Status of Applications of Cellulose Nanomaterials US and the World

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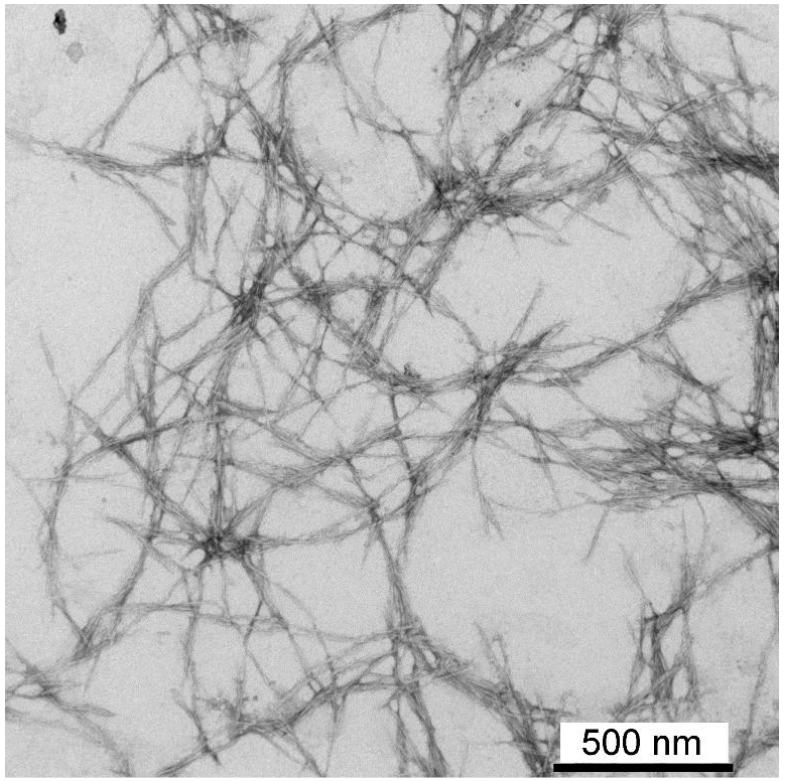
3 Types of Celluloe Nano Materials

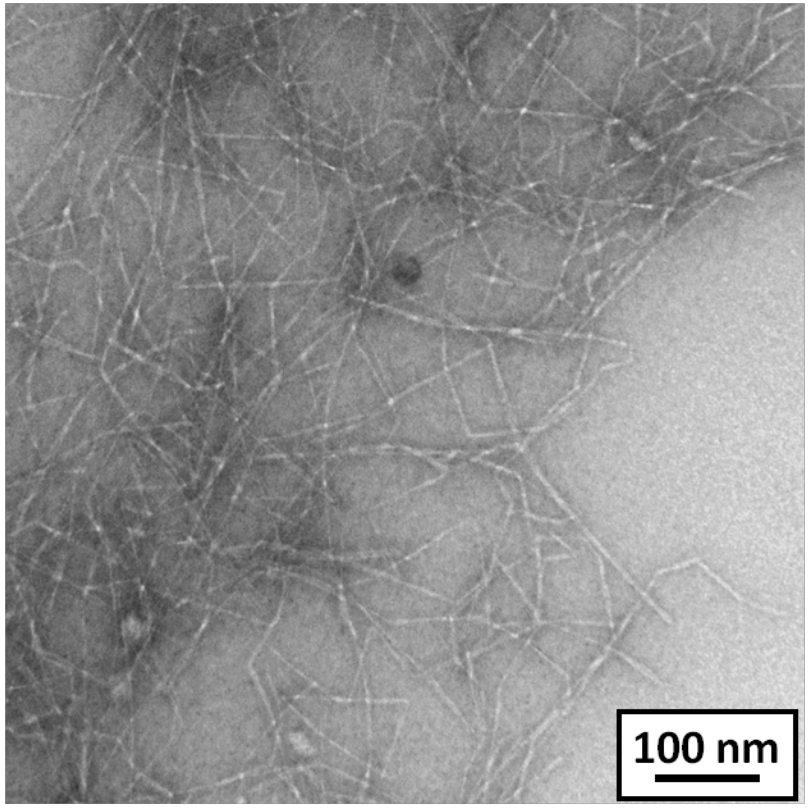
- Crystals – rod shaped particles approximately 6 nm in diameter and 100 nm long. Because crystals are reinforced by the H-bonding that maintains the crystalline order, this is the strongest for of CN
- Chemical fibrils – string or spaghetti-like particles approximately 6 nm in diameter and 1-2 microns long. Generally thought to be linear.
- Mechanical fibrils – A mixture of fibril ranging from 10-20 nm diameter up to 300-500 nm. Fibrils are not completely separated so the particles are branched and possibly cross linked.

