# Research into CELLULOSE NANOMATERIALS Spans the Globe

A host of international research organizations are hot on the trail of new applications and products that can be made from cellulose nanomaterials

ROBERT MOON, PH.D., and COLLEEN WALKER, PH.D.

The January/February 2012 issue of *Paper360°* described the unique properties of nanocellulose (made from cellulose fibers from the pulp process), some major industry collaborations looking to capitalize on it, as well as some attempts at commercialization. In this article, we take a closer look at some research efforts around the world and how these new advances will lead to new products and applications.

Jean Bouchard, Ph.D., Principal Scientist, FPInnovations

### USDA FOREST SERVICE, FOREST PRODUCTS LABORATORY (FS-FPL), WISCONSIN, USA

Since 2004, the FS-FPL has been expanding its research programs and building collaborative efforts with universities and industry in cellulose nanomaterials (CN). This program covers several broad areas including: pilot scale processing of CNCs and CNFs, composite processing, characterization technique development, specialized surface coatings (chemical or inorganic nanoparticles) and predictive modeling. CN composites (foams/hydrogels, thin transparent films, core-shell microspheres, continuous fibers) are being investigated for applications in high strength packaging materials, high strength substrates for printed electronics, barrier applications, multifunctional composites/coatings (antimicrobial, self-cleaning, electrical conduction, etc.), and structural materials. One of the key capacities within the program is the installation and startup of 25+ kg batch processing of CNCs and CNFs.

### FPINNOVATIONS, POINTE-CLAIRE, QUEBEC, CANADA

"Our research has led to two significant breakthroughs," reports Jean Bouchard, Ph.D., with FPInnovations' Biomaterial Program. "[We have] demonstrated the scale-up of a high-yield nanocrystalline cellulose (NCC) manufacturing process. This has led to the recent opening of the CelluForce demonstration plant with an NCC production capacity of one ton/day. The second breakthrough is the production of an NCC water-dispersible grade."

In addition to large scale NCC production, FPInnovations' research program focuses on

## HOT RESEARCH TOPIC: CELLULOSE NANOCOMPOSITES

During our informal survey we found that the research community was in almost unanimous agreement that the production of composites with incorporated cellulose nanomaterials, is the hottest area of research. With giant customers awaiting—such as the automotive industry—there are huge incentives to develop these products. The research activities are focusing on composite processing methods and controlling dispersion.

discovery and control of unique NCC properties, physical and chemical compatibilization of NCC, and toxicity and environmental assessment. "Regarding the development of new applications, we focus on three fundamental properties of NCC: reinforcement additive, barrier properties and optical properties of NCC chiral nematic films. As a result, the group has filed more than 20 patent applications," comments Bouchard. "Our collaborative efforts with universities, institutes and private companies have led to progress in very diverse fields of application such as: Li-ion batteries, food packaging, paint and varnish, polymer nanocomposites, textiles, adhesives, inks and printing, and optical devices."

### VTT TECHNICAL RESEARCH CENTRE OF FINLAND, ESPOO, FINLAND

"Our main focus has been in development of the production process together with UPM," states Pia Qvintus, VTT's Technology Manager, R&D. "When it is possible to produce different grades of nanocellulosic materials in a controlled way, you can focus on modification of materials according to the needs of selected applications."

In November of last year, UPM announced that it had started pre-commercial production of fibril cellulose in Otaniemi, Espoo, Finland. UPM is now able to provide different types of fibril cellulose for extensive customer testing. As part of this program, VTT has developed a very wide set of characterization methods and has identified new applications for nanocellulose.

### GRENOBLE INP-PAGORA, FRANCE

Dr. Alain Dufresne, Professor of Polymers and Composites, leads a team of researchers whose activity has focused on the processing and characterization of polymer nanocomposites reinforced with cellulose nanocrystals. "The hydrophilic nature of cellulose nanocrystals makes them poorly dispersible in hydrophobic matrix," says Dufresne. "Moreover, sulfuric acid–prepared nanocrystals present low thermal stability when heated at moderated temperatures. All these issues limit the processing of cellulose nanocrystal–based nanocomposites to wet processing such as solution casting, which was extensively studied."

Recently, Dufresne's team has found a way to process cellulose nanocrystal–based nanocomposites in the melt without any chemical modification. "We obtain a good dispersion of the filler in a highly hydrophobic matrix such as polyethylene. Moreover, from our method the thermal stability of the nanocrystals is significantly improved." These preliminary results have been recently published.

### UNIVERSITY OF EXETER, UNITED KINGDOM

"The main focus of my research is trying to obtain structure-property relationships of both the mechanics of cellulose nanofibres and their interfaces with polymeric resin materials," states Professor Stephen Eichhorn, Chair of Materials Science at the United Kingdom's University of Exeter's College of Engineering, Mathematics and Physical Sciences. "This enables direct understanding of the effects of processing variables (dispersion, aspect ratio, surface chemistry) to be probed so that we can make better decisions about the tailoring of mechanical properties."

"We showed that the modulus of highly crystalline cellulose nanowhiskers is close to the crystal modulus of cellulose. We have also shown that both orientation within and the interfaces between resins and cellulose nanofibres can be probed simultaneously. We also showed quite clearly that controlled orientation can direct the growth of muscle cells, which could lead to the development of implant technology."

### OREGON STATE UNIVERSITY, OREGON, USA

For many years, Dr. John Simonsen at Oregon State University's Department of Wood Science Engineering, has led a research team studying cellulose nanocrystals. "We are primarily concerned with composites," says Simonsen. "Few nanoparticles offer the versatility of cellulose nanocrystals in terms of ease of preparation and chemical modification."

