

## Foreword

**“Production and Applications of Cellulosic Nanomaterials”** was intended to help organize and highlight the wide range of research being conducted worldwide on the science and technology of cellulose nanomaterials. The format of this book consists of short research summaries, targeted for a level where they can be understood by non-specialists in the research fields, and with a lot of figures and pictures to help convey the science. Although we have tried to be thorough and inclusive in searching out authors, the world is still a big place in the 21st century, and we can guarantee that we have missed a lot of good science. The book has 106 contributions from about 45 institutions and 10 countries. Science on cellulose nanomaterials that is not included in the book is simply the result of limited time and limited resources. We believe there is sufficient on-going science on cellulose nanomaterials to support two or three books of this nature, maybe more, and encourage others to take up that challenge.

The book is organized into two main chapters, based on the two general cellulose nanoparticle types used to date: cellulose nanocrystals (rod-like particle types) and cellulose nanofibrils (fibril-like particle types). Each chapter is itself divided into several main sections: Preparation and Characterization, Health and Safety, Coatings-Films-Optics, and Composites. The chapter on cellulose nanocrystals also contains a section on modeling. This deviates somewhat from the main chapters in that most of the summaries deal with molecular modeling of cellulose crystals, but several papers deal rather with models of composite products and the interface. This latter group tends to be agnostic on material form and in general works well within the CNC chapter, but anyone with interests in composite models should make sure to check the modeling section of the CNC chapter.

Coupled with the irrational exuberance of taking on a book, the editing job is at times exhilarating, at times exasperating, exhausting, and ultimately when complete, rewarding, not in a personal or financial sense but with a real sense of achievement and contribution. Those emotions were increased in all of us when we realized that the initial response to the request for summaries was a book of 300 to 400 pages, approximately twice the initial target. But that response is a testament to the level of interest within the scientific community, and that knowledge helped propel us through that list of E's (exuberance, emotion, exasperation and exhausting). We hope that we have served this community of scientists well. We thank them all for their contributions and for bearing with us as we tried to assemble the book. Now it is for you to decide whether the effort was worthwhile. We hope you enjoy and learn.

This project has been a joint cooperation between the USDA Forest Products Laboratory (FPL), DOC National Institute of Standards and Technology (NIST), the University of Maine, and the Technical Association of the Pulp and Paper Industry (TAPPI). Inspiration for this book came from Michael Postek of NIST, while connections within the community and expertise with cellulose nanomaterials came from Robert Moon and Alan Rudie of FPL and Mike Bilodeau of the University of Maine. Having embraced TAPPI as publisher, the editors also loosely based the original distribution list of the call for summaries on the contributors to the TAPPI International Conference on Nanotechnology for Renewable Materials. In addition, the TAPPI Nanotechnologies Division became the formal book sponsor, and we would like to thank the Chairman, Sean Ireland, and the Division Council for their enthusiastic support.



# Cellulosic Nanomaterials: Sustainable Materials of Choice for the 21st Century

Theodore H. Wegner<sup>1</sup>, Sean Ireland<sup>2</sup> and J. Philip E. Jones<sup>3</sup>

<sup>1</sup>USDA Forest Service, Forest Products Laboratory, Madison, WI, USA

<sup>2</sup>Verso Paper Corp., Bucksport, ME, USA

<sup>3</sup>Imerys, Roswell, GA, USA

*“Production and Applications of Cellulosic Nanomaterials”* is intended to bring together current leading-edge knowledge and information on cellulosic nanomaterials from worldwide expert sources. This has been a joint cooperation between the USDA Forest Products Laboratory (FPL), DOC National Institute of Standards and Technology (NIST), the University of Maine, and the Technical Association of the Pulp and Paper Industry (TAPPI). This book is needed because during the past several years, discovery of the properties and performance of these materials has accelerated. However, by comparison with some other nanomaterials, the level of funding and effort has been modest, largely because most scientists and government bodies are unaware of their existence. The scope and breadth of the knowledge and information outlined in this book span the range of cellulosic nanomaterials research, process and product development, and commercial exploitation and include standards development and environmental, health, and safety issues. It is hoped that this book will help spread the knowledge of cellulosic nanomaterials and lead to further efforts in the broader scientific communities.

