Alternative uses for a plant fiber

Brazilian companies are investing in nanocellulose, a promising material for reinforcing plastic and cement, and the production of prostheses and sensors

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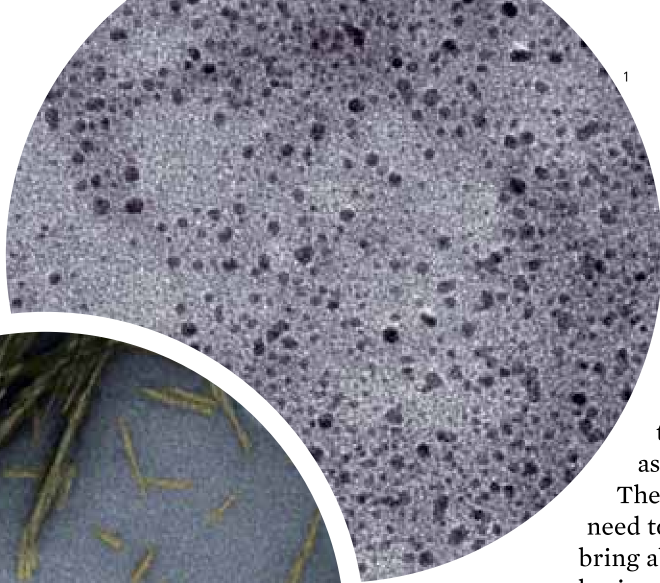
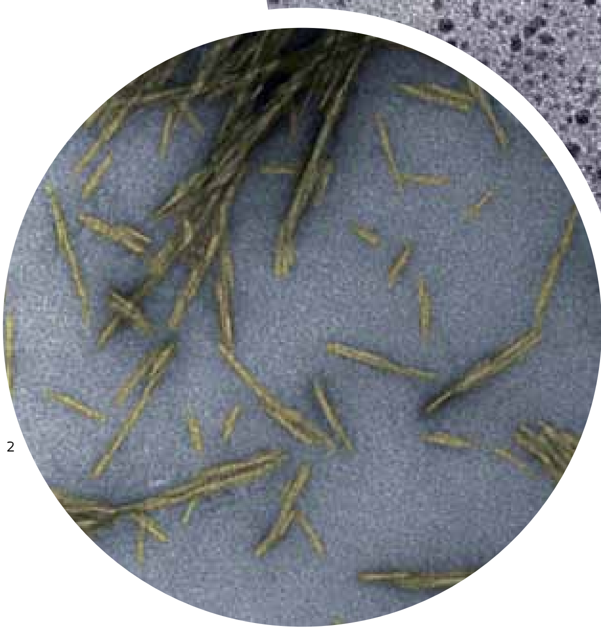
The decline of the paper industry, which has been associated with progress in materials technology, has drawn attention to cellulose, a new player that has kindled entrepreneurial interest. At the nanometric scale (in which at least one dimension must be less than 100 nanometers, or nm), cellulose can take the form of nanofibrils or nanocrystals. Nanofibrils are spaghetti shaped, can be easily interwoven, and are used mainly to strengthen plastic packaging. Cellulose nanocrystals, with dimensions of 5 to 20 nm in width and 100 to 500 nm in length, resemble rice and are regarded as a more useful material because they can have an electrically charged surface as well as chemical, optical and electronic properties. This new material is characterized by a nanometric crystalline structure found within any plant fiber.

Nanocrystals, which are extracted from cellulose, the raw material in paper-making, can be sourced from reforested wood as well as from waste wood, sugarcane bagasse, coconut husks, rice husks, and waste from the production of soybean and palm oils. Nanocrystals come from a renewable source and are lightweight and biodegradable, lending them an advantage over other synthetic materials—often sourced from petroleum by-products. They have several potential applications, including for the reinforcement of plastic materials and cement, in sensors for the oil and gas industry, in specialized wound dressings, and in inks, coatings, cosmetics and, when combined with other substances, in the electrical and electronics industry. At present, there are no commercial products made with nanocrystals: the global production of this material, still in the early stages, is targeted to customers who can develop applications and create markets.

Brazil has invested in this promising material by acquiring equity in foreign companies that produce nanocrystals. In 2013,



Small spheres of carbon dots can be used in electronic equipment screens



Nanocrystals used to reinforce cement

PHOTOS 1 FABIANO PEREIRA/UFMG 2 PURDUE UNIVERSITY

Granbio, a Brazilian industrial biotechnology company, acquired 25% of American Process Inc. (API), a U.S. company. In 2015, API announced a new low-cost technology for extracting nanocellulose from biomass and began pre-commercial production. Granbio, one of two Brazilian companies that has the technology to make second-generation ethanol from sugarcane bagasse (*see* Pesquisa FAPESP *Issue No. 235*), invested in API to gain access to biomass pretreatment technology. In a press release, the Brazilian firm said it has been investing in nanocellulose research and development (R&D) for four years and operates at a plant in the United States through its API affiliate. The nanocellulose samples it produces are offered to potential customers.