Cellulose Nano-particle Images

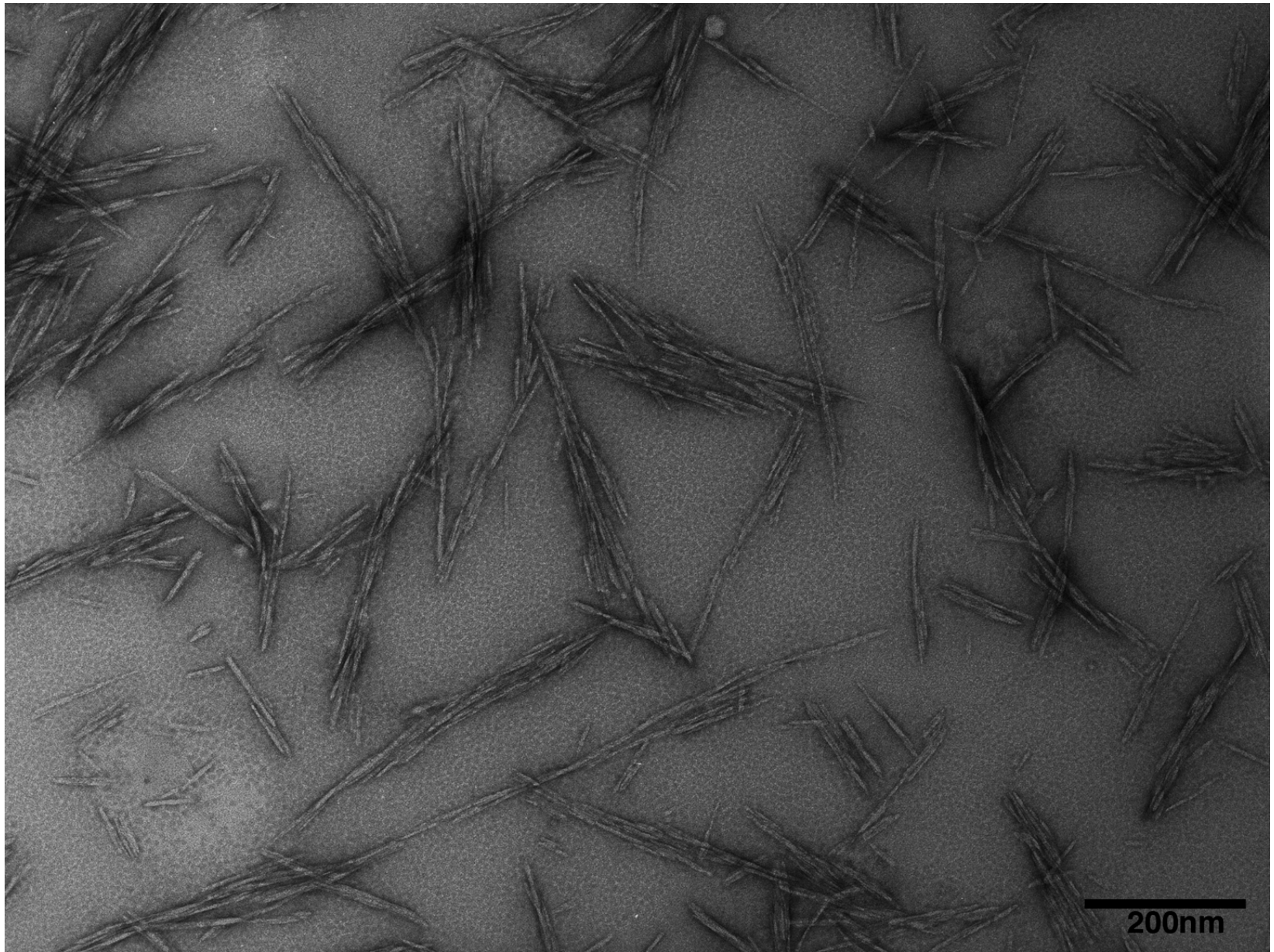
