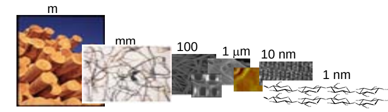
Conclusion: TEB analysis shows a typical sample of carboxylated CNXLs has a largely bimodal distribution with a small component around 100 nm in length and a larger component at about 350 nm length. In this analysis the cross sectional dimension was assumed to be constant at 7 nm.

Bioinspired Sustainable Nanotechnology at Georgia Tech

Georgia Tech

Art Ragauskas (Chemistry & Biochemistry, Institute of Paper Science & Technology): biorefinery chemistry, cellulose nanostructures
Bob Snyder (Materials Science & Engineering): engineering cellulose nanocrystal polymer composites
Rina Tannenbaum (Materials Science & Engineering): in-situ polymerization with cellulosic nanowhiskers
Carson Meredith (Chemical & Biomolecular Engineering): assembly of nanostructured renewable advanced optical materials

"Combining renewable bioresources with natural hierarchical nanoassembly to create novel advanced materials"



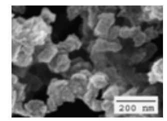
Extraction and application of cellulose nanowhiskers (CNWs) and nanoballs (CNBs)

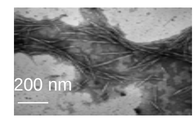
A. Ragauskas

Goal: Develop methods to extract cellulose nanocrystals from bioresources.
Approach: modified hydrolysis of bleached softwood kraft pulp

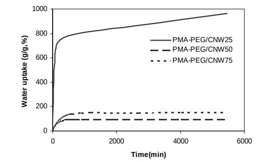
NaOH/DMSO
Acid, Sonication → cellulose nanoballs

Acid → cellulose nanowhiskers

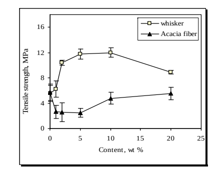




Application 1. CNWs and CNBs form super-absorbent hydrogels with hydrophilic polymers



Application 2. CNWs increase acrylic strength by > 110%



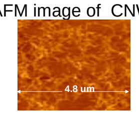
Acknowledgement: NSF EEC-0332554

Chemistry and Processing of Bio-based Multi-Component Nanocomposites

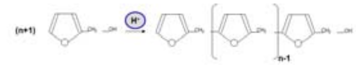
R. Tannenbaum & B. Snyder

Goal 1: explore novel chemical routes to CNW-polymer matrix nanocomposites

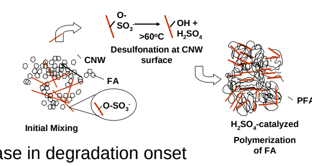
AFM image of CNWs



Approach: in-situ polymerization in presence of polymerizable solvent furfuryl alcohol (FA)



In-situ polymerization ensures a uniform distribution and orientation of the CNW phase.

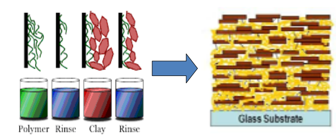


Result: 80 °C increase in degradation onset in polyfurfuryl-CNW nanocomposite

L. A. Pranger and R. Tannenbaum, *Macromolecules* **2008**, *41(22)*, 8682-8687.

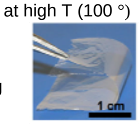
Goal 2: novel processing of CNW/nano-clay/polymer composites

Approach: ***layer-by-layer deposition*** coupled with ***in-situ polymerization***



Step 1. coat alternating monolayers of CNW and nano-kaolin particles in FA.
Step 2. polymerize FA at high T (100 °)

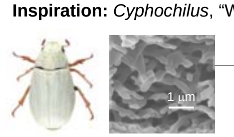
Result: transparent composites with strength approaching that of steel.



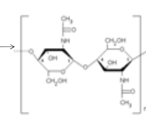
Self-Assembly of cellulose- and chitin-based bio-inspired optical materials

C. Meredith

Inspiration: *Cyphochilus*, "White beetle": Brilliant white due to efficient light scattering[1]

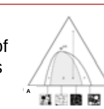


Nanofibrillar chitin: A cellulose analog

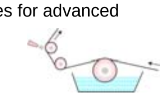


Approach :

(1)Mimic natural assembly of fibrous nanostructures



(2)Scale-up processes for advanced materials and paper



Applications for high brightness & whiteness

1. paper – use chitin or cellulose nanofibrils as green replacements of energy-intensive, nonrenewable whitening and sizing agents
2. renewable OLEDs, sensors

1. Vukusic et al. Science 315, 348 (2007)
2. Lee et al. JACS *131*, 5048 (2009)

Acknowledgement: IPST@GaTech