It is difficult to imagine anything on our planet more ubiquitous and environmentally friendly than plants—they grow using sunlight, carbon dioxide, water, and soil nutrients. What many people may not know is that plants, from the smallest algae cell to the largest redwood tree, contain cellulose. Cellulose is the most abundant polymer on Earth, representing about  $1.5 \times 10^{12}$  tons of total annual biomass production [1]. It consists of glucose-glucose linkages arranged in linear chains where C-1 of every glucose unit is bonded to C-4 of the next glucose molecule as shown in Fig. 1 [2,3].

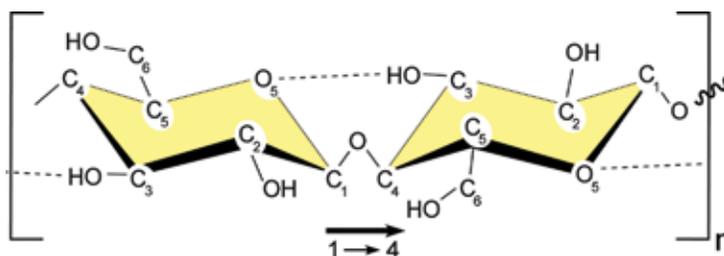
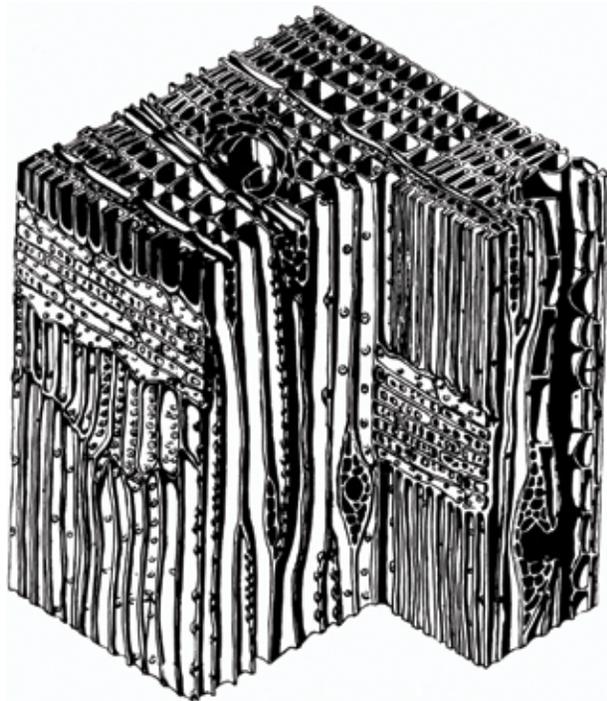


Figure 1. Cellulose Schematic. Adapted from reference [3].

These chains aggregate along the chain direction with intermolecular hydrogen bonds and hydrophobic interactions. They form 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 [4]. Because these cellulosic nanodimensional building blocks have crystalline regions, they have unique distinguishing properties. They have strength properties greater than Kevlar<sup>®</sup>, piezoelectric properties equivalent to quartz, can be manipulated to produce photonic structures, possess self-assembly properties, and are remarkably uniform in size and shape. In addition, because of their abundance, we can sustainably and renewably produce them in quantities of tens of millions of tons.

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 no new science to learn. However, the opposite is true. Because of the complex cascading hierarchical structure of wood (Fig. 2), many of the technologies used in the forest products industry were first developed through experience. The complexities of wood are just now yielding to newer and more robust qualitative and quantitative analytical tools. We are beginning to see and track



*Figure 2. Wood structure schematic*

how the mechanical, optical, and other physical properties of wood are related to its discrete hierarchical structures ranging from nanoscale to microscale to macroscale. As a result, we are now seeing growing but disjointed efforts worldwide to move research, development and deployment forward to commercialize cellulosic nanomaterials. Several small-scale pilot and pre-prototype facilities have been built to produce working quantities of cellulosic nanomaterials to support research and product applications development. Several different forms of cellulosic nanomaterials are being pursued. One form, cellulose nanocrystals, consists almost exclusively of nanodimensional cellulose crystals. Another form, cellulose nanofibrils, consists of regions of crystalline as well as amorphous cellulose. In addition, production methods that include acid hydrolysis, enzymatic treatments, chemical treatment, and mechanical treatment are being pursued. All this activity and more is leading to exciting but challenging times in the commercial development of cellulosic nanomaterials.