Mechanical



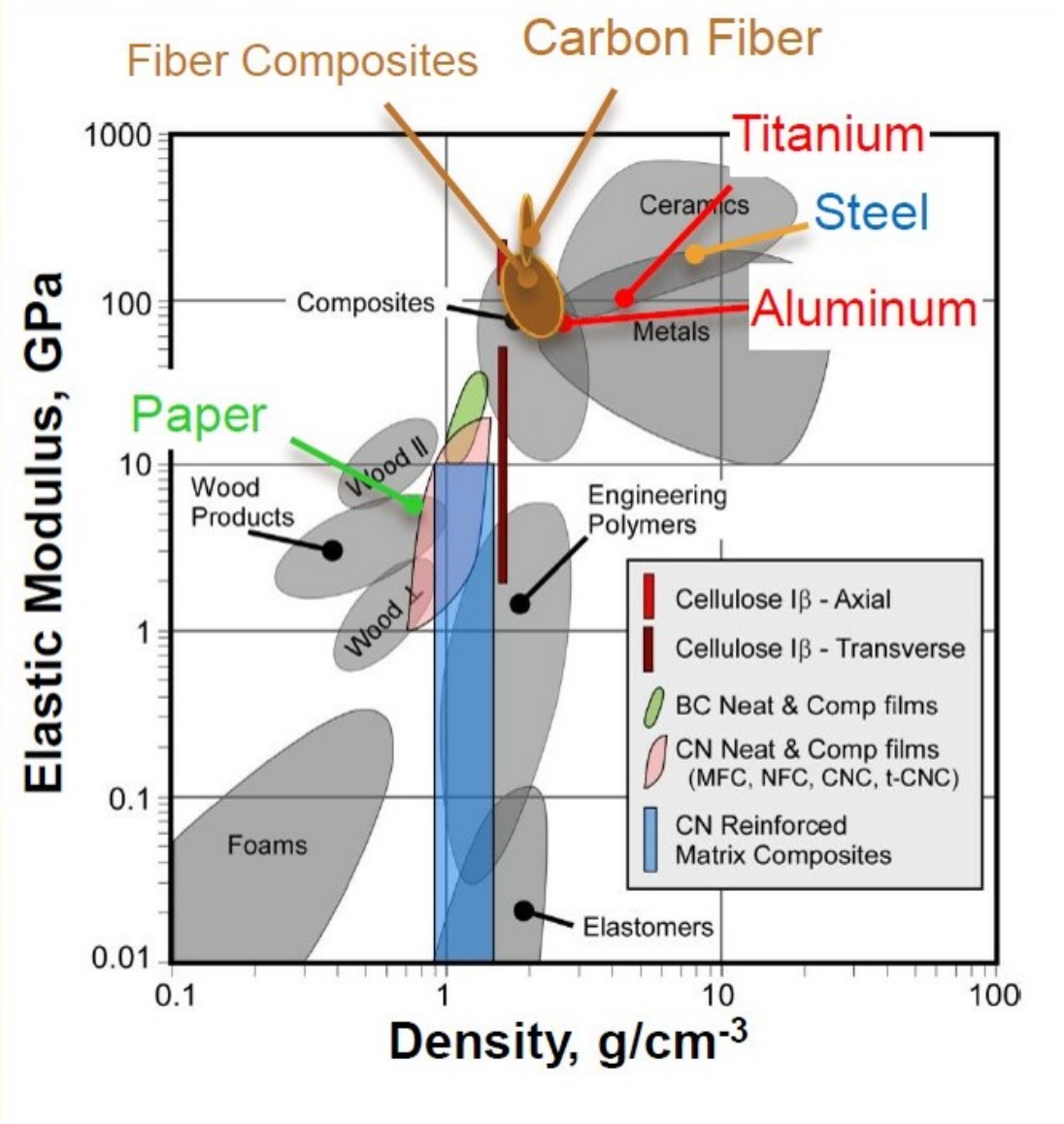
TEMPO CNF



CNC



