Cellulose Nanomaterials

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Research Roadmap

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Inside Cover

Acknowledgments

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This roadmap was created through the work of many individuals representing pulp and paper companies, industry suppliers, government agencies, universities, and other organizations. A full list of contributors can be found in Appendix D.

The principle writers were Victoria Brun and Fred Hansen of Energetics Incorporated, David Turpin, Kathleen Bennett, and several members of the Agenda 2020 Cellulose Nanomaterials Team. The document was designed by Julie Chappell of Energetics Incorporated.

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Executive Summary

During the 20th century, global economic development drove an eight-fold increase in global materials use. At the same time, there was a shift from the dominance of renewable biomass toward mineral and petroleum materials, such that non-renewable resources now account for more than 70% of total materials use.[1] As this trend continues, resources once easy to extract will become more difficult to find. Real concerns are emerging about longer-term sustainability of many materials. New, sustainable approaches are required to meet the needs of the growing global population.

Cellulose Nanomaterials Roadmap

Cellulose nanomaterials demonstrate great potential for meeting the need for new, sustainable approaches and products. They have a variety of unique distinguishing properties—including high strength, high absorbency, low densities, and self-assembly properties—that makes them promising for an array of commercial applications. In addition, because of their feedstock's abundance, they potentially could be sustainably and renewably produced in quantities of tens of millions of tons per year.

The range of potential applications of cellulose nanomaterials is substantial and provides a great opportunity to develop new biobased products that complement the industry's traditional pulp, paper, and paperboard products. Developing cellulose nanomaterials also aligns with national priorities, particularly in the area of developing new advanced manufacturing technologies and maintaining healthy, resilient forests.

This roadmap—which is part of a series of five Agenda 2020 roadmaps—specifically targets cellulose nanomaterials to develop new biobased products. The Agenda 2020 Cellulose Nanomaterials Team envisions a materials revolution, in which new market entries made from cellulose nanomaterials derived from sustainable, renewable forest resources are in wide use, supporting the everyday lives of millions around the globe.

This roadmap presents six concrete R&D projects that can help facilitate rapid commercialization of cellulose nanomaterials.

Agenda 2020's Strategy

Agenda 2020 utilized a methodical strategy (see Figure ES-1) to identify the R&D projects that will best achieve its vision and address industry needs. The Agenda 2020 Cellulose Nanomaterials Team first conducted an extensive assessment of the nanocellulose landscape in terms of current practices and technologies, potential applications of cellulose nanomaterials, and current challenges restricting commercialization. The team then identified areas where further research would have the greatest impact and established high-level R&D priorities for cellulose nanomaterials. Next, the team deconstructed the key priorities to determine the most important technical issues restricting solutions. This more focused analysis enabled the team to identify and map out specific, actionable projects to address the R&D priorities. Effective implementation of these projects will lead to meaningful progress in surmounting industry challenges and meeting national goals.

[1] Krausmann, Fridolin, Simone Gingrich, Nina Eisenmenger, Karl-Heinz Erb, Helmut Haberl, and Marina Fischer-Kowalski. 2009. "Growth in Global Materials Use, GDP and Populations during the 20th Century." *Ecological Economics* 68: 2696–2705.

Priorities and Projects

Based on an in-depth analysis of the current state of cellulose nanomaterial technology, research needs, and potential applications, the team identified two R&D priorities to focus further research:

- Dewatering and drying cellulose nanomaterials
- Enabling technologies to facilitate the use of nanocellulose in composite materials

The team identified the technical issues underlying each priority and translated the two R&D priorities into six actionable projects:

- Develop viable dewatering methods
- Develop viable drying methods
- Facilitate commercialization in high-volume composites
- Prepare an application for Generally Recognized as Safe (GRAS) designation by U.S. FDA
- Develop characterization standards for nanocellulose and composites
- Conduct a life-cycle analysis

The project maps for these six high-priority projects are presented in Appendix A. Each map provides a plan that is intended to guide the implementation of the R&D project and provide a basis for securing funding and establishing partnerships.

Path Forward

Developing breakthrough technologies that enable the production and application of cellulose nanomaterials is beyond the scope and means of a single organization. Effectively implementing the identified R&D projects and achieving the resulting benefits from the commercialization of more sustainable materials from nanocellulose will require collaborative effort with diverse partners.

This roadmap is designed to spur this critical collective action and serve as an invitation and as guidance for future R&D efforts.

We look forward to engaging the research community to address this challenge, and we welcome the input and engagement of industry, universities, research institutions, national laboratories, and public agencies in developing technology options—and in further defining the questions and challenges.

Agenda 2020

The Agenda 2020 Technology Alliance is a non-profit organization working to identify high-priority, pre-competitive technology challenges for the pulp and paper industry and to promote scientific R&D projects to address them.

The goals of the organization are the following:

- Reduce water consumption and enhance water reuse
- Reduce energy use and carbon emissions
- Increase manufacturing process efficiency
- Improve raw material yield
- Develop new biobased products

The Agenda 2020 Technology Alliance is committed to transforming the paper and forest products industry through innovation in its manufacturing processes and products. Agenda 2020 is uniquely qualified to meet this goal because of its ability to bring together subject-matter experts and promote cooperation among universities, research institutions, and government agencies. Collaborative R&D programs that bring together diverse expertise are essential for addressing industry needs and national sustainability goals.

Agenda 2020 has developed five R&D roadmaps:

- Reuse of Process Effluents
- Drier Web before Dryer Section
- Black Liquor Concentration
- Next-Generation Pulping
- Cellulose Nanomaterials

Each roadmap topic aligns with Agenda 2020's vision and was selected after a careful analysis of industry needs and current and emerging technology.

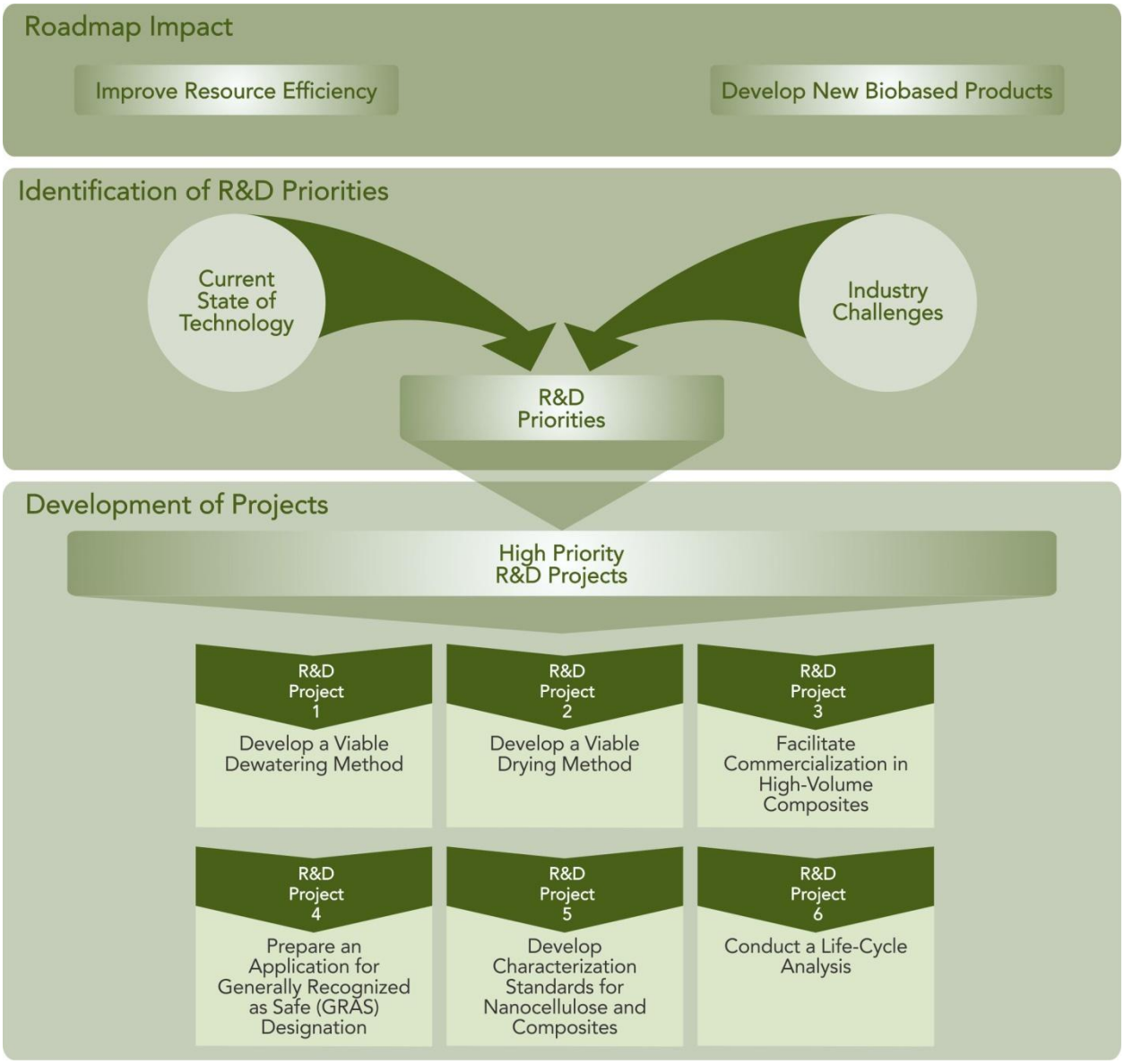

Figure ES-1. Roadmaps Driven by Vision and Need

1. Introduction

Background

This roadmap is part of a series of research and development (R&D) roadmaps developed by the Agenda 2020 Technology Alliance in part with funding from a National Institute of Standards and Technology (NIST) Advanced Manufacturing Technology Consortia (AMTech) Planning Grant.

After careful analysis of trends and drivers shaping the industry, key challenges and opportunities, and barriers to industry sustainability and competitiveness, a steering committee selected cellulose nanomaterials as an important roadmap topic area.

The development of this roadmap is based on a two-part strategy. First, the Agenda 2020 Cellulose Nanomaterials Team investigated best available technologies and identified the most promising R&D priorities to be explored further. Then the team determined the most critical technical issues within the R&D priorities, and identified and mapped out actionable R&D projects to address those issues.

In both phases, the team used workshops and other interactions to draw on the diverse expertise and perspectives of subject-matter experts from industry, national laboratories, government, and academia.

This roadmap presents concrete R&D projects to address cellulose nanomaterial technology needs, research challenges, barriers to commercialization, and market opportunities. This roadmap is designed to help prioritize and direct R&D work toward commercialization, with the specific objective of developing breakthrough technologies that can be implemented in 5 to 10 years.

Accordingly, the team's scope is limited to identifying the precompetitive research opportunities, potential applications, and scale-up priorities to steer cellulose nanomaterials toward rapid commercialization.

Agenda 2020 Vision

The U.S. pulp and paper manufacturing industry through Agenda 2020 is actively addressing national goals of sustainability, energy productivity, full employment, and healthy, resilient forests. Pulp and paper manufacturers need new breakthrough technologies that can meet key industry needs. However, such research is capital-, equipment-, and resource-intensive, and no company is likely to discover a breakthrough technology alone. These roadmaps seek to address specific needs and to encourage the interest of research institutes and government agencies in this challenging and promising endeavor in the national interest.

Vision 2030

The U.S. pulp and paper industry could accomplish the following by 2030:

- Reduce purchased energy by 50%, saving over 500 TBtu per year.
- Reduce water used per ton by 50%, reducing water discharge nationally by 480 billion gallons per year.
- Develop new biobased products worth $5 billion in sales per year.
- Protect 370,000 existing jobs by making 359 mills in 40 states more sustainable economically, environmentally, and socially.
- Dramatically improve the life-cycle sustainability of its products.

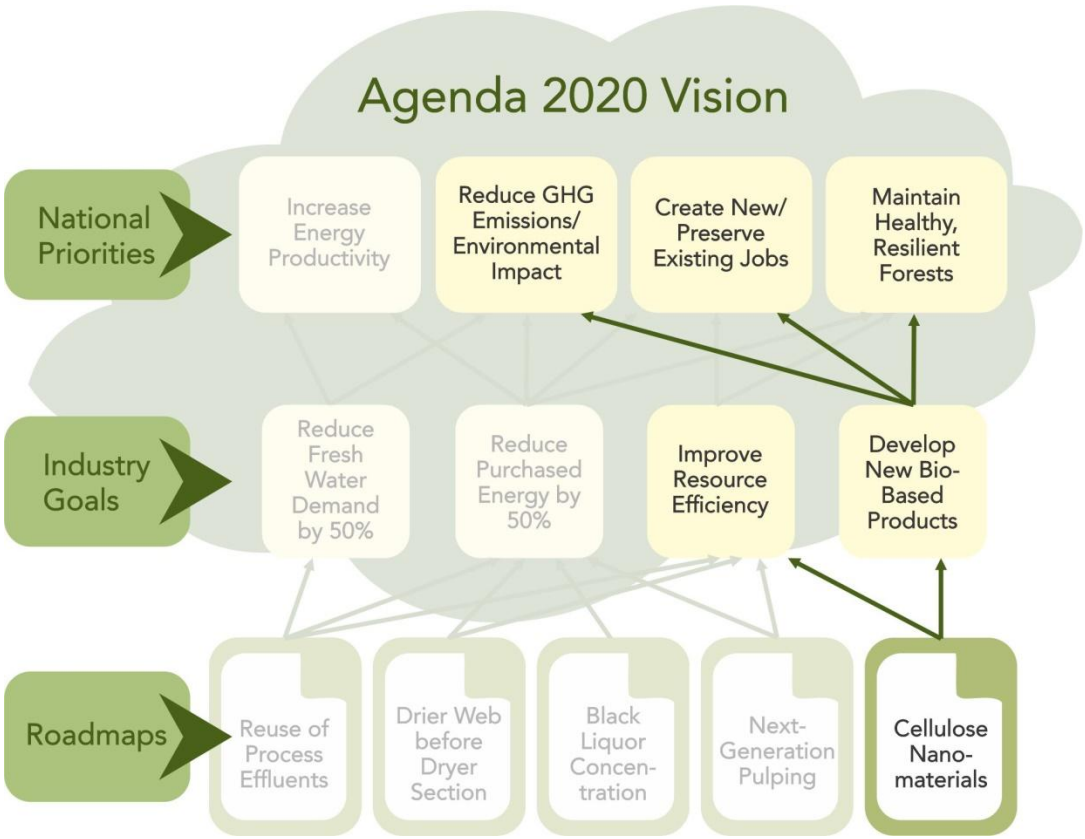

Figure 1. Roadmaps Driven by Vision and Need

The roadmaps are driven by the Agenda 2020 Vision for the pulp and paper industry. This vision encompasses specific industry goals and is aligned to broader national priorities (Figure 1). In identifying high-priority R&D projects for the industry, each roadmap maintains a line of sight to the vision and to particular industry goals and societal priorities. This line of sight ensures that the research described in the roadmaps will directly contribute to the realization of the Agenda 2020 Vision and thus provides the purpose, rationale, and measure of success for the roadmaps.

Focus on Development and Commercialization of Cellulose Nanomaterials

The Agenda 2020 Cellulose Nanomaterials Team envisions a materials revolution, in which new products made from cellulose nanomaterials derived from sustainable, renewable forest resources are in wide use supporting the everyday lives of millions around the globe.

The team has developed this roadmap to attract broad engagement in realizing the potential of these materials. The Agenda 2020 Technology Alliance seeks to enable the use of these renewable raw materials in a variety of applications. This roadmap captures the Cellulose Nanomaterials Team's vision for developing the technology needed for the advancement of cellulose nanomaterials and expanding the ways that the material could play a role in our future. The scope and breadth of the opportunities contained within this roadmap help provide a framework for research and development to address issues hindering commercialization. Development of standard definitions and test methods and addressing environment, health, and safety (EHS) questions are also in scope.

Potential Benefit

Cellulose nanomaterials have unique distinguishing properties, including high strength, high absorbency, and unique self-assembly properties. In addition, because of their feedstock's abundance, they can potentially be sustainably and renewably produced in quantities of tens of millions of tons per year.

The range of potential applications for cellulose nanomaterials is substantial. The development of this material provides a great opportunity to meet the Agenda 2020 Vision to develop new biobased products that complement the industry's traditional pulp, paper, and paperboard products. It also aligns with national priorities, particularly in the area of developing new advanced manufacturing technologies and maintaining healthy, resilient forests.

Several U.S. government agencies have already recognized the significant potential economic impact offered by cellulose nanomaterials. The National Nanotechnology Initiative (NNI)[2] and the U.S. Department of Agriculture Forest Service held a workshop in May 2014 entitled "Cellulose Nanomaterials—A Path Towards Commercialization." In addition, cellulose nanomaterials are one of three classes of sustainable materials targeted under the NNI's Sustainable Nanomanufacturing Signature Initiative to accelerate the development of industrial-scale methods for manufacturing functional nanoscale systems. The Department of Energy and the National Science Foundation have also recently provided funding to support projects based on cellulose nanomaterials.