### **Materials of the 21<sup>st</sup> Century Revisited**

As we move forward in the 21<sup>st</sup> Century, we are seeing an explosion in demand for materials, energy, food, and water driven by growing world population and the

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emergence of large numbers of middle-class consumers in emerging economies wishing to consume at Western-world levels. The supply of material building blocks as we know them today will not be sufficient, and we will have to revisit and look to materials from forest and agricultural-based resources as major sources of materials for products. In addition, for similar reasons, the rapidly increasing demand for higher-quality food types will require enhanced packaging performance to minimize loss of food in the supply chain. Sustainable, renewable cellulose-based nanomaterials have excellent oxygen barrier properties and can fill this need. Concerns about climate change are leading to a resurgence of interest in cellulose due to the increased focus on renewable materials that meet the material needs of society while at the same time sequestering carbon. The use of cellulose-based materials to produce products in a sustainable and ecologically preferable manner is furthered by the need to adhere to the principles of Green Chemistry and Green Engineering [5]. The forest products industry has substantial infrastructure already in place to harvest sustainably grown trees and transport them to centers for debarking, chipping, and pulping. Such a sustainable supply base will enable the rapid scaleup of nanocellulosic materials based on this existing platform.

### **Nanocellulose as a Green Material**

Society requires scientists and manufacturers to focus research on sustainable materials and develop them so they are easy to manufacture, affordable to the consumer, and widely available. A term, “Green”, has been developed not just as a label, but as a new measure of materials, technologies, and products. “Green” generally refers to materials, technologies, and products that have less impact on the environment and/or are less detrimental to human health than traditional equivalents [6]. For example, green products might be produced from sustainable raw materials, be manufactured in a more energy-conservative or environmentally friendly way, pose

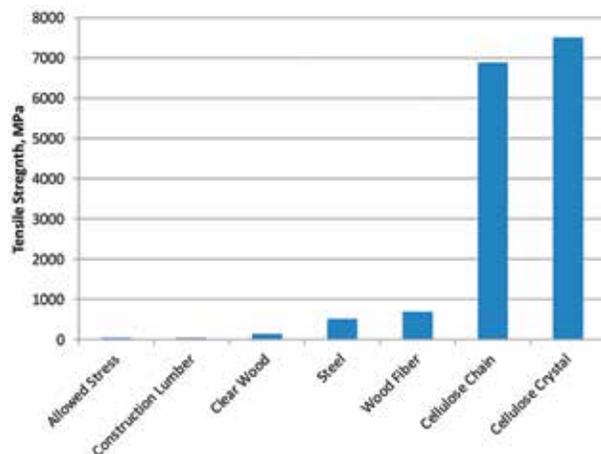
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few, if any, health and safety problems, sequester carbon, be recyclable, be compostable, be supplied to the market using less material, or all the preceding. Cellulosic nanomaterials have the capability to meet almost all the requirements for being “green” and with further responsible and thoughtful research, development, and deployment, have the opportunity to become sustainable materials of choice for the 21<sup>st</sup> Century.

Nanotechnology can also play an important role in the production of liquid biofuels from lignocellulosic biomass. For example, nanoscale cell-wall structures within trees could be manipulated so they are more easily disassembled into their constitutive materials through bio-conversion, thermo-conversion, or catalysis. Another approach would be to use nanocatalysis to break down recalcitrant cellulose. Recalcitrant cellulose is on the order of 15–25 percent of wood, and failure to convert this to sugars reduces bioconversion yields.