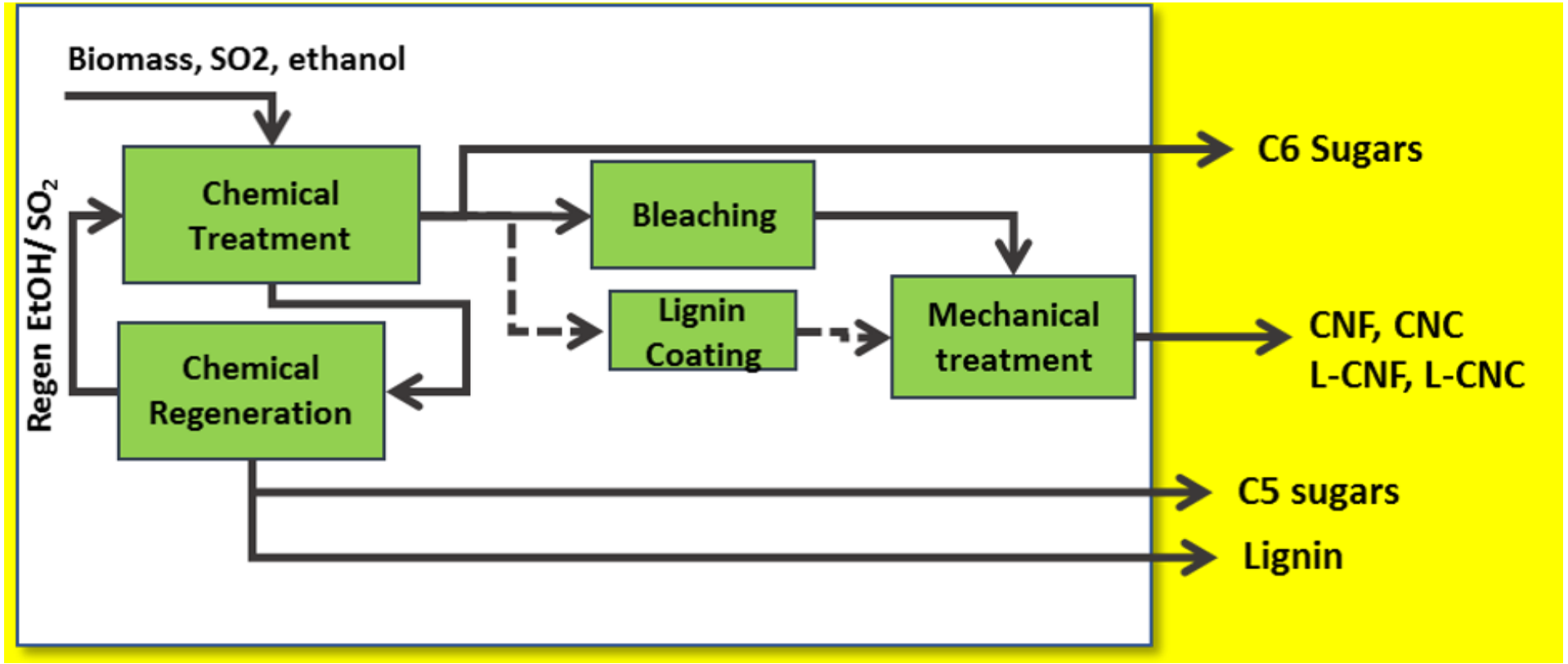
Elastic Modulus of Cellulose Nano-Materials