The research directions called for in this roadmap promise a significant step forward in developing the technologies needed for cellulose nanomaterials to play a key role in the future.

[2] Established in 2001, NNI is a U.S. government R&D initiative involving 20 federal departments and independent agencies and commissions working together toward the shared and challenging vision of "a future in which the ability to understand and control matter at the nanoscale leads to a revolution in technology and industry that benefits society."

Structure of this Report

The remainder of this report is organized as follows:

- Chapter 2, which follows, presents technical background on cellulose nanomaterials, including the current practices, best available technologies, and potential applications and uses.
- Chapter 3 presents the analysis of the research needs and opportunities that led to the identification of specific R&D priorities selected for further development.
- Chapter 4 presents an examination of the technical issues within each R&D priority, the development of potential solutions to address those issues, and the specification of actionable projects to implement those solutions. It also includes an action plan that describes what actions must be taken to pursue the promising research.
- Chapter 5 summarizes the key outputs of the efforts and discusses the need for collective action.

In addition, a series of appendices provides extensive detail of this roadmapping effort, including the project maps for the high-priority projects, additional technical review, and additional EHS information.

2. Current State and Best Available Technology

This chapter presents background on cellulose nanomaterials technologies. The purpose of this section is to provide the reader with access to and understanding of the technical information that informed the team's analysis presented in Chapter 3 (Additional background information may be found in Appendix B).

Overview

During the 20th century, global economic development drove an eight-fold increase in global materials use. At the same time, there was a shift from the dominance of renewable biomass toward mineral and petroleum materials, such that non-renewable resources now account for more than 70% of total materials use.[3] As this trend continues, resources once easy to extract will become more difficult to find. Real concerns are emerging about longer-term sustainability of many materials.

As a result, abundant cellulose materials are being investigated with great intensity as a way to provide a renewable source of materials, chemicals, and energy. Cellulose materials represent the most abundant renewable resource on our planet and can play a vital role in meeting the expanding demand globally for renewable materials. Building on the established infrastructures associated with pulp mills, cellulose nanomaterials are expected to be manufactured in large volumes,. The forest products industry has done an exceptional job in commercially realizing the market potential of wood-based materials from the macro- to micro-scales by cost-effectively producing an array of affordable products vital to our modern way of life. Developing the market potential for a new generation of products by liberating and modifying the basic nanoscale structural building blocks of wood represents a logical next step for the forest products industry. This next step capitalizes on the industry's vast knowledge base and infrastructure in new ways to leverage the inherent physical and chemical features of wood for the betterment of society and the economy.

Nanotechnology represents a major opportunity to generate both new products and new and revitalized industries in the 21st century. The ability to view and engineer materials down to atomic dimensions provides the opportunity to develop new materials and products in unprecedented ways.

A recent, first-of-its-kind study sponsored by the U.S. Department of Agriculture (USDA) Forest Service estimates the annual market potential for high-volume applications in the United States at around 7 million tons (oven-dried basis) of cellulose nanomaterials per year, based on current markets that are most likely to be affected.[4] The largest-volume uses in the United States for cellulose nanomaterials are projected to be in packaging, automotive applications, cement, and paper. In addition, cellulose nanomaterials are projected to be able to compete in numerous products in other existing and emerging markets (e.g., flexible electronics, photovoltaics, filters, viscosity modifiers, oil drilling fluids, and additive manufacturing).

The first edition of the U.S. roadmap for cellulose nanomaterials in the forest products industry was

[3] Krausmann, Fridolin, Simone Gingrich, Nina Eisenmenger, Karl-Heinz Erb, Helmut Haberl, and Marina Fischer-Kowalski. 2009. "Growth in Global Materials Use, GDP and Populations during the 20th Century." *Ecological Economics* 68: 2696–2705.

[4] Shatkin, J. A., et al. 2014. "Market Projections of Cellulose Nanomaterial-Enabled Products− Part 1: Applications." *TAPPI Journal* 13(5): 9–16.

developed in 2005 via a joint effort involving the USDA Forest Service, Agenda 2020, and Technical Association of the Pulp and Paper Industry (TAPPI).[5] In the intervening years, there has been significant progress in the understanding of the properties and performance of the materials, particularly in the United States, Canada, Japan, Finland, Sweden, and Norway. In several of these countries there appears to be a concerted effort among industry, government, and universities to work together, encouraged with an infusion of public funds from their governments, to accelerate the pace of advancement. Compared to some other countries, the level of funding and effort in the United States has been quite modest, despite the extent of forest resources and infrastructure in the country.

Current Practices and Technologies

Cellulose Nanocrystals vs. Cellulose Nanofibrils

Several forms of cellulose nanomaterials are being produced globally. One form, cellulose nanocrystals (CNC), consists almost exclusively of nano-dimensional cellulose crystals. Another form, cellulose nanofibrils (CNF), typically consists of regions of crystalline as well as amorphous cellulose. Worldwide there are more than 25 small-scale, pilot, and semi-commercial operations using a variety of methodologies to produce CNC and CNF.

Cellulose Nanocrystals

The preparation of CNC from biomass generally occurs in two primary stages. The first stage is a purification of the biomass to remove most of the non-cellulose components. These include lignin, hemicellulose, extractives, and inorganic contaminants. This is typically done by conventional pulping and bleaching. The second stage uses an acid hydrolysis process to deconstruct the "purified" cellulose material into its crystalline components. This is accomplished by removing the amorphous regions of the cellulose microfibrils. The resulting rod-like particles (3–20 nm wide and 100-300 nm long) are almost 100% cellulose and are highly crystalline (62%–90%, depending on cellulose source material and measurement method). The variations in CNC characteristics (e.g., particle morphology, surface chemistry, and percentage crystallinity) are strongly linked to the cellulose source material and the acid hydrolysis processing conditions.[6]

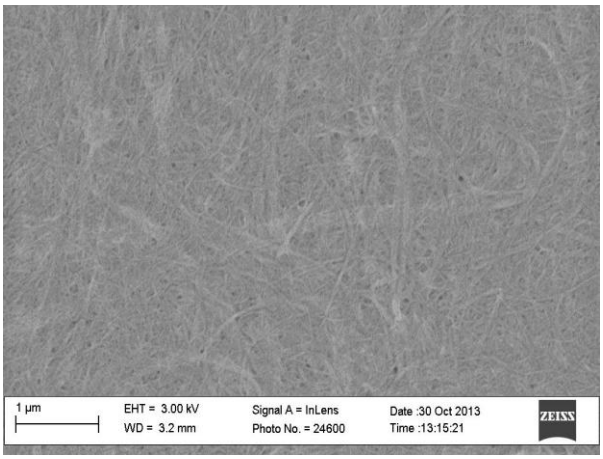

Figure 2. Cellulose Nanofibrils (Courtesy American Process, Inc.)

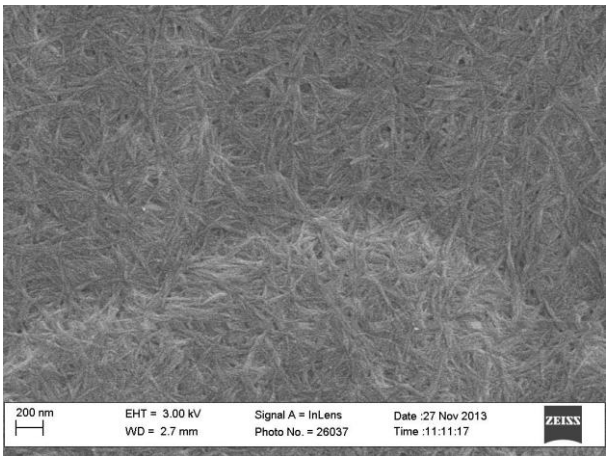

Figure 3. Cellulose Nanocrystals (Courtesy American Process, Inc.)

[5] Atalla, Rajai, et al. 2005. *Nanotechnology for the Forest Proeucts Industry: Vision and Technology Roadmap.* USDA Forest Service, Agenda 2020, and Technical Association of the Pulp and Paper Industry. http://www.ipst.gatech.edu/faculty/ragauskas_art/technical_reviews/fp_nanotechnology.pdf.

[6] Moon, R., J. Beck, and A. W. Rudie. 2015. "Cellulose Nanocrystals – A Material with Unique Properties and Many Potential Applications." In *Products and Applications of Cellulose Nanomaterials*, edited by M. T. Postek, R. J. Moon, A. W. Rudie, and M. A. Bilodeau, 9–12. Peachtree Corners, GA: TAPPI Press.

Cellulose Nanofibrils

CNF are generally manufactured by mechanical treatments—for example, in a refiner, grinder, homogenizer, or fluidizer. The resulting material consists of fibrils of many different sizes. The width of the smaller fibrils or aggregates is usually around 20–40 nm, while their length can be several micrometers. The fibrils are highly branched and flexible. The high-energy consumption of mechanical treatments may be reduced with different chemical or enzymatic pretreatments that act by facilitating the fibrillation of cellulose fibers by mechanical treatments in subsequent stages. Several different pretreatments for obtaining CNF have been published, including mild enzyme pretreatment using endogluconase, carboxy-methylation, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxly radial) mediated oxidation and AVAP® biomass fractionation.

Opportunities and Applications

Cellulose nanomaterials in various forms have a host of unique characteristics that, in conjunction with their origin from renewable materials, support a range of applications. As the basic properties of the materials become better known, applications development work will undoubtedly result in significant commercial opportunities. This section highlights the most promising application areas.

Features and Opportunities

The ability to liberate CNF and CNC at large scale would allow commercial utilization of their unique properties. The very high strength of cellulose nanomaterials, together with low densities, allows for the development of a wide range of high-strength, lightweight composites. Likely areas of application include automotive body panels, aerospace interior materials, lightweight construction materials with thermal and acoustic barrier properties, and paper and paperboard packaging with lightweight and enhanced barrier performance.

Table 1. Properties of Cellulose Nanomaterials

Material	Density	Tensile Strength	Tensile Modulus	Cost
	glcc	MPs	GPs	$/kg
High-strength steel	7.9	600	210	~1
Aluminum 6061-T6	2.7	275	70	~2
E-glass fiber	2.5	3,500	80	~2
Carbon fiber	1.8	4,000	230	>20
Nanocrystals*	1.5	7,500	135	4–10

Cellulosic nanomaterials are potentially useful as either primary or secondary reinforcements in polymer matrix composites

Source: Ted Wegner, seminar at Oak Ridge National Laboratory, November 2012

Development work is under way on the drying and surface treatments of cellulose nanomaterials to allow their use in reinforced plastic composites as a replacement for more expensive carbon fiber. Composites based on water-based resins or matrices are also under investigation.

The size, shapes, and water absorbency of cellulose nanomaterials allow thixotropic gelling at low solids concentrations that lead to applications in paints, drilling muds, cosmetics, and concretes.

Applications for Cellulose Nanomaterials

Table 2 lists the commercial applications identified in a recent cellulose nanomaterial markets report funded by the USDA.[7] The applications that appear most promising are summarized below.

High-Volume Applications (Excluding Paper Applications)

Automotive—Body Components: Because cellulose nanomaterials are inexpensive relative to other composite reinforcement fibers, it should be possible to use them in wide-scale structural applications.[8] In the near term, the most likely adoption will be in applications already using composite materials. CNF can be used as stable, extremely reactive raw materials for technical applications. It offers the added advantages of being renewable, biologically produced, and biodegradable. Applications include reinforcing biopolymers to create promising, environmentally

[7] Andrews, C. 2012. "Wood in Warfare." *Engineering & Technology Magazine* 7(9).
[8] Ibid.

Table 2. Commercial Applications for Cellulose Nanomaterials

High-Volume Applications	Low-Volume Applications	Novel and Emerging Applications
• Cement • Automotive body • Automotive interior • Packaging coatings • Paper coatings • Paper filler • Packaging filler • Replacement—plastic packaging • Plastic film replacement • Hygiene and absorbent products • Textiles for clothing	• Wallboard facing • Insulation • Aerospace structure • Aerospace interiors • Aerogels for the oil and gas industry • Paint—architectural • Paint—special purpose	• Sensors—medical, environmental, and industrial • Reinforcement fiber—construction • Water filtration • Air filtration • Viscosity modifiers • Purification • Cosmetics • Excipients • Organic LED • Flexible electronics • Photovoltaics • Recyclable electronics • 3-D printing • Photonic films

safe, and lightweight construction material for the automotive industry.

Automotive—Interiors: CNC has been incorporated in polyethylene, polypropylene, and biopolymers, where it enhances mechanical and barrier properties, as well as abrasion resistance. CNC is envisioned as improving prospects for using bio-plastics in interior automotive parts.[9] Further, the ability to create aerogels and structural foams can create lightweight decorative and interior panels such as dashboards and door panels.

Construction—Cement and Pre-stressed and Pre-cast Concrete: Concrete can be reinforced with a combination of cellulose nanomaterials and micro-cellulose fibrils to increase the toughness of an otherwise brittle material.[10] These fibers could provide the benefit of other micron-sized and nanofibril reinforcement systems at a fraction of the cost. The addition of up to 3% micro- and nanofibrils in combination increases the fracture energy by more than 50% relative to the unreinforced material, with little change in processing procedure. Benefits include reducing the amount of cement needed, which will lower material and labor costs and results in reduction in associated carbon emissions.

Packaging—Fiber/Plastic Replacement: Cellulose nanomaterial-based foams are being studied for packaging applications to replace polystyrene-based foams.[11] The advantage of using cellulose nanomaterials instead of wood-based pulp fibers is that the CNF can reinforce the thin cells in the starch foam, replacing a polymer produced from fossil fuel with a renewable material that decreases weight.

Packaging Film: The mechanical and optical properties of cellulose nanomaterials make them a promising material for reinforcing plastics. Cellulose nanomaterials have been reported to improve the performance of, for example, thermosetting resins, starch-based matrices, soy protein, rubber latex, and poly(lactide).[12] Such applications may be used as coatings, films, paints, foams, and packaging.

[9] Lyne, B. 2013. "Market Prospects for Nanocellulose." Presented at The Royal Institute of Technology Alberta Biomaterials Development Centre, February 12.

[10] Ardanuy, M., J. Claramunt, R. Arévalo, F. Parés, E. Aracri, and T. Vidal. "Nanofibrillated Cellulose (NFC) as a Potential Reinforcement for High Performance Cement Mortar Composites." *Bioresources* 7(3): 3883–3894.

[11] Svagan, A. J., My A. S. Azizi Samir, and Lars A. Berglund. 2008. "Biomimetic Foams of High Mechanical Performance Based on Nanostructured Cell Walls Reinforced by Native Nanofibrils." *Advanced Materials* 20(7): 1263–1269.

[12] Yua L., et al. 2006. "Polymer Blends and Composites from Renewable Resources." *Progress Polymer Science* 31: 576–602.

Personal Care—Hygiene and Absorbent Products: The super-absorbency of cellulose nanomaterials makes them an ideal biodegradable water-retention filler in incontinence pads and diapers.[13] There is likely to be high demand for lighter, thinner, and natural-product alternatives in this market.

Textiles—Clothing: Cellulose has long been used to make textiles. For example, rayon is made from pulp or cellulose. Recently, scientists have developed a highly processed form of cellulose nanomaterials that, once mass-produced, will provide stronger, lighter, more durable textile materials from which to make clothing.[14] The development of electrospinning techniques that produce continuous fibers can be used to develop cellulose nanomaterial composite fabrics.[15] The movement toward more natural materials from textiles creates a consumer driver, and biodegradability decreases the burden of textiles in the waste stream.

Low-Volume and Novel/Emerging Applications

Aerogels—Oil and Gas Industry: A novel type of sponge-like material for the separation of mixed oil and water liquids has been prepared by the vapor deposition of hydrophobic silanes on ultra-porous cellulose nanomaterials aerogels. The hydrophobic lightweight aerogels selectively absorb oil from water with a capacity to absorb up to 45 times their own weight. The oil can also be drained from the aerogel, and the aerogel can then be reused for a second absorption cycle.[16,17]

Aerospace—Structural: There is increasing attention on the performance advantages of nanocomposites, and particularly of polymer-based nanocomposites for weight-reducing initiatives. In the interest of sustainability, the specific use of bio-reinforced nanocomposite parts and nanostructured coatings within automotive, aerospace, construction, medical, and packaging applications is accelerating. These "green" nanocomposites can provide high mechanical strength at low density, low weight, and potentially low cost. New efforts are under way to develop and apply sustainable nanocomposites that improve structural properties for applications in the aerospace industry.[18] Typical property improvements as compared to existing composites include dimensional stability, structural strength, thermal resistance, chemical resistance, weight reduction, and electrical conductivity.