### Nanocellulose Form and Function

The various forms of nanomaterials that can be produced from cellulose are often collectively referred to as cellulosic nanomaterials or nanocellulose. For example, the extraction of cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC) from plants, bacteria, and some animals (e.g., tunicates) is leading to a wide array of worldwide research to use these nanomaterials in product applications [3, 7–10]. Examples include using CNFs as reinforcing agents in composites due to their high strength properties, relative low cost, and availability, or CNCs due to their incredibly high strength (Fig. 3), renewability, lightweight, high surface area, and unique photonic characteristics.



**Figure 3.** Tensile strength properties of selected wood-based products and constitutive hierarchical structures versus steel. Note—When using a linear scale, the allowable stress for lumber and the tensile strengths of construction lumber, clear wood, and wood fiber are barely distinguishable on the Y-axis.

As you will see when reading this book, research and development is currently taking place worldwide within academia, industry, and government agencies to study, characterize, and use these highly complex cellulosic nanomaterials. Nanocellulose in its various forms contains unique structures and self-assembly features that we can exploit to develop new nano-enabled green products. A specific example is use of cellulosic nanomaterials in lightweight, high-performance composites. Such nanocellulose-enabled composites could eventually replace carbon fiber mats and strands by weaving cellulose-derived nanomaterials and fiber into mats. This could lead to replacement of the nonrenewable and fossil-based materials currently used to make automotive parts such as dashboards, seats, floor mats, and even body panels or frames. The world may not be ready yet to step back into a wooden airplane, but the day will come when aircraft will have wings and fuselage components containing lightweight, high-performance nanocellulose-enabled composites. Fiberglass is a common composite with which most people have experience. It is used to manufacture diverse products including tool handles, sporting goods, bike frames, boats, and even the bodies of some sports cars. Fiberglass cannot be made transparent and is a heavy material for a composite. Replacing fiberglass mat with nanocellulose-containing mat could lead to new lighter-weight materials and the eventual replacement of nonrenewable products with sustainable and renewable cellulosic materials

Another valuable feature of cellulosic nanomaterials is their compatibility with human tissue, as evidenced by

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a number of research studies focused on their use as a tissue scaffold [10].

The area of nanomanufacturing science and technology has not received sufficient attention despite its being one of the most critical pathways to applying the benefits of nanotechnology. It is absolutely critical to build the nanomanufacturing science and technology base to the point where nanomaterials exhibiting unique nanoscale properties can routinely be placed into components or systems, retaining and combining their unique properties in a matrix of other materials and resulting in superior and controllable composite performance.

### Partnering Nationally and Internationally

To scientists, everything meets at the atom. All of us, whether we are scientists, engineers, materials producers, industrial product producers, or consumers, have something to learn from new technological advancements in nanoscale and atomic-scale science. These new advancements cannot come to fruition without focused and responsibly targeted efforts in research, development, and deployment led by government and industry in conjunction with academia. This also requires increased international cooperation due to the worldwide importance of trade, the need to engage collectively the best minds to achieve rapid use of cellulosic nanomaterials for the benefit of humankind, the need to meet the needs of all people sustainably, and the shared responsibility we all have to live within the carrying capacity of our planet Earth.

Nanotechnology and the development of the science and technology for producing and using cellulosic nanomaterials, although promising, are still high-risk and expensive. Cooperation, pooling of resources, and openly sharing of pre-competitive information is critical to moving the science and technology for exploiting cellulose nanomaterials expeditiously forward. In North America, Europe, and Asia, governmental agency partnerships with industry and academia are becoming common. For example, in the United States (U.S.), Federal government emphasis on renewable materials has led to increasing emphasis on these specific materials. The U.S. National Nanotechnology Initiative (NNI), which brings together 25 federal agencies and departments, serves as a natural focal point for government and industry to work collaboratively [11]. Within NNI, the U.S. Department of Agriculture (USDA) Forest Service is the lead federal agency advocating for cellulosic nanomaterials from forest biomass. The forest products industry, through the Agenda 2020 Technology Alliance, has also formed a relationship with the NNI. In addition, the NNI has recently developed a sustainable manufacturing “signature” initiative which includes renewable and sustainable

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cellulosic nanomaterials [12]. These NNI signature initiatives are aimed at enhancing the commercialization of nanomaterials and nano-enabled products for the benefit of humankind.