Producers

- American Process Inc. now GranBio
- University of Maine
- The U.S. Forest Service
- Product developments

GranBio: BioPlus® with AVAP®



CN Products Summary

	AVAP® CNC	AVAP® CNF	GreenBox® CNF
Feedstock	Any Biomass		
CN Yield	25%	42%	80-90%
Treatment	SO_2 and Ethanol	SO_2 and Ethanol	Water
Cellulose	100% (85%)	100% (94%)	50%
Hemicellulose	0	0	14%
Lignin	0 (15%)	0 (6%)	36%
Market	Performance Materials	Performance Materials	Commodities

Joint Venture with GL&V

- One ton per day mechanically produced CNF
- Uses paper industry stock preparation refiners with specialized refiner plates.
- U. Maine and the Turner Falls installation operated in a batch recirculation mode.
- The University of Maine is also the retail sales agent for the cellulose nanomaterials produced by Maine, and by the Forest Products Laboratory.

Forest Products Laboratory

- Pilot plant commissioned in 2012
- Produces sulfuric acid cellulose nanocrystals at 25 kg per batch
- Produces the TEMPO form of cellulose nanofibrils at 4 kg per batch
- FPL has been the bulk supplier of CNC and t-CNF to the University of Maine.

Delivery

- Sold by Maine:
- 687 pounds (308 kg) of CNC
- 11 pounds (5 kg) of t-CNF have been sold by Maine.
- 4 samples of CNC suspension and 10 samples of freeze dried CNC have been purchased by scientists in Japan. 1 sample of freeze dried t-CNF was purchased by a scientist in Japan.

The materials: Cellulose nanoCrystal

- Initially – 1949: Low concentration sulfuric acid to what was referred to at the time as the limiting degree of polymerization.
- Currently – 60-65% sulfuric acid
  - Concentrated sulfuric acid is a solvent for cellulose. 60-65% is the range where it will dissolve amorphous cellulose but not the crystalline regions.

TEMPO CNF

- FPL uses a scaled up version of the process developed by Professor Isogai at the University of Tokyo.
- 400 Liter stirred reactor
- 800 Liter pressure filter for collecting and washing the TEMPO treated wood pulp
- 3-valve homogenizer
- Membrane filtration system to concentrate.

Advanced level Applications

- Oil well drilling
- Concrete (Purdue/Oregon State University)
- Cosmetics
- Fiberglass (Georgia Institute of Technology)

Research

- PLA (FPL, Purdue, CAU/GT, nearly everyone)
- Epoxy (FPL, GT, ARL)
- Polyester, nylon
- PP/PE (Nearly everyone)
- Oil well applications (LSU)
- Barrier coatings (Maine)
- Films and film laminates (Purdue)
- Thread, reinforcing fibers (Purdue and GT)

Products

What	Type	How	Who	Where
Pen Ink	t-CNF	Shear thinning	DKS and UniBal	Japan
Toilet wipe	m-CNF	entanglement	Daio & Tentco Paper	Japan
Diapers	t-CNF	film	Nippon	Japan
Oil Wells drilling	CNC	Rheology/dispersant	Schlumberger	Canada/US
Running shoe	CNF	foam	Seiko PMC	Japan
Paper	M-CNF	Coating, or mixing	Some/many	NA, Europe, Asia

US vs the World

- US:
  - (CNC, t-CNF, m-CNF).
  - Not a lot of coordination between funding agencies. Generally not dedicated to Cellulosic nanomaterials
  - FS + US. Endowment P^3 grants are the exception: ~ $7 Million in three RFP
- Japan:
  - Largely CNF.
  - Large government and corporate level support.
  - Highly targeted at specialty applications
- Europe:
  - Largely CNF.
  - Scandinavian countries all have extensive government support.
  - Targeted at paper grades
- Canada:
  - CNC and m-CNF.
  - Extensive government support (>$50 million).
  - Both specialties and commodities.