Aerospace—Interiors: Much like aero-structures, interiors are being designed with lighter-weight materials. Beyond traditional applications in floorboards, ceilings, panels, and other similar components, seating has become a major focal point for composites applications.[19] Lightweight seats can enable major reductions in the weight of aircraft. The use of composites in seats and in a variety of small brackets, clips, trays, plinths, and other structures is increasing.

Construction—Gypsum Wallboard Facing: Cellulose nanomaterials in wallboard facing makes drywall lighter, stronger, and water-resistant, which ultimately makes it resistant to mold growth.[20] Light-weighting can reduce the

[13] Larsson, K., L. A. Berglund, M. Ankerfors, and T. Lindström. 2012. "Polylactide Latex/Nanofibrillated Cellulose Bionanocomposites of High Nanofibrillated Cellulose Content and Nanopaper Network Structure Prepared by Papermaking Route." *Journal of Applied Polymer Science* 125(3): 2460–2466.

[14] Lyne, B. 2013. "Market Prospects for Nanocellulose." Presentation at The Royal Institute of Technology Alberta Biomaterials Development Centre, Feb. 12, 2013.

[15] Moon, R., S. Beck, and A. W. Rudie. 2013. "Cellulose Nanocrystals – A Material with Unique Properties and Many Potential Applications." In *Products and Applications of Cellulose Nanomaterials*, edited by M. T. Postek, R. J. Moon, A. W. Rudie, and M. A. Bilodeau, 9–12. Peachtree Corners, GA: TAPPI Press.

[16] Cervin, N. T., et al. 2012. "Ultra Porous Cellulose Nanomaterials Aerogels as Separation Medium for Mixtures of Oil/Water Liquids." *Cellulose* 19(2): 401–410.

[17] Korhonen, J. T., M. Kettunen, R. H. Ras, and O. Ikkala. 2011. "Hydrophobic Nanocellulose Aerogels as Floating, Sustainable, Reusable, and Recyclable Oil Absorbents." *ACS Appl Mater Interfaces* 3(6):181 –1816.

[18] Future Markets Inc. 2012. *The Global Market for Nanocellulose to 2017*, Technology Report No. 60, Second Edition, 38.

[19] Red, C. 2012. "Composites in Aircraft Interiors, 2012–2022." *High-Performance Composites*, September.

[20] VTT. 2013. *Research Highlights in Industrial Biomaterials 2009–2012*, VTT Research Highlights 5. Kuopio: VTT

life-cycle energy and material impacts of building materials, adding green building credits toward Leadership in Energy and Environmental Design (LEED) certification, for example.

Construction—Insulation and Soundproofing: Over the past years, there have been advancements made toward creating cheaper, thinner, and more breathable insulating materials with higher R-values. Aerogel is one of the top insulation materials, having the lowest bulk density of any known porous solid as well as significant insulating qualities. [21]

Industrial—Viscosity Modifiers: Cellulose nanomaterials are used as viscosity modifiers, gelling agents, foaming agents, and binding agents.[22] Currently, hydroxyethyl methyl cellulose is used in the production of cellulose films.[23]

Industrial—Water Purification: Commercial companies are designing, developing, and optimizing novel bio-based foams, filters, membranes, and adsorbent materials with high and specific selectivity using combinations of cellulose nanomaterials and nano-chitin for decentralized industrial and domestic water treatment. A Swedish organization is developing a novel water purification approach combining the physical filtration process and the adsorption process exploring the capability of the cellulose nanomaterials and/or nano-chitin to selectively adsorb, store, and desorb contaminants from industrial water and drinking water while passing through a highly porous or permeable membrane.[24]

Paint: Cellulose nanomaterials can modify the viscosity of paints and coatings. A Finnish group improved the durability of a coat of paint using cellulose nanomaterials as an additive in water-based polyurethane varnishes and paints.[25] According to this research, cellulose nanomaterials improve finish durability, and they protect paint and varnish from attrition caused by ultraviolet radiation. Extending the life of paints and coatings reduces the environmental burden of replacing coatings and the underlying material.

Personal Care—Cosmetics: Cellulose nanomaterials may be used as a hydrating agent, non-allergenic rheology modifier, and as composite coating agents in cosmetics—e.g., for hair, eyelashes, eyebrows, or nails.[26] Demand for natural products as well as for high-performance colorants increases demand for these products.

Pharmaceuticals—Excipients: Cellulose nanomaterial drug carriers may be produced in a bid to fight various types of illness-causing bacteria such as ones that are resistant to antiseptics. The biocompatibility and biodegradability of cellulose nanomaterial are behind innovations to incorporate it into drugs and pharmaceutical delivery.[27]

Sensors—Medical, Environmental, and Industrial: CNC films are hygroscopic or water-absorbing, but individual crystals do not dissolve or even swell in water. For this reason, it is possible to use them in applications involving moisture, e.g., as humidity sensors or for real-time contaminant detection. Cellulose nanomaterial-based sensors could help in monitoring and detecting elevated stress in structures such as bridges. Modifying cellulose nanomaterials by double-walled carbon nanotubes and graphite carbon nano-powder expands applications for sensor applications.[28] The

Technical Research Centre of Finland. http://www.vtt.fi/publications/index.jsp.

[21] Forest Products Laboratory. 2013. *Forest Products Laboratory: Restoring America's Forests through the Wise Use of Wood*. USDA.gov, 13.

[22] Qvintus, P., T. Tammelin, S. Peresin, A. Harlin, E. Hellen, and U. Forsström. 2013. "Nanocellulose in Packaging." VTT.

[23] Dufresne. A. 2013. "Nanocellulose: From Nature to High Performance Tailored Materials." Walter de Gruyter.

[24] NanoSelect. 2012. "Functional Membranes/Filters with Anti/Low-Fouling Surfaces for Water Purification through Selective Adsorption on Biobased Nanocrystals and Fibrils (NANOSELECT)." University Campus, Porsoen Lullea, Sweden: Lulea Tekniska Universitet. http://www.nanoselect.eu/.

[25] VTT. 2011. "Innovation and Competitiveness from Nanocellulose." Accessed March 29, 2013. http://www.vttresearch.com/media/news/innovation-and-competitiveness-from-nanocellulose.

[26] Williamson, W. 2012. "Nanocellulose on the Cusp of Commercialization." *Focus on Nanotechnology*," 31–36. http://www.celluforce.com/upload/IPW_Nanocellulose_Final_131.pdf.

[27] Kolakovic, R., L. Peltonen, T. Laaksonen, K. Putkisto, A. Laukkanen, and J. Hirvonen. 2011. "Spray-Dried Cellulose Nanofibers as Novel Tablet Excipient." *AAPS PharmSciTech* 12(4): 1366–1373.

[28] Wang, M., I. V. Anoshkin, A. G. Nasibulin, J. T. Korhonen, J. Seitsonen, J. Pere, E. I. Kauppinen, R. H. Ras, and O.

electrical conductance of these materials displays a high sensitivity to strain when tensile stress is applied.

Sensors—Piezoelectric Properties: The asymmetric nature of the cellulose molecule can result in piezoelectric properties when CNC are well aligned.[29] These piezoelectric properties have potential as both a sensor and actuator, allowing their use in diverse applications.[30]

Uses of Cellulose Nanomaterial in Papermaking

Wet-End Applications

Currently, the most widespread use of cellulose nanomaterial in paper and paperboard is CNF addition to the wet end of the paper machine to achieve the following benefits:

1. *Increased strength*—The main mechanism by which cellulose nanomaterial creates property enhancement is through increased fiber-fiber bonding or bonded area in the sheet. CNF will work best as a dry-strength additive in poorly bonded sheets and less so in sheets made from highly refined pulps that already have a high bonded area. Increased strength can be leveraged in several ways:
    a. Increased filler/decreased fiber for cost savings and drying energy savings
    b. Decreased fiber at equal strength and/or stiffness for light-weighting of packaging
    c. Decreased use of expensive, reinforcing fibers
2. *Decreased air permeability or porosity*—Increased fiber-fiber bonding results in a more closed sheet, i.e., one with less porosity as measured by air-flow techniques. This can be leveraged in several ways:
    a. A less porous sheet has improved coating hold-out; less coating can be used to achieve the same benefit sought by the coating, be it print quality, smoothness, barrier, or other functional properties.
    b. A less porous sheet generally results in higher print quality because the ink is held out on the surface of the sheet.
    c. A less porous sheet results in better barrier properties for superior performance in paper packaging applications.
3. *Improved smoothness*—Use of CNF in the wet-end will improve smoothness but to a lesser degree than when it is used in a surface coating.

Most published wet-end work has been done with CNF.

Surface Treatments

The use of CNF and CNC in coatings is not as developed as its use in the wet-end applications, but it offers many potential benefits. CNF has been explored as a functional additive in traditional clay/carbonate coatings and also as the majority or sole ingredient in coatings. These coatings can be applied to the sheet as any other coating—rod/bar/blade coating, size-press coating, and spray coating—and foam-coating of CNF films has also been explored.

1. *Barrier properties*
    a. Gas permeability—CNF coatings have been shown to improve air and oxygen permeability because of the closure of pores in the base paper.
    b. Oil barrier—CNF coatings have been shown to decrease the penetration of oil into the paper, especially at high coat-weights.
2. *Coating viscosity*
    a. CNF suspensions have very high viscosity at low concentrations, making the material a good candidate for coating rheology control.

Ikkala. 2013. "Modifying Native Nanocellulose Aerogels with Carbon Nanotubes for Mechanoresponsive Conductivity and Pressure Sensing." *Advanced Materials* 25(17): 2428–2432.
[29] Csoka, L., et al. 2012. "Piezoelectric Effect of Cellulose Nanocrystals Thin Films." *ACS Macro Letters* 1(7): 867.
[30] Kim, J., and S. Yun. 2006. "Discovery of Cellulose as a Smart Materials." *Macromolecules* 39(12): 4202–4206.

b. CNF suspensions are highly shear-thinning or thixotropic, which helps to retard the flow of the coating into the base sheet and keep it on the surface after coating.

3. *Surface smoothness*—Smoothness is improved with CNF coatings because of their very small particle size and ability to fill in the pores and roughness of the base sheet.

4. *Physical properties*— CNF surface treatments have been shown to increase slightly the fracture toughness and bending stiffness of the coated structure compared to uncoated.

5. *Printing applications*—It remains a challenge to use CNF as a cost-effective and high-performing replacement for latex in coatings intended for printing by offset methods. Pick strength and gloss decrease with CNF as a binder. CNF-coated paper is less porous and absorptive to ink-jet inks and therefore could be beneficial in that application.

Most work to date with cellulose nanomaterial in paper and packaging applications has been done with CNF.

Table A-1 in Appendix B summarizes the opportunities and challenges associated with the most promising applications. The challenges highlight critical areas for research.

3. Identification of R&D Priorities

Introduction

The Agenda 2020 Cellulose Nanomaterials Team sought to identify the research and development (R&D) priorities that have the greatest potential for advancing both the manufacture and use of cellulose nanomaterials. The team considered current manufacturing practices as well as potential applications and opportunities to assess priorities among knowledge gaps and determine the most promising R&D needs.

While the research opportunities surrounding cellulose nanomaterials cover a broad range of topics, the team limited the focus to the non-competitive components that all Agenda 2020 members and other parties could address together.

Knowledge Gaps and Challenges

Progress in commercial utilization of cellulose nanomaterials requires deeper understanding of these materials and their interactions with other materials.

The Cellulose Nanomaterials Team found that the most critical knowledge gaps and challenges hindering commercialization are in the following areas:

- Measurement and standards for manufacturing
- Controlling interactions between water and cellulosic nanomaterials
- Dewatering and drying
- Management of interfacial properties
- Environment, health, and safety (EHS) considerations
- Characterization of cellulose nanomaterials

The following sections will discuss these areas in detail.

Measurement and Standards for Manufacturing

The terms "characterization" and "measurement" can be differentiated by the extent of analysis. "Characterization" is the detailed analysis to define the key properties of a given material and is not necessarily meant to be done on a routine basis. "Measurement," on the other hand, is the routine analytical work necessary for manufacturing and quality control, and for compliance with environmental, health, and safety (EHS) regulations.

For implementation of cellulose nanomaterials in industry, it is necessary that test methods are standardized. Several organizations worldwide are working on defining standard methods for cellulose nanomaterial, including the Canadian Standards Association,[31] Technical Association of the Pulp and Paper Industry (TAPPI), and National Institute of Standards and Technology (NIST).

Another challenge to the large-scale economical manufacture of cellulose nanomaterial is replacing the expensive, high-tech characterization methods employed within the field of nanotechnology to characterize submicroscopic particles with rapid, robust industrial methods. Measurement needs include the following:[32]

- Particle size distribution (current methods include scanning electron microscopy and transmission electron microscopy)
- Lignin content (tedious wet chemistry)
- Crystallinity (x-ray diffraction)
- Thermal stability (thermal gravimetric analysis)
- Purity (inductively coupled plasma/optical emission spectrometry)

[31] CSA Group. 2014. *CSA Z5100, Cellulosic Nanomaterials – Test Methods for Characterization.*

[32] U. S. National Institute of Standards and Technology (NIST), and Technical Association of the Pulp and Paper Industry (TAPPI). 2014. "Measurement Needs for Cellulose Nanomaterials." NIST and TAPPI Joint Workshop, June.

The principal disadvantages of the existing methods listed above are capital cost (estimated at $1.4 million total), length of time required for sample preparation and measurement (up to several hours), high level of technical expertise required, and high facility construction costs due to special environmental requirements for many of the instruments in terms of acoustic and mechanical vibrations, electromagnetic fields, etc. Manufacturers seek methods that can be performed on the operating floor or in a standard process control laboratory and that have low associated costs, short characterization and test times (minutes), and require minimal training and expertise. Development of these methods will require collaboration among academics, government, industry, and equipment suppliers.

The existing lower-cost measurement methods, such as equivalent spherical volume, rheology, and water retention, need to be evaluated for their effectiveness in quality control and other applications.[33,34]

The challenges are improving the resolution of the existing techniques, increasing the automation of the tests, and defining standard methods so the product may be characterized accurately and in a timely manner for manufacturing quality control and to satisfy potential regulatory requirements.

Controlling Interactions between Water and Cellulosic Nanomaterials

The presence of hydroxyl groups along the backbone of the cellulose polymer contributes to the high level of water interaction observed with plant-based fibers. Strong hydrogen bonds are formed between fiber surfaces as water is removed from a slurry of fibers, giving rise to a strong fibrous network upon drying without the need for the addition of any additional binders. As the surface area, degree of swelling, and/or flexibility of the fibers is increased through mechanical action or other means, the bonded area between fiber surfaces increases, resulting in higher strength in the fiber network. This phenomenon is the basis of modern paper and paperboard manufacturing.

As cellulose fibers are processed into cellulose nanomaterials, the number of hydroxyl groups available to interact with water increases significantly. The surface area, as measured by nitrogen gas absorption, increases from about 1 m^2/gm for cellulose fibers to more than 100 m^2/gm for cellulose nanofibrils (CNF). This increased surface area results in a dramatic increase in the low shear viscosity of a low solids slurry of cellulose nanomaterials compared to a slurry of cellulose fibers. A hydrogel can easily be formed from an aqueous slurry of CNF at 3% by weight or less.

Strong water interactions are a beneficial characteristic of cellulosic nanomaterials for many applications, such as controlling the rheology of coatings, slurries, food, and cosmetics. The strong water-holding properties of cellulose nanomaterials also make them useful as humectants and as aids in the curing of cement and mortars.

This same characteristic, however, presents challenges in the dewatering and drying of cellulose nanomaterial slurries, as well as in the processing and handling of slurries during manufacturing and in use.

Some emerging and promising applications involving cellulose nanomaterials, including additive manufacturing, polymer reinforcement, and composites, are currently challenged by the strong affinity for water that cellulose nanomaterials naturally possess. The control of water affinity of cellulose nanomaterials is therefore a specific knowledge gap and current research need.

[33] Kangas, et al. 2014. "Characterization of Fibrillated Celluloses." *Nordic Pulp Paper Research Journal* 29(1): 129–143.
[34] Suzuki, M., and Y. Hattori. 2008. "Method and Apparatus for Manufacturing Microfibrillated Cellulose Fiber," U.S. Patent 7381294, issued June 3.