In Canada, ArboraNano has served as the focal point for public-private partnerships [13]. ArboraNano is the Canadian Forest NanoProducts Network, made possible through the Government of Canada’s Business-led Centres of Excellence program, FPInnovations, and Nano-Québec. Its mission is to create new business opportunities using renewable forest resources and the advances made in nanotechnology, especially cellulosic nanomaterials, to develop novel or superior products with enhanced performance attributes.

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 products groups) [14]. The focus of the Center is to create new applications for nanocellulose as a raw material, substance, and end product.

To translate fundamental knowledge developed by investment in nanotechnology into manufacturing and create jobs, it will be necessary for industry to partner with national laboratories and academia both nationally and internationally. This is a critically important linkage. National laboratories and academia have the expensive infrastructure in place to conduct needed work on nanoparticles as well as the ability to carry out basic research. University faculty and students also bring enormous intellectual capacity to bear in providing innovative solutions and advancing the underlying science. To be effective, the work of academia and national laboratories must be focused and adequately funded. With respect to

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funding, government often supplies the bulk of the funding for the basic underlying science and technology. Industry often supplies leadership to focus government spending in a manner that leads through research to development and manufacturing for the consumer. Additionally, industry involvement ensures that material development will be in alignment with modern manufacturing processes and workplace and consumer product regulatory requirements. When technically and economically viable pathways to commercialization become clearer the result is that, industry funding increases exponentially and government funding decreases exponentially as the science moves into commercial development and deployment. Industry generally funds commercial deployment, which is very expensive, on the order of 12 to 20 times the cumulative research and development costs.

### The Path Forward

In responsibly and efficiently moving cellulosic nanomaterials through research, development, and deployment in partnership, we need to concentrate our efforts in the following five general areas:

- *Economically viable and environmentally preferable production of the various forms of cellulose nanomaterials*
- *Characterizing cellulosic nanomaterial morphology and properties*
- *Exploring new applications for using cellulosic nanomaterials and tailoring them to perform well in those applications*
- *Elucidating and quantifying EHS (environment, health, and safety) and ELSI (ethical, legal, and social implications) information for responsible use, recycling, and disposal*
- *Developing national and international codes and standards to support responsible use and trade*

There is ample opportunity for national and international cooperation, sharing resources and avoiding needless duplication of efforts to develop and commercialize uses of cellulose nanomaterials. TAPPI, through its annual International Conference on Sustainable Nanomaterials, has created a welcoming forum to share information and convene like-minded people seeking to advance research, development, and deployment of cellulosic nanomaterials to make them a material of choice for the 21<sup>st</sup> Century [15].

The uniqueness, abundance, and potential low cost of cellulosic nanomaterials from trees will serve many industrial materials needs. In our immediate future, we can envision automobiles and trucks made with cellulosic nanomaterials, wind turbines producing green power, ships crossing the oceans, and medicines and medical diagnostics. Electronic devices, including photovoltaics, electrical storage devices, and sensors, all will be made with cellulose nanomaterials produced from trees. We hope the vision that we and others share will open your mind to the potential opportunities presented by this new material. Hundreds of millions of dollars are being spent worldwide in a race to discover and patent the capabilities of cellulosic nanomaterials. Small-scale facilities to produce limited quantities of cellulosic nanomaterials have already been built in Asia, North America, and Europe. Governments cannot stand by and leave the rewards to international competitors; academia cannot do research without support; and industry has to step up and work cooperatively with others to exploit these materials. We need to reach out to others, work collaboratively, and share information. The potential benefits of using cellulosic nanomaterials are too great for us to fail to harness them for the benefit of humankind.

Everything meets at the atom—unless you are a physicist, in which case, it all comes down to quarks...

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