In November 2016, Fibria, Brazil's global leader in commercial cellulose sales, became a shareholder in CelluForce, a Canadian company that is the leading producer of cellulose nanocrystals. Fibria invested about $4 million to acquire an 8.3% equity interest in the company, which is a startup from FPInnovations, a research center in the Canadian forest products industry. FPInnovations (formerly Pulp and Paper Research Institute of Canada) holds the first patent on the production of cellulose nanocrystals, granted in 1997. In addition to FPInnovations, the other shareholders of CelluForce are Domtar, a Canadian cellulose and paper-manufacturing company, and Schlumberger, a French company that is the leading manufacturer of systems and equipment for the oil industry. Established in 2010, CelluForce launched its pilot plant in Montreal, Quebec, in 2012. With an annual production capacity of 300 tons, the company also offers its product as samples to potential customers.

According to Vinicius Nonino, director of new business at Fibria and now a board member of CelluForce, nanocrystals have potential uses in such industries as paper, cement and medicinal products. These applications, which Nonino says still need to be developed for each industry, could bring about a major diversification of Fibria's business. The company holds production rights in Brazil and distribution rights for nanocrystals throughout Latin America. Both CelluForce and Fibria will be initial suppliers of raw material. Fibria plans to set up a pilot plant to produce cellulose nanocrystals at its Technology Center in Aracruz, in the state of Espírito Santo, in 2017.

The new material has awakened interest as a substitute for previously used raw materials and as a basis for developing new products. Estimates indicate that the price of nanocellulose crystals could run more than 20 times higher than that of cellulose. According to a study by the American consulting firm Market Research Store, the nanocellulose market was $65 million in 2015. The company estimates that this figure could climb to $530 million in 2021—a 30% annual increase.

INTEREST FROM INDUSTRY

The first scientific paper on the production of nanocellulose crystals was published in the early 1950s by Swedish chemist Bengt Rånby of the Royal Institute of Technology (KTH). Having established a strong tradition in the paper and cellulose industry, in 2011, the Swedes inaugurated the world's first pilot plant that extracted cellulose nanofibrils, operated by the Innventia research institute. The use of nanocellulose to reinforce materials such as paper, composites and plastics was already awakening interest on the part of industry, but the extraction process required much energy and rendered the process unviable.

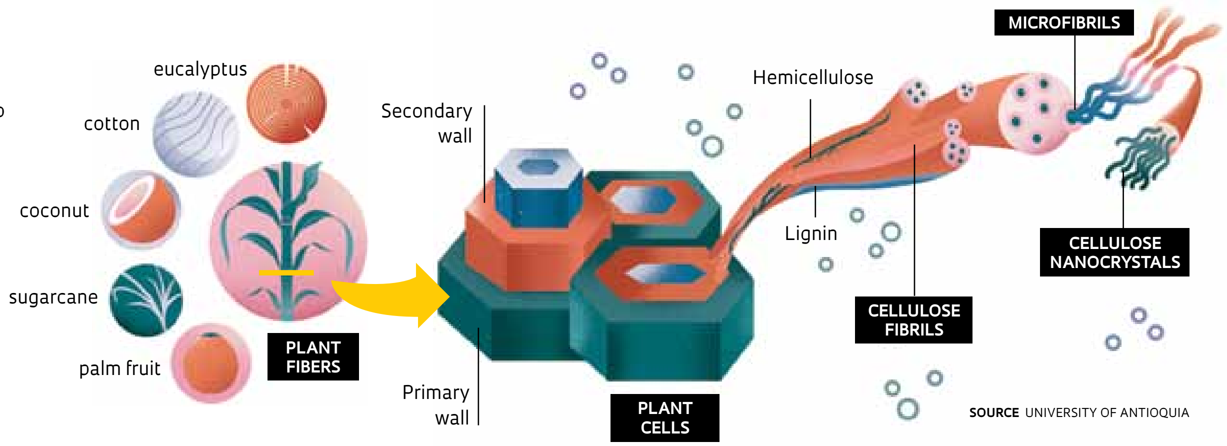
Holmen AB, a Swedish paper and cellulose company, became the principal shareholder in the Israeli firm Melodea, developer of an industrial process for extracting cellulose nanocrystals from paper manufacturing slurry. The company conducts research on the use of this material in foams without any type of plastic component and as a way to increase the strength of packaging, paper, acrylic adhesives and inks. In a partnership between Melodea and Holmen AB, the RISE Research Institutes (a Swedish government

Raw material extracted from inside plants

New material is created from the cellulose found in many plants

EXTRACTION OF CELLULOSE NANOCRYSTALS

The first step is to separate cellulose from hemicellulose and lignin. Smaller cellulose fibers are produced until they become nanocrystals. All the processes use chemicals, usually acids



SOURCE UNIVERSITY OF ANTIOQUIA

initiative in the field of innovation that encompasses Innventia and other institutes) and MoRe Research (a Swedish R&D company in the forest products industry) are building the first cellulose nanocrystals pilot plant in Europe, 500 kilometers from Stockholm.