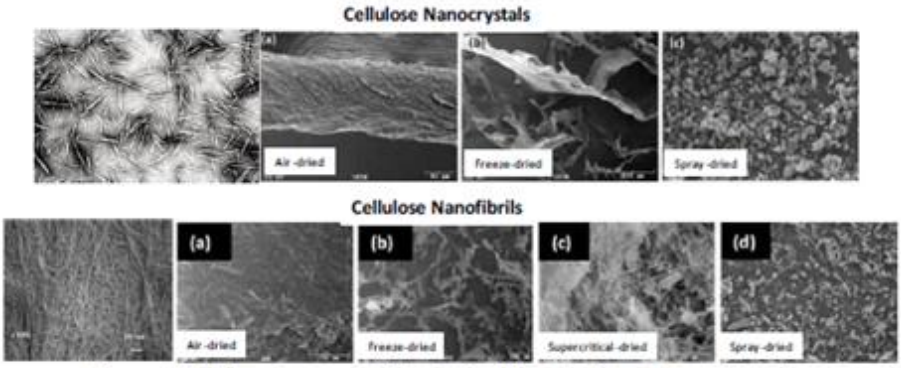

Figure 4. Cellulose Nanomaterials Obtained from Different Dry Technology

Dewatering and Drying

Dewatering

Dewatering of cellulose nanomaterials is inherently difficult because of the tremendous water-holding capacity of these materials. Conventional filtration techniques have proven to be ineffective in dewatering aqueous slurries of native cellulose nanomaterials. Centrifugation has shown promise in dewatering these slurries, but enhanced processing techniques and equipment are needed to realize commercial efficiencies and scale. In addition, surface modification of the materials can aid in the rate of dewatering and increase the final solids content. However, more exploration of this approach is needed.

Drying

Shipping cellulose nanomaterial gels with high water content (90–97 wt.% water) to their end-use destination is costly and impractical at large volumes and long distances. A cellulose nanomaterial drying method must be developed that is scalable, low-cost, and maintains product quality and particle morphology. The most common drying technologies for cellulose nanomaterials reported in the literature are freeze drying and spray drying, although air drying and critical drying have also been reported. However, researchers have shown that all of these drying methods can have a negative impact on cellulose nanomaterial properties, including crystallinity, thermal stability, and irreversible inter-particle aggregation/bonding, known as hornification.[35, 36, 37] Hornification clumps particles into large agglomerated structures that lose the individual nanoparticle morphology, as shown in Figure 4. Cellulose hornification is a significant challenge across all conventional drying methods for both CNF and cellulose nanocrystals.[38, 39]

Recently, Missoum et al. showed that freeze-drying is a promising method to prepare dried CNF that maintains discrete particle morphology by adding inorganic salt to a CNF suspension before drying.[40] The study indicated that the salt separates the CNF during the drying process so that aggregation and bonding of the particles during drying could be avoided. The salt acts as an inter-particle hydrogen bonding blocker. As a result, the dried CNF could be redispersed in water as individual nanoparticles. This method, however, has several disadvantages. The large amount of salt used has to be removed by dialysis in water before end-use. In addition, the method is not

[35] Peng, Y., D. J. Gardner, Y. Han, Z. Cai, Mandla, and A. Tshabalala. 2013. "Drying Cellulose Nanocrystal, Suspensions." Presented at the 2013 International Conference on Nanotechnology for Forest, Stockholm, Sweden, June 23–27.

[36] Peng, Y., D. J. Gardner, and Y. Han. 2012. "Drying Cellulose Nanofibrils: In Search a Suitable Method," *Cellulose* 19: 91–102.

[37] Y. Peng, D. J. Gardner, Y. Han, A. Kiziltas, Z. Cai, M. A. Tshabalala, 2013. "Influence of Drying Method on the Material Properties of Nanocellulose I: Thermostability and Crystallinity." *Cellulose* 20: 2379–2392.

[38] Y. Peng et al. 2013. *Drying Cellulose Nanocrystal Suspensions, Production and Applications of Cellulose Nanomaterials*. TAPPI Press.

[39] Y. Peng et al. 2013. *Drying Cellulose Nanofibril Suspensions, Production and Applications of Cellulose Nanomaterials.* TAPPI Press.

[40] Missoum, K., J. Bras, and M. Belgacem. "Water Redispersible Dried Nanofibrillated Cellulose by Adding Sodium Chloride." *Biomacromolecules* 13: 4118–4125.

applicable for dispersion of cellulose nanomaterial in hydrophobic polymers or solvents.

Managing the Interfacial Properties of Cellulosic Nanomaterials

The resulting properties of any composite material are dependent upon the physical and chemical properties of their various component materials, the relative amounts of the various component materials, the resulting composite structure, and the interfacial interactions among the component materials. When using cellulosic nanomaterials with other bulk and additive materials to produce composites of commercial interest, the producer selects the type(s) of cellulosic nanomaterials and the loadings of the various composite materials that will give rise to the resulting composite structure. Manipulating the interfacial interactions of the composite components and the interfacial zone then becomes important in controlling the efficacy of the cellulosic nanomaterials and the resulting composite material properties.

Therefore, the understanding, manipulation, and modification of the interfacial interactions of cellulose nanomaterials with other materials are of critical importance for their successful commercial use in a wide array of composite end-use applications. For example, cellulose nanomaterials are envisioned to be used in an array of composites such as for polymer/polymer-blend reinforcement, concrete and cement additives, epoxy coatings, packaging, automotive and aerospace components, construction and building materials, bio-mimetic composites, and filters. It is safe to say that the use of multiphase, multicomponent composite materials is expected to grow significantly in the future. If successfully applied, tens of millions of tons of cellulose nanomaterials would be required to meet the theoretical demand for such composite applications worldwide on an annual basis.

To achieve large-scale market penetrations in a variety of end-use applications, it will be critical to tailor the interfacial properties of cellulosic nanomaterials in multiple applications to achieve optimal performance. Approaches to modifying cellulosic nanomaterial chemistries and control their subsequent interactions with other materials include treatments such as acetylation, plasticization, silylation; use of coupling agents, polymer grafting; use of surface active agents; polyelectrolyte adsorption; and use of surfactants. The role and importance of interfaces are the same for all multicomponent composite materials and cellulosic nanomaterials surface modification. Manipulation must always be selected according to the end-use properties targeted, as well as to the characteristics of the specific system in which they will be used.

As we move forward, it will also be important to monitor developments in interfacial phenomena, as the principles and techniques developed for other materials may find application for cellulose nanomaterials.

Environment, Health, and Safety Considerations

Quantifying the EHS impacts of cellulose nanomaterials was identified as an important area of research in several areas:

- Measurement—to enable reliable and comparable research in all other areas
- Physicochemical data— to characterize key properties that may influence biological and environmental behavior
- Safe exposure levels—primarily to understand potential inhalation impacts in the workplace
- Development of workplace monitoring methods

A more detailed description of the EHS needs identified by the team is included in Appendix D.

Characterization of Cellulose Nanomaterials

Materials characterization is needed to enable quantitative description of a material's structure and properties. Measurement of materials properties at the nanoscale is particularly difficult. In addition, nanomaterials have properties that differ fundamentally from those at the micro-scale and macro-scale and can be size-dependent at the nanoscale. As a result, oftentimes the physical properties of nanomaterials, such as tensile and compressive strength, are based upon theoretical calculations and not actual measurements. The

International Organization for Standardization (ISO) has developed a technical report that comprehensively reviews an array of structural, mechanical, physical, and chemical properties to be measured for nanomaterials.[41] Examples are as follows:

- Structural (e.g., aspect ratio, size, size distribution, shape, surface area, surface morphology, and crystallinity)
- Physical properties (e.g., thermal, optical, electrical, and acoustical)
- Mechanical properties (e.g., tensile, compressive, stiffness, elasticity, plasticity, viscoelasticity, rheology, creep, fatigue, and abrasion)
- Chemical properties (e.g., absorptiveness, lyophillicity and lyophobicity, biocompatibility, biodurability, and toxicity)

Other important measurements include Young's modulus, emissivity, luminosity, coefficient of thermal expansion, heat capacity, thermal conductivity, torsional strength, rigidity, shear strength, creep properties, frictional coefficient, roughness, fatigue, and solubility. The list is long, and it would be a daunting and time-consuming task to determine all of these properties for cellulose nanomaterials or any nanomaterial.

As a result, the best strategy for characterizing cellulose nanomaterials appears to be to let end-use applications, EHS information needs, and production quality control requirements ultimately dictate the characterization measurements required. To date, interest has been to measure cellulose nanomaterials dimensions to include aspect ratio and aspect-ratio distribution, crystallinity, surface charge, surface contamination, and acid content. Because development of reliable and accurate methodologies for characterizing cellulose and other nanomaterials is evolving, and because it is not a trivial matter to avoid measuring artifacts when making measurements at the 10^{-9} meter scale, interested manufacturers should work with universities, private laboratories, government laboratories, and organizations such as NIST that have the specialized instrumentation focused on nanomaterial characterization. The prospect that cellulose nanomaterials are available and likely to be used in many consumer products and in large volumes may provide enough incentive for some entities such as government laboratories to help in the characterization of cellulose nanomaterials.

Selected R&D Priorities

The Cellulose Nanomaterials Team's analysis of knowledge gaps and challenges across these six areas identified several areas in which further research has the potential to advance commercialization and create market opportunities for cellulose nanomaterials products. After careful consideration of industry needs, the team decided to focus on the area of dewatering and drying. Progress in this area would enable efforts across a wide range of processes and products and contribute to the formation of platforms for all participants in cellulose nanomaterials markets. In addition, the team also decided that commercialization of nanomaterials would require advancement of technologies to enable their use in composites. Progress in this area would open significant market opportunities.

Accordingly, the Cellulose Nanomaterials Team identified the following two R&D priorities as the most promising areas for further exploration:

A. **Dewatering and drying**: Develop an economically viable dewatering and drying method that allows for re-dispersion. As an industry, we want to dry cellulose nanomaterials (or increase dewatering) in a form that can be completely re-dispersed or used in a cost-effective manner (e.g., reasonable shipping solids content—targets 30% or higher—up to 100% solids).

B. **Enabling technologies to facilitate the use of nanocellulose in composite materials**: Develop commercially viable surface functionalization methods for improved compatibility with end-use composite materials. Determine composite systems and resins that will work with

[41] ISO. 2010. *Nanotechnologies—Methodology for Classification and Categorization of Nanomaterials,* ISO/TR 11360.

cellulose nanomaterials—conventional polymers and/or biodegradable varieties. Develop other strategies for using nanocellulose in composite materials.

4. Identification of R&D Projects

Introduction

Having identified the two key research and development (R&D) priorities for addressing industry needs, the Agenda 2020 Cellulose Nanomaterial Team sought to develop concrete R&D projects that, when implemented, would achieve meaningful progress on these priorities.[42]

The team began this effort by identifying critical, technical issues within each of the R&D priorities. These issues manifest in a variety of forms, including knowledge gaps and technical challenges.

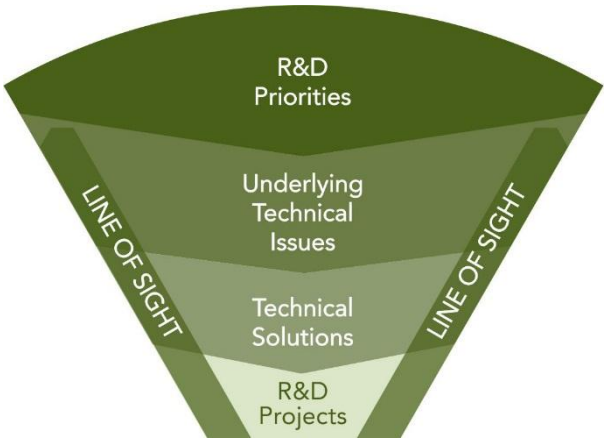

Figure 5. Line of Sight to Industry Needs

Next, the team identified technical solutions to address the most pressing technical issues. Based on the specified solutions, the team generated a set of high-priority R&D projects that would result in important advancements, breakthroughs, or new technology solutions.

For each of these projects, the team developed project maps (see Appendix A) to guide the implementation of the high-priority projects. The R&D project maps represent the ultimate output of this roadmap. They are intended to provide a business case and research plan that engages funding sources, informs and shapes request for proposal development, and guides the actual implementation of research projects.

This process ensures that implementation of the high-priority R&D projects will be guided by a line of sight to industry needs. Figure 5 illustrates this line of sight that helps align research and industry need.

Technical Issues and Technical Solutions

For each of the two R&D priorities, the team identified the underlying challenges and/or knowledge gaps. Then the team identified technical solutions to address the highest-priority issues identified.

Dewatering and Drying

Technical Issues

For the ***Dewatering and Drying R&D*** priority, the team grouped the technical issues into four major themes, which are summarized below:

- **Energy Requirements**: The energy required for drying cellulose nanomaterials poses a significant technical challenge. Current dewatering and drying techniques are energy-intensive and add significant cost to producing cellulose nanomaterials.
- **Water-Cellulose Interaction Properties**: As cellulose fibers are processed into cellulose nanomaterials, the number of hydroxyl groups available to interact with water increases significantly. The material is difficult to dewater

[42] To gather the content for this phase of work, the Agenda 2020 Cellulose Nanomaterial Team hosted a workshop to bring together a select group of subject-matter experts and industry representatives. For more information on the workshop and workshop results, see Appendix C.

and difficult to handle as a viscous gel. Many drying methods appear to significantly modify properties of cellulose nanomaterials, particularly particle size. The hydrogen bonds that form during drying are strong and difficult to break when dispersing. Current techniques are not able to control the formation of interfacial hydrogen bonds.

- **Technical Limitations**: Mechanical dewatering techniques to high solids content do not appear commercially viable. The losses of yield in drying methods attempted to date are high. In addition, dewatering by filtration is too slow for economical production. Hydrogen-bonding blockers serve as a potential solution to prevent irreversible agglomeration during drying; however, most reported additives cannot be efficiently removed or washed out after dispersion. Hence, they need to be compatible with end-use systems.
- **Knowledge:** There is a significant knowledge gap regarding the technologies and expertise employed by other industries to remove water from other nanomaterials. There is also a lack of knowledge related to technical customer specifications, which could pose a barrier to establishing important industry partnerships.

Technical Solutions

For the ***Drying and Dewatering R&D*** priority, the team grouped the promising technical solutions into four themes, which are summarized below:

- **Dewatering Research:** To reduce energy usage for drying, R&D is needed to develop and implement new commercially viable dewatering technologies. Research should evaluate available dewatering technologies, determine relative performance, and identify issues. A critical aspect of this research will involve exploring chemistries for modulating temporary hydrophobicity that decay with time, thus enabling redispersion post-decay. Research should define a means to dramatically improve the drainage rate of cellulose nanomaterials and develop additives allowing reversible or temporary flocculation. Exploiting shear-thinning properties of cellulose nanofibrils (CNF) could improve mechanical dewatering.
- **Drying Research**: R&D is needed to evaluate drying methods that have higher yields and are less sensitive to feed concentration. Research should examine current drying technologies to determine and compare the relative performance and issues for each method. Ultimately, research would result in a novel approach for drying so that cellulose nanomaterials are redispersible and lower-density. Such R&D could include the impact of atomizer droplet size on redispersion for spray drying, rheology of cellulose nanomaterials suspension, and dewatering under electric field. For composite applications, research should determine whether a polymer or monomer can be implemented into the cellulose nanomaterial production process, thereby reducing the drying need as well as making them easier to use in subsequent polymer composite processing into end-use products.
- **Crosscutting Research**: Research is needed to investigate known methods for processing other nanomaterials and to assess the applicability of those techniques for cellulose nanomaterials. Alternative solvent mediums that can replace water and be removed and recovered more easily should be investigated. An analysis method needs to be developed to reveal how CNF and CNC change during processing.
- **Agglomeration Research:** Additional research is required to study techniques used to prevent agglomeration and identify issues with each one. Research should identify a coating or additive that can be applied to cellulose nanomaterials in water that blocks hydroxyl groups.

Enabling Technologies

Technical Issues

For the ***Enabling Technologies R&D*** priority, the team grouped the technical issues into six major themes, which are summarized below:

- **Performance Issues**: A variety of performance issues inhibit the use of cellulose nanomaterials in composite materials. For example, traditional sulfuric acid CNC's are not universally dispersible in polymeric hydrophobic mediums, which prevents the materials' potential from being fully realized. Limited information has been reported on the performance advantages of CNC addition to plastics, hindering the market

pull of cellulose nanomaterials. Another issue is that cellulose nanomaterials generally have limited thermal stability, meaning that they may not be compatible with polymer melt processing. The impact of the materials' hydrophilic nature, and knowledge of how to make surface modifications to improve compatibility without changing performance characteristics, is an additional challenge. Adoption would be accelerated with better understanding of cellulose nanomaterials' impact on performance properties in end-use applications.