Experiments in the Simonsen lab have shown the effect of different interphase chemistries on nanocomposite performance. Dr. Simonsen's team has observed increases from two to approximately five times in modulus (stiffness) for various polymer systems.

"A big step forward has been collaborating with Prof. John Nairn at OSU and his development of a new set of mathematical models for cellulose nanocrystal (CNC) composites. We hope to work with him to validate and utilize these equations to design and fabricate new composite materials using CNCs."

### UNIVERSITY OF FRIBOURG, SWITZERLAND

At the Adolphe Merkle Institute at the Univeristy of Fribourg, Professor Christoph Weder's research team is focused on the design, synthesis, and investigation of structure-property relationships of novel functional polymers. Together with colleagues Profs. Stuart Rowan and Jeffrey Capadona, both at Case Western Reserve University in Cleveland, Ohio, Weder, Executive Director and chair of the Polymer Chemistry and Materials team, recently reported on stimuli-responsive, mechanically adaptive polymer nanocomposite. These materials were inspired by the defense mechanism used by sea cucumbers, in which they switch the modulus of their skin on a physiological time scale. "Our adaptive nanocomposites adopt the architecture of this adaptive skin and are comprised of low-modulus polymer matrices and rigid cellulose nanocrystals," notes Weder.

The non-covalent interactions between the percolating cellulose fibers can be mediated by chemical and other stimuli. For example, through modest aqueous swelling, the reinforcing cellulose network can be disrupted, resulting in a dramatic modulus reduction. These chemo-responsive mechanically-dynamic "smart" nanocomposites are potentially useful for biomedical and other applications.

Expanding on these efforts, Weder's team is also developing processes to create non-adaptive nanocomposites of a range of polymers and cellulose nanocrystals. Together with biologists Prof. Barbara Rothen-Rutishauser and Dr. Martin Clift, he has further launched a program that seeks to explore the interactions of cellulose nanocrystals with living cells. A recently established in-vitro cell model of the epithelial airway barrier is used to assess the potential toxicity of cellulose nanofibers, and to establish knowledge regarding the potential risks of nanocellulose-based materials over their entire lifecycle.

### KYOTO UNIVERSITY, JAPAN

Professor Hiroyuki Yano at Kyoto University's Research Institute for Sustainable Humanosphere has been studying extraction of nanocellulose from wood and other biomaterials using grinding, hi-speed blending, and twin-screw extrusion. Yano's team is incorporating cellulose nanofibers (CNF) into polypropylene and other traditional polymers to form composites for use in the automotive industry.

### ADDITIONAL RESEARCH EFFORTS

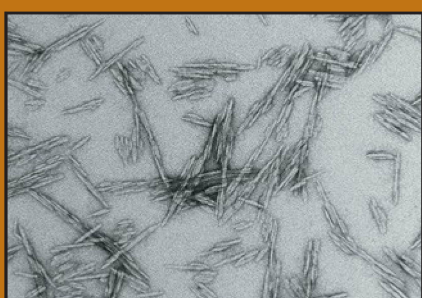
Due to space limitations, it is not possible to feature every research group working in this area. Below are a number of more teams that should be on your nanotechnology radar:

- University of Queensland, Australia
- University of Natural Resources and Life Sciences (Boku University), Austria
- University of Alberta, Canada
- National Institute for Nanotechnology (NINT), Canada
- University of Tokyo, Japan
- The Hebrew University Jerusalem, Jerusalem
- Norwegian University of Science and Technology, Norway
- Innventia, Sweden
- Lulea University of Technology, Sweden
- Royal Institute of Technology (KTH), Sweden
- Empa, Switzerland
- IPST @ Georgia Tech, USA
- National Institute for Standards and Technology (NIST), USA
- North Carolina State University, USA
- Pennsylvania State University, USA
- Purdue University, USA
- University of Maine, USA

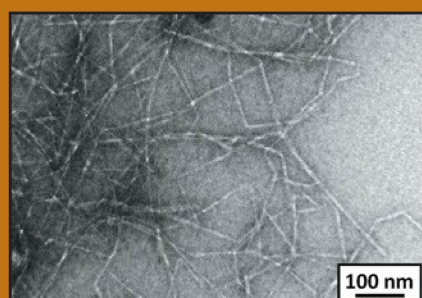
## CELLULOSE MICROCRYSTALS AND CELLULOSE NANOFIBRILS

The feature article in the January/February 2012 issue of *Paper360°* included a review of the developing language for cellulose nanomaterials. As a reminder, there are two general classifications: cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNF).

CNCs are rod-like particles produced through acid hydrolysis of wood fiber and are 3-20 nm wide, 50-500 nm in length. CNFs are longer and more branched particles produced from chemical-mechanical refining of wood fiber, and are 4-20 nm wide, greater than 500 nm in length.



TEM view of Cellulose nanocrystals. Photo courtesy of Rick Riener and Alan Ruide of the Forest Products Laboratory.




TEM view of celllulose nanofibrils. Photo courtesy of Rick Riener and Alan Ruide of the Forest Products Laboratory.

### KEY CHALLENGES TO COMMERCIALIZATION

Researchers around the world seem to be concerned about the same challenges in moving towards commercialization: continued funding, reducing production costs, and technology transfer.

"We need to press ahead with large scale production, driving down costs and industrial integration of the materials into products and to market," says Professor Stephen Eichhorn. "If consumers are not buying products containing these materials, then [these products] will continue to only be an academic curiosity. Costs for production are still too high, but the demonstrable functionality of the materials needs to be more widely publicized."

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