Conclusion

- In spite of a less organized and less well funded process, U.S. Scientists are contributing to the science and applications of cellulose nanomaterials.
- In comparison, Japan has 6 or more, Canada at least two, and Scandinavia presumably several, incorporating in existing products and new products.
- In terms of large market applications – fiber glass and concrete, US R&D shows great promise; paper and other functional additives internationally.

Generally Regarded as Safe

- A consortium of potential producers and potential users is supporting an application to NIH for GRAS status.
- Feeding studies of CNF have been completed.
- Fiber is known to reduce cholesterol. This is the only observable impact of the addition of CNF to the animals diet.
- To date, inhalation studies have been inconclusive but generally, at low and probably realistic exposure levels, there has been nothing observed beyond (shorter) term inflammation.
- Does not seem to fit the fiber paradigm and behaves more like PSLT dust.

International Standards Development in Cellulose Nanomaterials

- ISO TC229 Nanotechnologies
  - Published ISO/TR 19716 Nanotechnologies – Characterization of cellulose nanocrystals published in 2016.
  - Published ISO/TS 20477 Nanotechnologies – Standard terms and their definition for cellulose nanomaterials published in 2017.
  - There are currently three other projects in ISO TC229 either waiting for publication or in the developmental stage.
- ISO TC6 Pulp, paper and board
  - Broadened their scope to include cellulose nanomaterials.
  - Added cellulose nanomaterials in some of the existing standards.

International Standards Development in Cellulose Nanomaterials

- Canadian Standards Association (CSA)
  - CSA-Z5100-17 Cellulose nanomaterials-Test methods for characterization published in 2017.
  - CSA –Z5200-17 Cellulose nanomaterials-Blank detail specifications published in 2017.
  - The Canadian government considers international standards development to be a key action to commercialize cellulose nanomaterials.
- The Technical Association of the Pulp and Paper Industry (TAPPI)
  - No active projects.
- International standards reflect the status of nanotechnology development in different areas.

Forest Service and NNI

- The mission of the Forest Service is “To sustain the health, diversity, and productivity of the Nation's forests and grasslands to meet the needs of present and future generations”. We administer the nation's 154 national forests and 20 national grasslands, which encompass 193 million acres.
- We are one of the smaller NNI participating agencies. We review our NNI investments against our mission and the value in return.
- NNI can connect us to stakeholder outside our traditional network.

Forest Service and NNI

- Cellulose nanomaterials – A Path towards Commercialization workshop in May 2014, co-sponsored by the FS and the NNI.
  - About 130 experts from government, industry and academia attended the workshop.
  - Workshop participants shared and discussed commercialization barriers from their perspectives.
- The APPTI Advancing Commercialization of Nanocellulose: Critical Challenges Workshop, in collaboration with the FS and the NNI, in support of the Sustainable Manufacturing Signature Initiative, May 2019.
  - This industry-lead workshop is a follow-up to the May 2014 workshop.
  - The workshop focused on dewatering-drying and compatibilization of cellulose nanomaterials, both are barriers identified in the 2014 workshop.
  - About 50 people attended the workshop.

NNI and other National Initiatives from the FS Perspective

- The Bioeconomy Initiative
  - More and more products will be produced from renewable (bio) materials.
  - Renewable (bio) materials from the forest and agricultural sources will be a major contributor towards a bioeconomy.
- Manufacturing USA®
  - VTT in Finland is a major research organization in cellulose nanomaterials and other renewable polymers from wood.
  - RISE in Sweden has a division on renewable (bio) polymers from wood.
  - Fraunhofer has a wood research institute and has renewable polymer research in a few other institutes.
  - ITRI in Taiwan is interested in renewable (bio) polymers from wood per request from their customers.
  - AIST in Japan provides secretarial service or leadership to the Japan Nanocellulose Forum and internationals standards development in cellulose nanomaterials.