- **Processing Issues:** There is a significant knowledge gap regarding the changing rheological properties during the process of mixing and how to address the challenging rheological behavior. A better understanding of rheology is needed for manufacturing at scale. Currently, there is no scalable method for introducing cellulose nanomaterials into composite manufacturing lines. The processing techniques for inclusion of cellulose nanomaterials in a polymeric matrix must be more fully developed.
- **Marketability Issues:** Cellulose nanomaterials have wide market potential, but there is a lack of market pull. From an end-use perspective, the specific product applications where cellulose nanomaterials provide the most benefit are not clear. The performance information needed to interest buyers and achieve market penetration is lacking. Greater market understanding is needed to generate the right information for buyers.
- **Product Standard Issues:** Product standards are needed to enable reproducibility and comparison with existing materials. The lack of standards defining the physical properties of cellulose nanomaterials and cellulose nanomaterial-based films makes it difficult for researchers to design experiments and make appropriate material selections.
- **Safety Issues:** The safety of cellulose nanomaterials when in contact with food needs to be established with credible research studies. It would be beneficial if cellulose nanomaterials were to achieve U.S. Food and Drug Administration (FDA) Generally Recognized as Safe (GRAS) status to unlock markets and reassure customers. To verify safety, techniques that can effectively measure any potential release of cellulose nanomaterials from composites are needed.
- **Metrology Issues**: There is currently no economical technique that allows for the accurate and timely measurement of cellulose nanomaterials used or retained in composite products. Test methods have not been standardized. A method for evaluating the consistency and purity of the material and for conducting quality control is required. Specifically, test methods are needed that can be run by shift operators on the operating floor.

Technical Solutions

For the ***Enabling Technologies*** R&D priority, the team organized the technical solutions around seven major research areas, which are summarized below:

- **Application Needs/Opportunities:** R&D is needed to investigate the reinforcing attributes of cellulose nanomaterials in composite systems to create components for major sectors such as automotive, aerospace, and construction. Addressing pre-competitive scalability and compatibility issues will facilitate commercialization of cellulose nanomaterials in a variety of high-volume manufacturing applications. This effort will involve the investigation and development of scalable dispersion techniques and alternate modes of incorporating cellulose nanomaterials.
- **Safety/Environment Benefits:** A food safety study would be helpful in demonstrating the safety of cellulose nanomaterials for GRAS designation for food contact. Collaboration with government and industry would be critical for the success of this investigation. To demonstrate environmental benefits, research should be conducted to determine the environmental performance of cellulose nanomaterials and composites and compare it to plastics.

- **Standards:** Further work is needed to develop characterization standards for the structure and mechanical properties of cellulose nanomaterials and composites. The work should build on existing techniques for measuring other types of nanoparticles. The characterization of cellulose nanomaterials should determine acceptable means of measurement, develop criteria or specifications for labeling, and allow manufacturing to create a Certificate of Authenticity for the product. An ideal end-state would include a comparison of cellulose nanomaterials available for research and development work.
- **Marketability:** To amplify market pull, a life-cycle assessment (LCA) for cellulose nanomaterials production and application pathways is needed. The LCA should consider multiple production pathways and key near-term applications. In addition, fostering partnerships with end users will help establish a better definition of customer needs, requirements, and value proposition. Customers may also provide metrics that could be utilized by cellulose nanomaterials producers.
- **Performance:** R&D is needed to develop a compatibilization scheme to introduce cellulose nanomaterials into complex multicomponent materials and systems, including polymer systems, resin mixes, ceramics, innovative health care applications and printed electronics. Research should also investigate surface functionalization of cellulose nanomaterials to tune hydrophobicity. Multiscale predictive modeling of cellulose nanomaterials could help increase understanding of the impacts of cellulose nanomaterials integrated to larger multi-component structures and materials. Modifications that improve thermal stability and water resistance of cellulose nanomaterials should be developed.
- **Metrology:** Research is needed to understand cellulose nanomaterials size distribution, interfacial interactions, and how those relate to composites and rheology behaviors. A detection method such as fluorescent tagging for cellulose nanomaterials in cellulose substrates might be employed. New methods to evaluate interfacial shear stress would help improve understanding and mechanical properties of cellulose nanomaterials.

R&D Projects

Based on the technical issues and solutions, the team identified an integrated set of six high-priority R&D projects (see Table 5), two for the Dewatering and Drying R&D priority and four for the Enabling Technologies R&D priority.

Using a structured format, the team developed detailed R&D project maps for each of these six high-priority projects. These project maps are intended to guide the implementation of the R&D projects and provide a basis for securing funding and establishing partnerships. The project maps are presented in Appendix A.

Table 5. High-Priority Projects

Dewatering and Drying
1. Develop Viable Dewatering Methods – Find a cost-effective solution that meets EHS goals and preserves nanocellulose characteristics and properties by modulating hydrophilicity, drainage rates, and rheology. – Explore additives to create temporary or reversible flocculation. – Explore alternative solvents.
2. Develop Viable Drying Methods – Explore and compare existing drying technologies for cellulose nanomaterials and for other nanomaterials via literature review and bench and pilot evaluations. – Explore chemical aids to prevent agglomeration/hysteresis. – Conduct process simulation modeling viability of scaling up to commercial size.
Enabling Applications
1. Facilitate Commercialization in High-Volume Composites – Develop scalable dispersion technologies by investigating alternative modes of incorporation and surface functionalization. – Test composites and evaluate value propositions.
2. Prepare an Application for Generally Recognized as Safe (GRAS) Designation – Conduct toxicological investigation for publication and expert peer review to obtain FDA GRAS status for cellulosic nanomaterials.
3. Develop Characterization Standards for Nanocellulose and Composites – Develop standardized descriptions and characterization methods of materials and structures to facilitate comparisons and commercialization.
4. Conduct Life-Cycle Analysis – Model various nanocellulose production methods and develop cradle-to-grave LCA to support low-carbon footprint claims.

Stakeholder Actions to Support Commercialization

In addition to mapping out R&D projects to benefit the production and application of cellulose nanomaterials, the Agenda 2020 Cellulose Nanomaterials Team also developed specific recommendations for stakeholders in the materials science community, including government, academia, and industry, to realize the potential of cellulose nanomaterial:

- Establish public–private partnerships
- Support government research investments
- Stimulate research at national laboratories and universities
- Raise awareness
- Gather EHS data
- Support the development of internationally recognized standards

These recommendations are discussed in detail below.

Establish Public–Private Partnerships

Establishing public–private partnerships will help address the opportunities embodied in cellulose nanomaterials. In particular, private companies with strategic interest in developing these materials should support a Manufacturing Innovation Institute for Bioproducts. Establishment of such a partnership would be reflective of company interests and of the interests of the National Nanotechnology Initiative, the U.S. Department of Agriculture (USDA) Forest Service, the National Institute of Standards and Technology and other agencies

Support Government Research Investments

The Agenda 2020 Technology Alliance strongly supported the investment of supplemental research funding by the Forest Products Laboratory/USDA Forest Service to accelerate the efforts to develop the potential of cellulose nanomaterials. The USDA/US Forest Service recently announced another such round of funding to continue to propel progress. We urge other agencies to do so as well, within their areas of interest, and encourage USDA to continue this much-needed funding in future years.

Stimulate Research at National Laboratories and Universities

To translate fundamental knowledge developed by the investment in nanotechnology research into manufacturing and job creation, private companies and consortia should seek partnerships with national laboratories and academia on a national and international level. This is a critically important linkage. National laboratories and academia have the infrastructure to conduct needed work on nanoparticles and the capability to carry out basic research. University faculty and students also bring intellectual capacity to bear on providing innovative solutions and advancing the underlying science. To be effective, the work of academia and national laboratories must be focused and adequately funded.

Raise Awareness

The team urges forest products industry associations to collaborate in promoting awareness of the possibilities inherent in cellulose nanomaterials and create support for manufacturing and commercialization. This would include promoting visibility in the executive branch, Congress, and the general public. Execution of the recommendations in this roadmap can support initiatives such as the Advanced Manufacturing Initiative, additive manufacturing initiatives, the Materials Genome Initiative, and other national efforts.

Support Development of Environment, Health, and Safety Data

The team supports the work of the P^3Nano Initiative sponsored by the U.S. Endowment and Forest Communities and the USDA Forest Service to complete its contracted work on development of a Material Safety Data Sheet for cellulose nanomaterials. This will facilitate work on developing safe workplace practices and LCAs as applications are developed.

A level playing field in the marketplace depends on a rigorous base of data to support statements

related to the sustainability, low-carbon footprint, biodegradability, etc., of cellulose nanomaterials compared to competitive materials. We support continued development of such data, and we fully support efforts of organizations such as the National Council for Air and Stream Improvement and the American Forest and Paper Association to pursue such scientific data.

Support Development of Internationally Recognized Standards

We support and encourage efforts of the International Organization for Standardization community, Technical Association of the Pulp and Paper Industry, and other bodies to develop the international codes, standards, and test methods to develop common nomenclature and measurements. These are critical to international trade, effective regulation, and development of a shared understanding of scientific research.

5. Conclusion

This roadmap serves to facilitate the manufacture and use of cellulose nanomaterials for the benefit of the pulp and paper industry and for national goals. Cellulose nanomaterials demonstrate great potential for use across a wide array of industries and markets because of their unique distinguishing properties. The range of potential applications of cellulose nanomaterial is substantial and includes packaging, automotive applications, cement, paper, flexible electronics, photovoltaics, filters, viscosity modifiers, oil drilling fluids, and additive manufacturing.

Cellulose nanomaterials also offer the added advantages of being renewable, biologically produced, and biodegradable. They could be sustainably and renewably produced in quantities of tens of millions of tons per year.

Therefore, commercialization of cellulose nanomaterial can play a critical role in meeting the national goals of sustainability, full employment, and healthy, resilient forests. The Agenda 2020 Cellulose Nanomaterials Team envisions a materials revolution, in which new market entries made from cellulose nanomaterials derived from sustainable, renewable forest resources are in wide use supporting the everyday lives of millions around the globe.

To help accomplish this vision, this roadmap identifies six high-priority research and development (R&D) projects intended to focus and direct R&D work toward the rapid commercialization of cellulose nanotechnologies. The projects are designed to lead to breakthrough technologies that can be implemented in 5 to 10 years.

However, moving the promising concepts presented in this roadmap quickly from bench-scale through pilot-scale demonstration and into commercial implementation will require adequately funded public–private partnerships and collaborations. This roadmap is designed to spur the necessary collective action and serve as an invitation and as guidance for future research and development efforts.

We look forward to engaging the research community to address this challenge, and we welcome the input and engagement of industry, universities, research institutions, national laboratories, and public agencies in developing technology options—and in further defining the questions and challenges.

We are grateful to all those who have contributed to the development of this roadmap as well as to those who will read and consider its content.

Appendix A: R&D Project Maps

The following pages present the project maps for the six high-priority projects. These project maps are intended to guide the implementation of the research and development (R&D) projects and provide a basis for securing funding and establishing partnerships.

The initial sections of the project map describe the larger context for the proposed effort, including the specific problems being addressed, keys to success and potential implementation challenges, and potential partners. Understanding this larger context is especially important to entities that are considering funding or contributing to the project. Funding sources are more likely to back projects that demonstrate alignment to industry needs and address key technical challenges.

Each project map also includes a specific plan for carrying out the R&D project, potential funding options, and additional guidance for carrying out the research.

The projects maps are presented in the following order:

- Develop Viable Dewatering Methods
- Develop Viable Drying Methods
- Facilitate Commercialization in High-Volume Composites
- Prepare an Application for Generally Recognized as Safe (GRAS) Designation
- Develop Characterization Standards for Nanocellulose and Composites
- Conduct a Life-Cycle Analysis

Project 1: Develop a Viable Dewatering Method

Proposed R&D Effort

Develop dewatering solutions that are cost-effective, scalable, do not negatively impact characteristics of nanocellulose, and meet environmental, health, and safety (EHS) and sustainability goals.

Problem Statement

- Nanocellulose materials have a high affinity for water, which is difficult to remove.
- High-water-content nanocellulose is expensive to transport, and many applications cannot tolerate water.
- Dehydration specification may vary from ~30% to >95%.

Current State of Technology & Knowledge	Keys to Success & Implementation Challenges
Many technologies have been explored, such as centrifugation and evaporation, but cost and scale-up issues are believed to be obstacles in a commercial environment.	Dewatering solutions must be cost-effective (e.g., low capital and operating costs), be scalable, must not negatively impact characteristics of nanocellulose, and meet EHS and sustainability goals.

Potential Partners

PARTNERS	HOW THEY COULD CONTRIBUTE
TBD	

Project 1: Develop a Viable Dewatering Method
(continued)

Project Plan

ACTIVITIES	EXPERTISE/PARTNERS	TIMEFRAME
1. Explore chemistries for modulating nanocellulose hydrophobicity (e.g., as a function of time, pH, other environmental parameters, or end use).		
2. Explore additives to improve the nanocellulose-water drainage rate.		
3. Explore additives allowing reversible or temporary flocculation.		
4. Develop a fundamental understanding of nanocellulose suspension rheology, including how it relates to processing, and explore additives enabling control of rheology.		
5. Explore novel methods, including use of electric fields, magnetic fields, ultrasonics, and other "blue sky" approaches. Benchmark approaches used in other industries.		
6. Explore the production of nanocellulose in alternative solvents.		

Funding Options

- Public–private partnerships
- National Science Foundation (NSF) grants

Other Guidance

- Fund projects and implement the workshop plan immediately to make a positive impact on the U.S. forest products industry.
- Promote the value of nanocellulose materials as an enabler of other technologies that are highly funded: automotive, electronics, biomedical, aerospace, defense, etc.
- Develop partnerships with customers and other in the product value chain, which can aid in the development and implementation of technologies.
- Data from this project can also feed into the life-cycle analysis (LCA) study for cellulose nanomaterials manufacturing (on energy and water usage). Also, approaches used in this research can be helpful in dispersing cellulose nanomaterials in composite matrices.

Project 2: Develop a Viable Drying Method

Proposed R&D Effort

Develop viable approaches to dry cellulose nanomaterials focusing on cellulose nanofibrils (CNF) so that it is redispersible and lower-density. Document performance of available technologies and identify gaps.

Problem Statement:

- Energy required to dry the material is high.
- CNF forms strong bonds once dried and is difficult to redisperse.
- Material is lost in redispersing.

Current State of Technology & Knowledge	Keys to Success & Implementation Challenges
• Spray drying – capital cost and redispersibility • Freeze drying – scale and cost	• Minimal agglomeration at acceptable economics

Potential Partners

PARTNERS	HOW THEY COULD CONTRIBUTE
• Forest Products Laboratory (FPL)	• Equipment and expertise
• Universities	• Equipment and expertise
• Industry partners	• Equipment and expertise

Project 2: Develop a Viable Drying Method *(continued)*

Project Plan

ACTIVITIES	EXPERTISE/PARTNERS	TIMEFRAME
1.a. Review available drying technologies; compare performance (feed concentration yield) vs. cost (energy, capital, and operating cost). b. Review known technologies for other nanomaterials (freeze dry, spray, solvent flash, drum, and microwave belt). c. Review literature to identify potential chemical pathways to do the following: • Minimize agglomeration • Assist drying	• Equipment supplier • Subject-matter experts	4 months
2.a. Evaluate the most promising options for cellulose nanomaterials at bench scale. b. Evaluate the most promising options at pilot scale.		6 months 12 months
3. Build a process model for promising options.		3 months
4. Determine properties vs. percentage solids content.		
5. Conduct a LCA of cellulose nanomaterials production options (carbon emissions).		

Funding Options

- Agenda 2020 Technology Alliance
- P^3Nano
- U.S. Department of Energy (DOE)
- AMTech Phase 2
- Private sector
- Renewable Bioproducts Institute (RBI) Endowment

Other Guidance

What types of interfacial properties can be measured to correlate with drying? Consider particle adsorption at an interface.

Project 3: Facilitate Commercialization in High-Volume Composites

Proposed R&D Effort

Address pre-competitive scalability and compatibility issues to facilitate commercialization of cellulose nanomaterials in high-volume composite applications.

Problem Statement

There are large risks in adopting cellulose nanomaterials composites because of unknowns in scalable manufacturing. Cost and scale issues are fundamental problems. There is an insufficient understanding of the effects of dispersion state and interface interactions on performance.

Current State of Technology & Knowledge	Keys to success & Implementation Challenges
• Cellulose nanomaterials composite fabrication is done at laboratory scale. • There are few if any industrial-scale examples. • Chemical functionalization is done in beakers now. • Knowledge on shear history that would be important in large-scale forming is limited.	• Demonstrate ways to repeatedly introduce cellulose nanomaterials to large-volume components addressing compatibility and dispersion properties. • Achieve light-weighting and performance at same cost (time and energy) as existing manufacturing. • Develop metrology for better characterization of the dispersion state and interface interaction.

Potential Partners

PARTNERS	HOW THEY COULD CONTRIBUTE
• Oak Ridge National Laboratory (ORNL)	• Carbon fiber experience
• Universities with manufacturing research centers (Georgia Tech Manufacturing Institute, University of Akron, etc.)	• Research at scale
• U.S. Forest Service – FPL	• Sourcing and compatibilization at scale
• Industrial end-users (e.g., automotive, aerospace, and consumer products)	• Pilot runs
• National Institute of Standards and Technology (NIST)	• On-line metrology of manufacturing

Project 3: Facilitate Commercialization in High-Volume Composites *(continued)*

Project Plan

ACTIVITIES	EXPERTISE/PARTNERS	TIMEFRAME
1. Investigate and develop scalable dispersion techniques.		5 years
2. Investigate alternative modes of incorporating cellulose nanomaterials (coating, laminates, spray, filler, and neat films).		5 years
3. Develop scalable chemical functionalization schemes.		5 years
4. Apply new dispersion/functionalization schemes in pilot runs.		5 years
5. Characterize and test large components (mechanical properties).		5 years
6. Evaluate costs to manufacture and value creation		1 year

Funding Options

- DOE
- NSF
- Industrial partners
- U.S. Department of Defense

Project 4: Prepare an Application for GRAS Designation

Proposed R&D Effort

Conduct a collaborative study to demonstrate the safety of cellulose nanomaterials in food and food contact packaging and achieve GRAS designation by the U.S. Food and Drug Administration (FDA).

Problem Statement

- Need to demonstrate safety of cellulose nanomaterials for food composite applications through oral exposure studies.
- Need FDA approval to utilize cellulose nanomaterials in food and food contact packaging.

Current State of Technology & Knowledge	Keys to Success & Implementation Challenges
Commercially available testing has challenges for nanomaterials requiring additional research beyond standard testing.	• Develop milestones to allow for interim/ongoing use • Peer review • Publication of results • Detection • Study quality • Collaboration between organizations • Manufacturing consistency (standards)

Potential Partners

PARTNERS	HOW THEY COULD CONTRIBUTE
• P^3Nano* • A2O2O* • FPL • Natural Resources Canada • Academic laboratories • Commercial toxicology laboratories • Government granting agencies *Various partner companies may come through A2O2O or P3Nano	Finance, materials, testing, methods development, characterization, manufacturing, etc.

Project 4: Prepare an Application for GRAS Designation *(continued)*

Project Plan

ACTIVITIES	EXPERTISE/PARTNERS	TIMEFRAME
1. Characterization, assay development		2016–2018
2. Preliminary toxicity testing		2016–2018
3. Toxicological screening assays		2016–2018
4. Peer review and publication		2016–2018
5. Submission to FDA		2016–2018

Funding Options

- P3Nano
- Industry
- Government granting agencies

Partners could contribute analysis in lieu of funding

Project 5: Develop Characterization Standards for Nanocellulose and Composites

Proposed R&D Effort

1. Develop characterization standards for structure and mechanical properties of nanocellulose and composites.
2. Conduct blind comparison of NFC producers' products, including image analysis.

Problem Statement

Lack of product specification creates ambiguity of claims approval.

Current State of Technology & Knowledge

1. Individual producers generate individual data.
2. Different isolation methods produce different properties.
3. No quality standards exist that correlate to value.

Keys to Success & Implementation Challenges

1. Cellulose nanocrystals (CNC) and CNF require very different characterization methods.
2. Each characterization should be done by the same laboratory. Establish center of excellence for each test required, i.e., the National Renewable Energy Laboratory (NREL) for imaging and NIST for mechanical.

Potential Partners

PARTNERS	HOW THEY COULD CONTRIBUTE
• Oregon State • NIST • NREL • Georgia Tech RBI • FPL • University of Maine • Oak Ridge National Laboratory (ORNL)	Each partner specializes in one or two product properties: • Oregon State – modeling • NIST – mechanical • NREL – structural • Georgia Tech – composite processing/fabrication • FPL – surface area, environmental testing (degradability) • University of Maine – production of samples, films • ORNL – 3-D printing, composite center of excellence

Project 5: Develop Characterization Standards for Nanocellulose and Composites *(continued)*

Project Plan

ACTIVITIES	EXPERTISE/PARTNERS	TIMEFRAME
1. Confirm study outline, inputs, outputs (metrics), and timeframe. – Solicit industry input for desired metrics		
2. Confirm participants and capabilities.		
3. Generate samples/distribute.		
4. Perform characterization; analyze results.		
5. Report – include reference materials to compare against existing products such as amorphous polylactic acid. – Sets the stage for commercialization		

Funding Options

- Make a case: moving toward a bio-based economy, lightweighting to replace plastics
- Consider DOE, USDA, and NIST (AMTech)
- Consider cellulose nanomaterial producers. They get some indication of certification for the funds.

Other Guidance

- Properties of raw cellulose nanomaterials: size, true aspect ratio CNC-only, diameter, width, “effective aspect ratio” of CNF using rheological properties, and BET surface area
- Capture different techniques for different types of nano particles.
- The following tests should be conducted:
  - Mechanical properties of composites: elastic modulus, compressive strength, and tensile strength (strain to failure)
  - Structure: TEM tomography correlated to x-ray scattering
  - Thermal: thermal conductivity, thermogravimetric analysis (degradable)
  - Other: degradability to focus on market application

Project 6: Conduct a Life-Cycle Analysis

Proposed R&D Effort

Conduct LCA of cellulose nanomaterials production and application pathways.

Problem Statement

- Need guidance to producer and user communities on quantifying sustainability profiles.
- Need to overcome barriers to market entry of cellulose nanomaterials with verifiable claims.

Current State of Technology & Knowledge

- LCA data is lacking for bio-based nanomaterials.
- Bio-based nanomaterials area is lagging far behind biofuels.

Keys to Success & Implementation Challenges

Some small-scale manufacturing is coming online, but data will still come from laboratory- and pilot-scale operations.

Potential Partners

PARTNERS	HOW THEY COULD CONTRIBUTE
• Small-scale cellulose nanomaterial manufacturers	• Provide data
• Near-term applications adopters/leaders	• Review models
• P3Nano/FPL	• Advice on getting others
• LCA consulting firms in biomaterial space	• Peer review
• Academic researchers	

Project 6: Conduct a Life-Cycle Analysis *(continued)*

Project Plan

ACTIVITIES	EXPERTISE/PARTNERS	TIMEFRAME
1. Develop cradle-to-grave LCA framework for multiple production pathways and key near-term applications.	• Sources of data for LCA and a common framework with accepted functional units	2016–2018
2. Assemble input/output data and identify data gaps.	• Public domain open access database	2017–2018
3. Identify comparison benchmarks.	• Documented case studies that can serve as suitable	2018

Funding Options

- LCA of bio-based nanomaterials – USDA, NSF, and the Environmental Protection Agency
- Cellulose nanomaterial producers
- Cellulose nanomaterial adopters

Appendix B: Additional Materials about the Identification of R&D Priorities

Nanocellulose Background

It is amazing that the most available and one of the oldest resources on this planet—plant matter—contains one of the most recently discovered and least understood materials: cellulose nanomaterials. It is difficult to imagine anything on Earth more ubiquitous and environmentally friendly than plants. Plants, from the smallest algae cells to the largest redwood tree, contain cellulose. Cellulose is the most abundant polymer on Earth, representing about 1.5 x 1,012 tons of the total annual biomass production.[43] It consists of glucose linkages arranged in linear chains where C-1 of every glucose unit is bonded to C-4 of the next glucose molecule.[41,42]

These sugar units aggregate along the chain direction with intermolecular hydrogen bonds and hydrophobic interaction. This cellulose chain further assembles into fibrous structures called nanofibrils 2 to 20 nm wide depending on biological species. These nanofibers make up the structure of all plants as well as some fungi, animals, and bacteria.[44] Because these cellulose nanodimensional building blocks have crystalline regions, they have unique distinguishing properties: strength properties comparable to Kevlar®, superabsorbancy, piezoelectric properties equivalent to quartz, the ability to be manipulated into photonic structures, self-assembly properties, and a remarkably uniform distribution of size and shape. In addition, because of their abundance, they could be sustainably and renewably produced in quantities of tens of millions of tons per year.

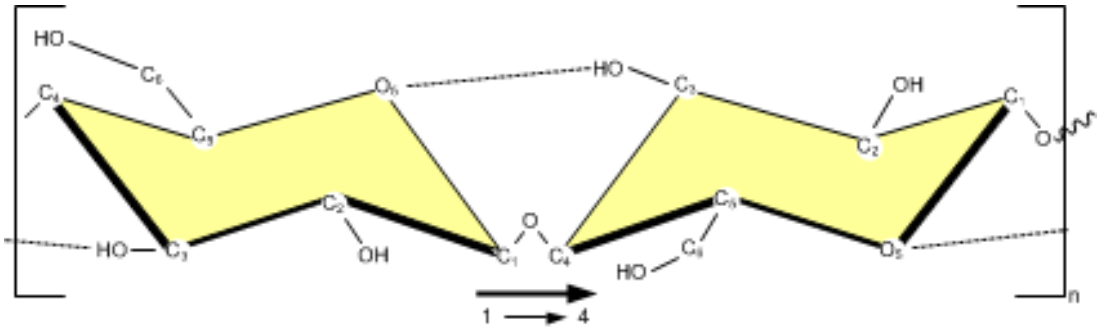

Figure A-1. Cellulose Schematic

Plants have been a major source of raw materials and products for humankind for millennia. For example, products derived from trees such as wood and paper have been with us so long and are used so widely in society that they are largely taken for granted as part of traditional industries with the assumption that no new science is left to learn. However, the opposite is true. Because of the complex cascading hierarchical structure of wood (Figure A-2) many of the technologies used in the forest products industry were first developed empirically through trial and error. The

[43] Klem, D., et al. 2005. *Angewandte Chemie International* 44: 3358.

[44] Kadla, J., and R. Gilbert. 2000. *Cellulose Chemistry and Technology* 34: 197.

complexities of wood are just now yielding to newer and more robust qualitative and quantitative analytical tools. We are beginning to see and track how the mechanical, optical, and other physical properties of wood are related to its discrete hierarchical structures ranging from nanoscale to microscale. As a result, we are now seeing growing efforts worldwide to move research, development, and demonstration forward to commercialize cellulose nanomaterials.

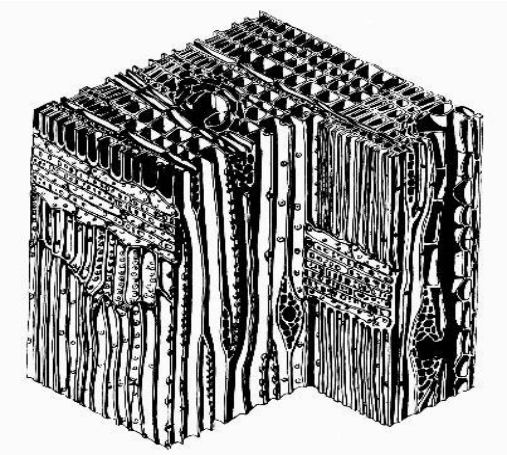

Figure A-2: Wood Structure Schematic

Current Manufacturing Practices

Cellulose Nanocrystals

The preparation of cellulose nanocrystals (CNCs) from biomass generally occurs in two primary stages. The first stage is a purification of the biomass to remove most of the non-cellulose components in the biomass. These include lignin, hemicellulose, extractives, and inorganic contaminants. This is typically done by conventional pulping and bleaching. The second stage uses an acid hydrolysis process to deconstruct the "purified" cellulose material into its crystalline components by removing the amorphous regions of the cellulose microfibrils. The resulting whisker-like particles (3–20 nm wide, 50–2000 nm long) are almost 100% cellulose, and are highly crystalline (62%–90%, depending on cellulose source material and measurement method). The variations in CNC characteristics (e.g., particle morphology, surface chemistry, and percent crystallinity) are strongly linked to the cellulose source material and the acid hydrolysis processing conditions.[45]

The U.S. Department of Agriculture (USDA) Forest Service, Research and Development Division, has a pilot facility for production of up to 50 kg CNC aqueous suspension per week (5%–10% solids) at the Forest Products Laboratory in Madison, Wisconsin. The process is based on concentrated sulfuric acid hydrolysis methods published by Grey et al.[46]

Typically, machine-dried pre-hydrolysis kraft rayon-grade dissolving wood pulp is shredded, placed under nitrogen atmosphere, and heated to 45ºC. Sulfuric acid (64 wt.%) at 45ºC is sprayed over the top of the shredded pulp strips and the mixture is stirred at 45ºC for 90 minutes. The reaction is quenched by diluting approximately 0-fold with water. Hypochlorite solution (household Clorox) is added to remove color formed during the reaction. The use of dissolving pulp as a starting material gives less color than with bleached kraft pulp. The CNC suspension is then neutralized by slow addition of 5%–8% wt.% sodium hydroxide, diluted about four-fold, and

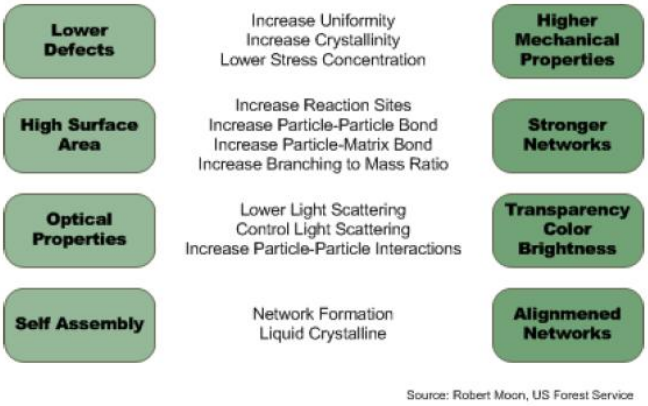

Figure A-3. Properties of Nano

[45] Moon, R., S. Beck, and A. W. Rudie. 2013. "Cellulose Nanocrystals – A Material with Unique Properties and Many Potential Applications." In *Products and Applications of Cellulose Nanomaterials*, edited by M. T. Postek, R. J. Moon, A. W. Rudie, and M. A. Bilodeau. Peachtree Corners, GA: TAPPI Press, 9–12.

[46] Grey et al. 1998. "Effect of Microcrystallite Preparation Conditions on the Formation of Colloid Crystals of Cellulose." *Cellulose* 5: 19–32.

allowed to settle. The salt/sugar solution is then decanted from the solids, which are diluted a second time. At this point, the sodium sulfate concentration drops to about 1 wt.% and the CNC particles begin to disperse in the solution. The CNC is then circulated through a tubular ultrafiltration membrane system where the salt/sugar solution passes through the membrane and the CNCs are retained. Reverse osmosis (RO) water is added as needed to maintain the CNC concentration to 1 wt.%. Diafiltration is continued until the residual salt concentration is reduced to about 8 µM (requiring about 24 hours and 20,000 L RO dilution water). The colloidal CNC suspension is filtered using a 20 µm cartridge-style filter to remove dirt and concentrated to at least 5 wt.% solids using the tubular ultrafiltration system. The cellulose yield is about 50% based on the starting bleached pulp. Each bath of CNC requires about 8 hours for CNC reaction and neutralization, 24 to 48 hours for settling and initial purification, and 24 hours for membrane filtration for final salt removal. Current production is 25 kg per batch, with up to two batches per week.[47,48]

Cellulose Nanofibrils

Cellulose nanofibrils (CNF) are generally manufactured by mechanical treatments, for example in a refiner, grinder, homogenizer, or fluidizer. The resulting material consists of fibrils of many different sizes. The width of the smaller fibrils or aggregates is usually around 20–40 nm, while their length can be several µm. The fibrils are highly branched and flexible. The high energy consumption of mechanical treatments may be reduced with different chemical or enzymatic pretreatments that act by facilitating the fibrillation of cellulose fibers by mechanical treatments in subsequent stages. Several different pretreatments for obtaining cellulose nanofibrils have been published, including mild enzyme pretreatment using endogluconase, carboxy-methylation, and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxly radial) mediated oxidation.[49]

The University of Maine operates a pilot plant capable of producing up to one ton per day (dry basis) of CNFs. The plant was funded through a joint venture with the USDA Forest Service and, as of summer 2014, is the only one of its kind in the United States. Typically, machine-dried northern bleached softwood kraft pulp is blended with water to 3 wt.% solids before processing through a modified, mechanical disc refiner. The pulp is refined using a series of progressively finer plates until a nanofibril gel is formed and the target particle-size range is reached. This series of specific mechanical treatments significantly lowers the energy required to produce CNF (~2,000 kWhr/MT) compared to prior-art mechanical methods like homogenizers and grinders. Refining is carried out with recirculation to provide nominally 30 passes through the refiner. The pilot plant is equipped with a spray dryer with the capacity to dry several pounds of cellulose nanomaterials per day.

The USDA's Forest Products Laboratory cellulose nanomaterials pilot plant also produces TEMPO-pretreated CNFs at the 2–3.5 kg scale. Using machine-dried market pulp, the yield of cellulose nanomaterials on original pulp is ~90% when using sodium hypochlorite at the primary oxidant. The method is based on laboratory work by Saito et al., which demonstrated that the energy required to produce a nanoscale fibrillated product was reduced by TEMPO pretreatment.[50] The pilot method alters the method by Saito et al. by using a sodium carbonate buffer to control the pH to 10. Typically, commercial machine-dried eucalyptus bleached kraft pulp is blended with water and then pretreated by mixing at 2 wt.% solids, pH 2, and 2

[47] Reiner, R.S., Rudie, and A.W. 2013. "Process Scale-Up of Cellulose Nanocrystal Production to 25kg per Batch at the Forest Products Laboratory." In *Products and Applications of Cellulose Nanomaterials*, TAPPI Press.

[48] Nelson, Kim, Theodora Retsina, Mikhail Iakovlev, Adriaan van Heiningen, Yulin Deng, Jo Anne Shatkin, and Arie Mulyadi. "Production of Low-Cost Nanocellulose for Renewable." In *Materials Research for Manufacturing: An Industrial Perspective of Turning Materials into New Products*, edited by Madsen, Lynnette D., and Erik B. Svedberg. New YorK: Springer International Publishing.

[49] Kangas, H. 2013. "Cellulose Nanofibrils – A Class of Materials with Unique Properties and Many Potential Applications." In *Products and Applications of Cellulose Nanomaterials*, edited by Michael T. Postek, Robert J. Moon, Alan W. Rudie, and Michael A. Bilodeau. Pachtree Corners GA: TAPPI Press.

[50] Saito, T. et al. 2007. "Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation of Native Cellulose." *Biomacromolecules* 8: 2485–2491.

wt.% sodium chlorite (NaClO2) on pulp. The mixture is stirred overnight at room temperature, then filtered and washed to collect the pulp.

Pretreated pulp is combined with sodium carbonate and stirred for an hour at room temperature. Sodium bicarbonate, sodium bromide, and TEMPO are added, and the reaction is heated to 30ºC. Sodium hypochlorite (NaClO) solution is added and the reaction is stirred overnight at 30ºC. The treated pup is filtered, washed, diluted to 2 wt.%, and refined using a disc refiner.

Refining is carried out with recirculation and run long enough to provide nominally 25 passes through the refiner. A heat exchanger is included in the recirculation loop to control the temperature near 50ºC. After refining, the pulp is diluted to 0.1 wt.% in water and treated with an ultrasonic probe for six seconds with an energy input of 300 W, passed through a centrifuge operating at 12,500 G, and concentrated to at least 0.5 wt.% solids using a tubular ultrafiltration system with a 200,000-MW cutoff membrane.

Final clarification is performed by passing the material twice through a homogenizer (Microfluidics M-110EH-30) equipped with series 200- and 87-micron orifices.[51,52]

Manufacturing Capacity around the World

Research into cellulose nanomaterials is occurring in many parts of the world. There are currently ten pilot and semi-commercial operations reportedly producing CNF and an additional six with the capacity to produce CNC. It is likely that additional unannounced capacity is located on company sites within the pulp and paper industry. Cooperation, pooling of resources, and open sharing of pre-competitive information is critical to moving the science and technology of cellulose nanomaterials forward in the most expeditious manner possible. In North America, Europe, and Asia, it is becoming common for governmental agencies to partner with industry and academia.

United States

In the United States, the federal government's emphasis on advanced materials has led to increasing interest in nanomaterials and ultimately to the formation of the National Nanotechnology Initiative (NNI).

NNI brings together 25 federal agencies and departments to serve as a natural focal point for government and industry to work collaboratively.[53] Within NNI, the USDA Forest Service is the lead federal agency advocating for the development of cellulose nanomaterials from forest biomass.

The forest products industry, through the Agenda 2020 Technology Alliance, has also formed a relationship with NNI to promote research and development (R&D) of cellulose nanomaterials. In addition, NNI has recently developed a sustainable manufacturing signature initiative that includes renewable and sustainable cellulose nanomaterials.[54] These NNI signature initiatives are aimed at enhancing the commercialization of nanomaterials and nano-enabled products for the benefit of humankind.

Within the United States, as of summer 2014, there are two cellulose nanomaterial pilot facilities: one at the USDA Forest Service Forest Products Laboratory and the other at the

[51] Nelson, Kim, Theodora Retsina, Mikhail Iakovlev, Adriaan van Heiningen, Yulin Deng, Jo Anne Shatkin, and Arie Mulyadi. "Production of Low-Cost Nanocellulose for Renewable." In *Materials Research for Manufacturing: An Industrial Perspective of Turning Materials into New Products*, edited by Madsen, Lynnette D., and Erik B. Svedberg. New YorK: Springer International Publishing.

[52] Reiner, R.S., and A.W. Rudie. 2013. "Pilot Plant Scaleup of TEMPO-Pretreated Cellulose Nanofibrils," In *Products and Applications of Cellulose Nanomaterials*, edited by Michael T. Postek, Robert J. Moon, Alan W. Rudie, and Michael A. Bilodeau. Pachtree Corners GA: TAPPI Press.

[53] Moon, R., A. Martini, J. Nairn, J Simonsen, and J. Youngblood. 2011. "Cellulose Nanomaterials Review: Structure, Properties and Nanocomposites." *Chemical Society Review* 40(7): 3941–3994.

[54] Moon, R., S. Beck, and A. W. Rudie. 2013. "Cellulose Nanocrystals – A Material with Unique Properties and Many Potential Applications." In *Products and Applications of Cellulose Nanomaterials*, edited by M. T. Postek, R. J. Moon, A. W. Rudie, and M. A. Bilodeau, 9–12. Peachtree Corners, GA: TAPPI Press.

University of Maine's Process Development Center. The main focus of these pilot plants is to manufacture large quantities of cellulose nanomaterials to facilitate R&D. In addition, as of November 2014, the Herty Advanced Materials Center (Savannah, Georgia) is installing a 500-L reactor that is capable of producing nanocrystalline cellulose and functionalized cellulose.

Canada

In Canada, ArboraNano served as the focal point for public–private partnerships until March 2014 when it completed its mandate.[55] ArboraNano was the Canadian Forest NanoProducts Network made possible through the Canadian government's Business-led Centres of Excellence program, FPInnovations, and NanoQuébec. Its mission was to create new business opportunities using renewable forest resources and to leverage the advances made in nanotechnology, especially cellulose nanomaterials, to develop novel or superior products with enhanced performance attributes. These centers worked with private industry to create two main production plants in Canada. The first is Celluforce, which is a demonstration-scale facility for the production of CNC. The second, run by Kruger and FPInnovations, focuses on a product the company calls "cellulose nanofilaments."

Blue Goose Biorefineries, Inc., is producing cellulose nanomaterials from a variety of biomass sources at a pilot plant in Saskatoon, Saskatchewan, reported to be able to produce approximately 250 lbs. per month of cellulose nanomaterials for research and technical evaluation. The process involves an oxidative method using hydrogen peroxide and citric acid to remove lignin, hemicellulose, and amorphous cellulose. The process is reported to be commercially scalable using off-the-shelf process equipment in a non-corrosive environment.

Scandinavia

Similarly, in Finland, the Finnish Centre for Nanocellulose Technologies was established as a public–private partnership by the federal VTT Technical Research Center of Finland, Aalto University, and UPM (one of the world's leading forest product groups).[56] The focus of the Centre is to create new applications for cellulose nanomaterials as a raw material, substance, and end product. In addition, significant activity has been reported and a number of patent filings covering both process and applications have come from Innventia, the Pulp and Fiber Research Institute in Norway (a subsidiary of Innventia), UPM-Kymmene, and Stora-Enso. UPM has been particularly prolific in its patent activity and, per a November 2011 announcement, has commissioned a pre-commercial CNF pilot plant at Otanieme, Espoo, Finland. As of 2013, UPM and Ashland have entered into an agreement to develop market applications for UPM's Biofibrils technology. In 2011, Stora-Enso also announced the start-up of a pre-commercial CMF plant in Imatra, Finland. Additional players in the space are Lulea University of Technology (Sweden), and Norske Skog. On November 5, 2014, Borregaard announced its intention to build a new microfibrillar cellulose plant at its site in Sarpsborg, Norway.

Asia

In Japan, a joint research program by New Energy and Industrial Technology Development Organization (NEDO), led by Kyoto Institute and funded by NEDO and industry, developed high-performance cellulose nanofibers. A second NEDO and industry-sponsored program led to the development of high-barrier functionalized packaging materials. These technologies have created manufacturing opportunities in Japan for Nippon Paper and Oji Holdings, Inc. According to Resource Information Systems, Inc., Nippon Paper is Japan's largest producer of CNF and has a significant patent portfolio related to the TEMPO-oxidation process. In November 2013, Nippon reported that it had commissioned a pre-commercial plant at its Iwakuni mill with an annual capacity to produce more than 30 tons per year of CNFs.

[55] Grey et al. 1998. "Effect of Microcrystallite Preparation Conditions on the Formation of Colloid Crystals of Cellulose." *Cellulose* 5: 19–32.

[56] Reiner, R. S., and A. W. Rudie. 2013. "Process Scale-Up of Cellulose Nanocrystal Production to 25kg per Batch at the Forest Products Laboratory." In *Products and Applications of Cellulose Nanomaterials*. TAPPI Press.

In India, a 2.5 Kg per day cellulose nanofiber pilot plant has been established at the Central Institute for Research on Cotton Technology at Mumbai with plans to expand to 10 Kg per day. While based on cotton fibers/linters, it expects to work with the growing pulp and paper industry as well as in areas of life science and medicine.

Applications and Challenges

Table A-1 presents an overview or the applications and challenges for cellulose nanomaterials.

Table A-1. Promising Applications and Challenges

General Application	Specific Application	Specific Challenges
Composites/Automotive body parts	Lighter weight than glass fiber	Dry cellulose nanomaterial in a way that avoids agglomeration
	High-strength fibrils	Develop appropriate interface chemistry/surface treatment to provide compatibility with resins
	Lower cost than other nanomaterials	Develop effective dispersion methods in resins
		Liberate cellulose nanomaterial in non-aqueous media to avoid drying challenges
		Develop water-based chemistries for composites to take advantage of hydrophilic properties
Aerogels/Foams	Lightweight sandwich structures with high strength	Develop cost-effective drying techniques
	Thermal insulation for wall-board, freezer packaging, and hot drink packaging	Develop interface chemistry
	Acoustic insulation	Ensure effective dispersion
	More robust foams with minimized brittleness	Ensure appropriate strength properties
Painting and coatings	Higher-strength, more robust coating; scuff resistance	Develop functional base materials together with interface chemistries
	Scratch-free floor coatings	
	Spackle, cover blemishes	
	Clear films and protective panels	
Medical	Wound healing	Identify and address environment, health, and safety issues, if any
	Tissue scaffolding	Conduct clinical trials
	Hemorrhage control	Understand interactions with human tissues
Viscosity Control	Oilfield applications	Understand rheological effects and component interactions
	Paint thixotrope	Develop formulations
Filtration/Separation	Water purification	Evaluate filtration options especially with other media
	Oil from water, clean-up	Develop broader separation technologies
	Separation of oil from water using foam as a sponge, made robust with use of cellulose nanomaterial	

General Application	Specific Application	Specific Challenges
Concrete	Improved fluidity through providing plasticizer effects	Understand reaction mechanisms
	Improved reaction rates through enhanced hydration	
	Bendable concrete through use of nanofibrils	
	Self-healing concrete	
Electronics/Optical	Photonic colors	Manipulation
	Batteries	Achieve necessary paper smoothness
	Super-capacitors, taking advantage of the low-cost/high surface-areas and abilities to form gels and foams with enhanced strength	Develop necessary strength and electrical properties
		Identify ways to assemble cellulose nanomaterial in aligned fashions to maximize effects
	Recyclable Electronics	Develop recyclable or recoverable electronic materials to complement the recyclable nature of lignocelluloses
Paper	Higher-strength paper grades	Drainage of wet end is slowed down
	Lighter-weight paper	Overcome reduced light scatter and lower brightness/opacity caused by increased bonded area
	Higher filler levels	Address cost-benefit ratio versus other chemistries such as starch
		Develop a mobile portable unit to run mill trials
		Achieve competitive capital and operating costs
		Develop measurements of characteristic properties and process controls
		Develop continuous process
		Develop adequate retention package
Surface treatments/ Paper coating	Coating hold-out for reduction in coat-weights	Develop excellent dispersion of CNFs to avoid buildup behind blades of coater
	Replacement of conventional binders	Achieve uniform fibril sizes
Packaging	Barrier coating films	Achieve moisture stability
	Lighter-weight paperboard	Develop good dispersion of cellulose nanomaterial
	Reinforcement of extrusions on board	Develop interface chemistries

Uses of Cellulose Nanomaterial in Papermaking

The use of cellulose nanomaterial in paper and packaging represents the largest segment of the high-volume applications for cellulose nanomaterial. Because paper, board, and coating operations are done in aqueous environments, the compatibility of cellulose nanomaterial with the raw materials and solvents (water) represents no barrier to its utilization. Furthermore, the opportunity of making cellulose nanomaterial within paper and board operations eliminates many of the challenges associated with concentrating, drying, and transporting nanocellulose from a remote production site to the point of use. Cellulose nanomaterial can be made in-house and simply pumped to the wet end of the paper/board machine at very low solids content (consistency). Cellulose nanofibrils show the most

promise for paper and packaging, and the equipment used in the mechanical processes being proposed are common to the paper industry. Recent advances in reducing the energy requirements and equipment costs for producing CNF have increased the interest and activity level in this material as a raw material in paper and packaging production.

Several attempts have been made to estimate market size, and they remain quite speculative. Assessments of key markets range from 23 million tons per year to 35 million tons/year globally (6.5 in the United States).[57]

The estimated market sizes for cellulose nanomaterial in paper and packaging applications from two studies are shown in Table A-2.

Table A-2. Markets for Cellulose Nanomaterial in Paper/Packaging Applications (in thousand tonnes per year)

Product	Market Size (U.S.)	Market Size (Global)
Paper Filler	310–724	1,427–3,352
Packaging Filler	310–724	1,427–3,352
Paper Coatings	351–585	1,625–2,798
Packaging Coatings	855–1,425	3,958–6,297

[57] Shatkin, J.A., et al. 2014. "Market Projections of Cellulose Nanomaterial-Enabled Products− Part 1: Applications." *TAPPI Journal* 13(5): 9–16.

Appendix C: Additional Materials about the Identification of R&D Projects

Introduction

The Cellulose Nanomaterials Workshop was held on September 22–23, 2015, at the Georgia Tech Renewable Bioproducts Institute (RBI) in Atlanta, Georgia. The workshop brought together a select group of subject-matter experts and industry representatives to refine key research and development (R&D) priorities and to map out actionable R&D projects for advancing technologies that help realize the potential of cellulose nanomaterials and enable the use of this renewable raw materials in a variety of applications.

The following sections provide a brief summary of the structure and outcomes of the workshops. The results provided here are a verbatim record with only minor editing to maintain cogency and meaning. These results served as the raw material for the development of this roadmap.

Technical Issues

The following tables present the results of the discussion of the technical issues for each breakout group. The black dots following each item indicate the number of votes it received during the prioritization; more votes indicate a higher priority.

Technical Issues – Drying & Dewatering

Energy Requirements
• Energy required to dry nanocellulose is excessive due to large number of -OH groups and affinity for H2O: ▪ Cost of dewatering/drying has significantly impacted application models that price the material off users' radar; ▪ Energy cost to freeze-dry, heating, spray - water was entrapped; cannot be filtrated or evaporated; gelation ●●●●●●
• Spray drying must be fed with low-concentration nanocellulose (<3%) for atomization – very energy-intensive to remove this much water

Water-Cellulose Interaction Properties
• Drying by various methods appears to modify the properties (surface area, strength) significantly ●●●●●●
• Cellulose has high affinity for water (high water retention value) ●
• Lack control of interfacial hydrogen bonds ●
• Bonds formed during drying are strong and difficult to break when redispersing ●
• High surface area that holds onto water
• Prevent hornification: ▪ Crystallinity – reduce hydrogen bonding capability; ▪ Hydrophobicity

Technical Issues – Drying & Dewatering (continued)

Process Challenges

- Mechanical dewatering does not appear commercially viable ●●●●●
- Produced at low solids content (we have a lot of water present); Let's do without the water, i.e., dry-based fibrillation ●●●●
- Product handling 3% liquid to solid (viscosity increases dramatically) ●●
- Any "hydrogen-bonding blockers" used must be compatible with end-use system – impractical to remove/wash them out after dispersion ●●
- Dewatering by filtration (including pressurized filtration) very slow – filter blinds easily/quickly ●
- Losses of yield in dewatering and drying methods attempted to date appear too high ●
- Drainability of wet cellulose
- Health and safety (dried materials) during storage and transport
- We are dealing with large volumes (fluffy)

Knowledge

- Unknown availability of technology and expertise from other industries to remove water from fiber nanomaterials; – On neat nanocellulose: Do we know everything about - spray, freeze, solvent, etc.?
- ●●●●●
- Do we know any technical customer specifications? Barrier: Partnerships ●●
- On functionalized/ modified nanocellulose: What are limitations on: M.W. → solvent; D.S.; Toxicity; Target polarity; Type of bonding; Allowable change in the nanocellulose ●●
- How can you measure interfacial water?

Technical Issues – Enabling Technology

Performance Issues

- The potential of CNC is not realized because it is not universally dispersible in polymeric hydrophobic mediums. It must be dispersed in the nano state. ●●●●●
- Validating value proposition of CNCs vs. plastics ●●●●●
- Generally, limited thermal stability of cellulose nanomaterials, not always compatible with polymer melt processing ●●●●
- Key composite performance properties that need to be enhanced and cannot be sacrificed – other than strength or toxicity! ●●●
- We lack a fundamental understanding of the relationship between cellulose and water; end material needs to be less susceptible to moisture ●●●
- Surface modification changes performance characteristics, including bio-compatibility and safety and biodegradability ●●●
- CNC is a new material, and we are eager to commercialize without in-depth development of how to use ●●
- Don't have a computation model of NC/composite and physical property compatibility ●●
- Do we need individually dispersed fibrils/crystals, or is having an interconnected network better?
- What is the strengthening mechanism?
- What level of surface modification is best? ●●
- Need to precisely control mesoscale architecture of composites
- Integrating hydrophilic material with lipophilic current production methods
- We do not understand whether CNC can be used as an additive or as the sole material for products; CNC as produced is end-use-specific; must be produce for one or the other
- As a biomaterial, NC in "raw form" will degrade over time (especially at higher moisture and temperature)
- Poor dispersion of nanocellulose in blends and agglomeration; better dispersion means better properties of material
- Lack of smart functional NC

Lack of Market Story

- Lack of market pull – Don't have a clear idea of what applications need cellulose nanomaterials ●
- As a manufacturer of CNF, we do not have the available information to sell into other markets; we use it for our own needs but cannot guide another end user with questions
- Surface functionalization tailored to specific end use is lacking

Technical Issues – Enabling Technology (continued)

Processing Issues

- Need better understanding in shear/mixing and modification of rheological properties and overcoming that for manufacturing ●●●●●
- Scalable method to introduce cellulose nanomaterials into composite manufacturing lines ●●●●●
- We lack high-speed manufacturing and scalable grafting reactions ●●
- The processing techniques for CNC inclusion in a polymeric matrix are not fully developed ●●
- Need region-selective surface modification ●
- Difficulty of retaining small molecules and effect on economics
- CNCs & CNFs rapidly viscosify suspensions, making functionalizing, pumping, and mixing high-energy or impossible
- Do we need to prepare and dry the cellulose and surface functionalize prior to compounding? Or should we find a way to do it in the middle of the process? We don't know the right order
- Do not know what is in source material going into composite

Standards Issues

- Lack of standards to define physical properties of CNC-based materials and films ●●●●●●
- Need list of "property–value range" needed to achieve "compatibility" in various host mediums – more than hydrophobicity
- Determining a criterion that deems a surface functionalization method as commercially viable; Application-specific? Success definition?

Safety Issues

- Food contact safety of nanocellulose composites is not established; studies not done ●●●●●●
- FDA GRAS status needed to unlock markets and reassure customers ●●●●●
- Hard to measure the release of cellulose nanomaterials from composites ●●
- Effect of cellulose nanomaterials production on greenhouse gases (compared to other reinforcements)? ●
- Retaining low toxicity/ environmentally favorable status for cellulosic nanomaterials after surface functionalization ●
- Compatibility of nanocellulose with mammalian system and ecosystem – generation, product, and waste stream
- End-of-life options (recycling/composting) of cellulose nanomaterials composites not established – unknown impact on environment or reuse

Metrology Issues

- We cannot accurately measure CNF; we have only been able to generalize customers requiring COA ●●●●●
- Generally remains challenging to "see" or visualize CNCs/CNFs in a matrix; challenge in assessing composite ●●
- Lack of "apples-to-apples" comparisons – what is/is not working? ●
- No economically accurate way to measure quantity used (retained in final product) ●
- How to evaluate purity and quality control; lack of techniques to assess purity; lack of sensors and protocols and definition of purity

Technical Solutions

The results of the discussion on technical solutions are presented in the tables below. The black dots following each item indicate the number of votes it received; more votes indicate a higher priority.

Technical Solutions – Drying & Dewatering

Drying Research

- Evaluate drying methods that have higher yield and are not sensitive to feed concentration; determine relative performance and issues with each one: spray, freeze, solvent, flash drying, drum drying; Develop novel approach to dry, dewater nanocellulose ●●●●●●
- Study atomizer droplet size for impact on redispersion for spray drying ●●●●
- Study rheology of nanocellulose suspension: Viscosity (dynamic); Compacity; Pumpability ●
- For composite applications, search if a polymer/ monomer can be implemented into the NC production process ●
- Dewatering under electric field ●
- Comprehensively examine current drying technologies and relate to redispersion effectiveness in a given application
- Build simulation model and perform comparison of alternative heat integrations
- To reduce drying energy, control OH- groups functionally and perhaps temporarily to enhance drying
- Study whether it is possible to dry under shear
- Search for a plasticizer to lower viscosity of NC slurry at high solid contents for further dewatering ease
- Evaluate additives to reduce the viscosity of nanocellulose gels to improve dewatering, drying, and handling efficiency

Cross-Cutting Research

- Research known methods for processing other nanomaterials – assess applicability to cellulose nanomaterials ●●●●
- Water–cellulose properties: investigate alternative solvent mediums to replace water that might release from the cellulose; displace water with a volatile solvent that is more easily removed and recoverable ●●●●
- Develop analysis method for how to know if the CNC/CNF are the same as their original one ●●●
- To address process challenge: produce NFC without water present or at high solids (start with dry-up; mechanical action; solvent)
- To achieve nanocellulose hydration level specification – R&D approach: develop specifications based on specific applications →build a matrix of needs ●
- Search for a way to transfer NC into another solvent cost-effectively (solvent exchange)
- Modeling study of dewatering/drying
- To address water + cellulose interaction: develop a unique method to remove water from cellulose (ultrasonics, electromagnetic, need space program “out-of-sight” new breakthroughs)
- Determine a percent solids (>70%) vs. redispersability vs. functionality relationship; study relation between water content & physical properties

Technical Solutions – Drying & Dewatering (continued)

Dewatering Research

- To reduce drying energy, develop chemistry for temporary hydrophobicity (i.e., temporary wet-strength) that decays with time, thus allowing redispersion post-decay ●●●●●●
- To address process challenges, define a means to dramatically improve the drainage rate of cellulose nanomaterials (chemical additives, i.e., drainage aids) ●●●●
- Develop on/off flocculating agent for nanocellulose concentration step ●●●●
- To address process challenges, exploit shear thinning properties of CNF to devise mechanical dewatering strategy ●●●●
- Evaluate available dewatering technologies, determine relative performance, and identify issues with each one ●●
- Develop nanocellulose functionalization scalable process sensitive to EHS that minimizes need for new/expensive capital and meets application needs ●

Agglomeration Research

- Review techniques that have been employed to prevent agglomeration and identify issues with each one ●●
- Search for a coating/ additive that can be applied NC in water and partially blocks OH- groups (with hydrophobic and hydrophilic ends)

Technical Solutions – Enabling Technology

Processing

- Biorefinery approaches for producing nanocrystalline cellulose (NCC) – other high-value chemicals ●●●
- Develop strategies to control surface properties of CNC films (wetting) ●
- Pilot-scale comparison of unit operations ●
- Develop drying technology that allows for a redispersible nanomaterial
- Identify rheological methods and appropriate material functions for understanding processing behavior of NC–polymer, NC–solvent mixtures
- Develop techniques to redisperse dried (powder) CNC in aqueous or nonpolar solutions to the nano level (for shipping and economic reasons)

Metrology

- Comprehensive study of NC size distribution, interfacial interactions and how those relate to rheology in solution, melt ●●●●●●
- Develop a detection method for cellulose nanomaterials in cellulose (paper) with fluorescent tagging ●●●●●
- New methods to evaluate interfacial shear stress; result – improved understanding and mechanical properties ●●
- Develop measurement methods and corresponding models to accurately describe interfacial behavior of NCs (physical–chemical connection) ●
- High-throughput multiscale imaging nano
- Study to develop methods to measure fiber length in CNF; result→ improved predictability and design of composites

Application Needs/Opportunities

- Investigate the reinforcing attributes of CNC in composite systems to create lightweight and other structural components for automotive, aerospace, and construction products ●●●●

Standards

- “Round robin” characterization studies ●●●●●
- CNF measurement: (1) Initiative to determine acceptable means of measurement, (2) Develop criteria or specifications that need to be met to label results as CNF based on results of testing; (3) Allows manufacturing to create a COA for the product ●

Technical Solutions – Enabling Technology *(continued)*

Safety/ Environmental Benefits

- Create consortium to fund GRAS determination project; solicit funding from government, industry ●●●●●●●
- Study the chelating efficiency of CNC on micro-plastics ●●
- Conduct FDA-compliant migration testing ●●
- Study NC migration, degradation, release and transfer from composites (solids/liquids); develop quantification and characterization protocols
- Study the breathing effects of CNC dust compared to other fine particles
- Measure cellulose nanomaterials/composite environmental performance and compare to plastics (greenhouse gas, energy, water, end-of-life – i.e., recycling or compost)
- FDA studies to allow food contact/consumption, etc.
- Food safety study – GRAS designation by FDA
- Gather enough partners to expedite GRAS status and food contact approval

Performance

- Conceive and design compatibilizers, either grafted or added to facilitate the nano dispersion of CNC into hydrophobic polymeric system and resin mixes (for reinforcement) ●●●●●
- Study surface functionalization of NCC to tune hydrophobicity ●●●●
- Modeling/simulation of NCC composites ●●●
- NC for innovative health care – dry delivery, skin and tissue ●
- Create a testbed center to evaluate cellulose nanomaterials materials for printed electronics, with benchmarking to plastics ●
- Develop “treatment” or modifications to cellulose nanomaterials to improve thermal/water resistance → Dispersions ●
- Develop family of continuous surface functionalization/in situ polymerization schemes
- Advance the understanding of the mechanical properties of NC
- Investigate the rejuvenating effect of CNC on the reuse of recycled papers and plastics

Market Requirements/Story

- Tap into end users’ technical expertise to create “market pull”; create partnerships with end users to establish a better definition of customer needs, requirements & value proposition – they may also have metrics we could use ●●●●●●●●
- Life cycle assessment of NCC/CNF in composite applications to quantify environmental benefits ●●●●
- Study of consumers’ perception of nanocellulose ●●
- Market study for CNF:
- (1) Determine markets for wet & markets for dry (2) Determine what the benefits are for each customer in each market, (3) Begins as a push and converts to a pull ●
- “Screening” study to compare cellulose nanomaterials performance with key polymeric materials used in composites → Value proposition vs. currently used materials

Appendix D: Additional Material on Environment, Health, & Safety Research Opportunities

Introduction

Environment, health, and safety (EHS) data gaps and priorities relative to cellulose nanomaterial materials have been identified based on three prior assessments:

- An evaluation by the National Institute for Occupational Safety and Health
- A life-cycle risk analysis by Vireo Advisors, LLC, that evaluated the available data and identified and prioritized gaps for occupational, environmental, and consumer safety
- An assessment by P^3Nano in collaboration with Vireo Advisors of data availability and gaps to complete a Material Safety Data Sheet (MSDS) compliant with the Globally Harmonized Standard format, required by the Occupational Health and Safety Administration

Environment, Health, and Safety Research Needs

Measurement

One of the first challenges in understanding the EHS aspects of the two most common forms of cellulose nanomaterials—cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF)—is a lack of measurement techniques. Measurement needs are identified as critical to EHS assessment because, without them, none of the other needed studies can be conducted reliably or results compared. This includes confirmatory detection techniques, quantitative measurements, and standardized protocols for sampling and analysis in environmental media, including air, water, and solid matrices. It would be helpful to develop material detection methods in environmental media such as aerosolized dust, aqueous solutions, non-aqueous solutions that may be used to deliver cellulose nanomaterials, and solid matrices such as composites and biological matrices.

Physicochemical Data Needs

The assessment of safety for nanomaterials requires better characterization of key properties that may influence biological and environmental behavior. These measurements are required for dry and aqueous solutions as well as delivered forms in toxicology experiments to measure dose. Information related to standardized measurement and reporting techniques for cellulose nanomaterials, flammability, and explosivity are not available.

Safe Exposure Levels

Currently there are no established and vetted occupational exposure limits specific to cellulose nanomaterials. As with many other nanomaterials, the dimension and possibly the surface area of these nanomaterials may be critical factors with respect to the potential toxicological risks and biological effects. Based on current information, the primary potential hazard for an occupational user appears to be the inhalation of pure, dried material. Manufacturers and researchers have regimens in place to protect against known inhalation risks; whether such methods would also be protective against cellulose nanomaterials in all manufacturing situations and applications is not yet known.

Appendix E: Contributors

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Arthur Ragauskas	University Tennessee
Ken Schelling	Southworth/Paperlogic
Lewis Shackford	GL&V USA, Inc.
Jo Anne Shatkin	Vireo Advisors, LLC
Meisha Shofner	Georgia Institute of Technology
John Simonsen	Oregon State University
Halil Tekinalp	Oak Ridge National Laboratory
David Turpin	Agenda 2020 Technology Alliance

Appendix F: Roadmap Workshop Agenda

Day 1: **12:00pm–5:30pm**

Time	Activity
1:00–1:45pm	**Opening Plenary Session** *The purpose of the opening is to provide important background information on the AMTech award, the purpose of the current workshop, and the progress of work to this point. The session will also describe the R&D priorities that came out of the 2014 roadmap and that represent the starting point for this workshop.*
1:45–3:00pm	**Plenary Presentations: *Review of Capabilities, Solutions, Problems*** *Experts and suppliers are invited to present short case histories and capabilities they bring to the workshop, and mention what they see as core problems. The purpose of these presentations is to provide context on the current state and to tee up the breakout discussions. The presentations also provide an opportunity for participants to understand the range of capabilities that exist in this area and to identify areas of common interest and collaboration. For the presenters, the presentations offer a business opportunity to showcase their capabilities and offerings.*
3:00–3:30pm	**Break**
3:30–5:00pm	**Breakout Session 1: *Develop Problem Statements*** *In this first breakout session, participants will confirm and/or modify the priority that is to be the focus of the breakout discussions. Participants will also begin the process of clarifying and further specifying their respective R&D priority in order to arrive at an actionable plan for moving forward. In particular, the focus of the discussion is on "problem definition" rather than "solution specification" — participants will form the problem statements that will be the basis of the project concepts.*
5:00–5:30pm	**Plenary Session: *Review & Wrap-up*** *Participants will reconvene as a large group to discuss breakout discussion, including additions or changes to the R&D Priority. The purpose is to have each group understand where the other groups is so that we keep the groups together given that they are both working on the same roadmap. At the end of the session the plan and instructions for Day 2 will be presented as well as the options for evening dinner.*
6:00–15 pm	**Optional No-host Dinner & Networking Opportunity**

Day 2: **8:00am–12:30pm**

Time	Activity
8:00–8:30am	**Opening Plenary Session: *Day 2 Kickoff & Networking*** *This is a chance for networking and discussing collaboration opportunities. At 8:20am there will be a brief introduction to Day 2, after which participants will move to their breakout rooms.*
8:30–9:40pm	**Breakout Session 2: *Pathways and Approaches*** *In this session, the breakout groups will dissect the problem statements and devise promising approaches and research pathways to reach solutions. The group will create project concept statements – a 2-3 sentence statement that indicates the nature of the research to be conducted, the anticipated R&D output, and the technical problem(s) that would be addressed. The project concept statements are intended to influence the development of RFPs by various funding sources.*
9:45–9:55am	**Break**
9:55–10:55am	**Breakout Session 3: *Completing the roadmap to success*** *For this session, participants within each breakout group will subdivide into small groups of 3-5 people. Each small group will select a project concept statement and complete a planning worksheet to map out the accomplishment of the project concept statement.*
11:00–12:30 pm	**Break to reconvene in the plenary room**
11:00–12:30am	**Plenary Session 4: *Jump Starting the Implementation*** *The purpose of this session is to engage participants in thinking about ways they can participate in and contribute to the implementation of the integrated roadmap. The session will begin with brief presentations from funding agencies. Participants will then be given a chance to review and comment on the R&D plans developed in Breakout Session 3. Finally, participants will discuss pathways to both funding and collaboration opportunities to implement the R&D plans.*
12:30–12:45pm	**Conclusion** *To close the workshop, participants will be asked for any closing comments. Team leads/Agenda 2020 will review next steps, and thank the participants and speakers.*