In Canada, another country with a strong tradition in the paper and cellulose industry, both CelluForce and Blue Goose Biorefineries sell nanocrystals in the form of a clear, nearly transparent gel, for $1,000 per kilogram (kg). The buyers are companies and research institutions that test the raw material in various situations and products. The company's plant, in the Canadian city of Saskatoon, produces 35 kg of nanocrystals per week, sourced from products with a high cellulose content, such as tree pulp, recycled paper, cotton linter (fuzz that clings to cottonseed hulls), and flax fibers.

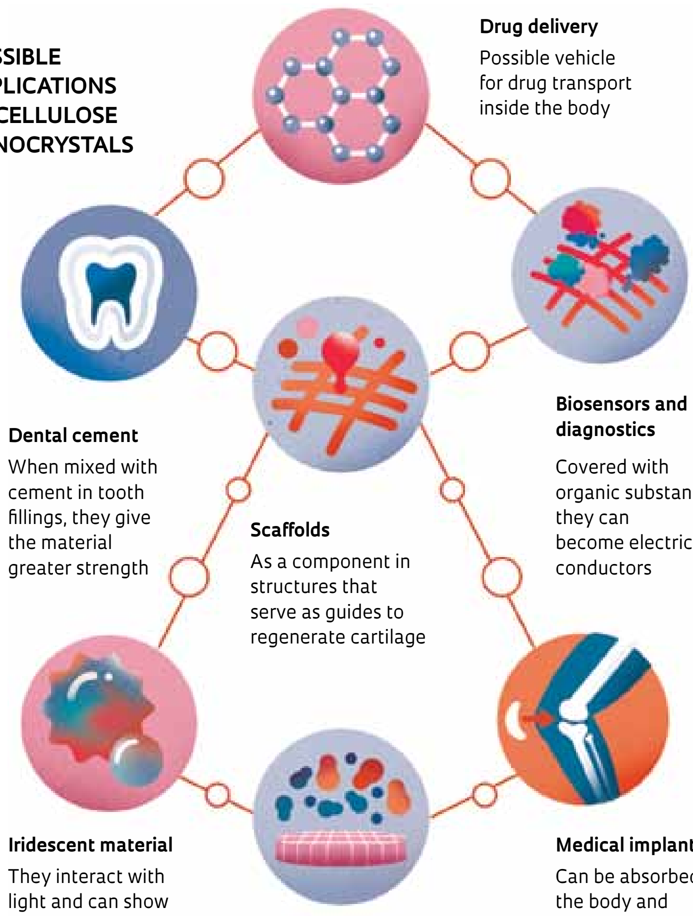
Blue Goose has developed an oxidative, nanocatalytic process that requires fewer chemicals and would therefore be more environmentally friendly for converting biomass into a nanometric-scale crystal. Nanocrystals are currently produced by acid hydrolysis (separation of wood fibers until the cellulose can be extracted in nanocrystalline form), in most cases using sulfuric acid but also using phosphoric acid or hydrochloric acid.

One bottleneck in R&D lies in the production of pieces of nanocellulose in larger dimensions. The challenge is to begin to efficiently produce the material in meters rather than in centimeters so that scientists can analyze its mechanical and functional characteristics and assess its benefits and uses as an end product. Melodea and MoRe Research are collaborating on a project to convert prototypes of films, papers and foams made in small dimensions in the laboratory using cellulose nanocrystals and nanofibrils into market-ready products. Under the leadership of KTH in Stockholm with participating Swedish universities and Processum, a biorefinery R&D company, the pilot plant now under construction in Sweden is expected to produce nanocrystals, nanofibrils and derivative products.

The project research team includes Daniele Oliveira de Castro, a Brazilian chemist who has an undergraduate degree from the Federal University of São Carlos (UFSCar), and a master's and sandwich doctorate from the Grenoble Institute of Technology in France, defended at the University of São Paulo (USP) under the advisorship of chemist Elisabete Frollini. In Sweden, Castro is developing processes to produce stronger paper with nanocellulose. "I'm also involved in creating foams made from nanocellulose that have fire retardant properties," she says. She has been at MoRe Research since September 2016, and her project ends in 2018.

Chemist Juliana Bernardes of the Brazilian National Nanotechnology Laboratory (LNNano) at the Center for Research in Energy and Materials (CNPEM) is coordinating a line of research using cellulose nanocrystals and nanofibrils extracted from sugarcane bagasse as thickeners in fluids. "These nanomaterials in small quantities can, for example, convert water into gel—an important feature in cosmetics," she explains. Bernardes will receive FAPESP funding for a three-month stint at Stockholm University to develop a dressing in gel form made of cellulose and wound-healing drugs.

One attention-grabbing use of cellulose is its application to reinforce cement. In a paper in the journal *Cement and Concrete Composites*, from February 2015, this use was evidenced by a study conducted at Purdue University. Researchers led



by engineer Pablo Zavattieri demonstrated that cellulose nanocrystals can increase the traction strength of concrete by up to 30%. The results indicated that the biomaterial increases concrete hydration, which strengthens the material. This would make it possible to use less cement in the mixture. These findings led the Purdue group to set up a partnership with P3Nano, a public-private organization created to conduct research using nanomaterials sourced from wood. The initiative is being funded by the Silviculture Office of the United States Department of Agriculture (USDA). P3Nano intends to advance the technology and commercialize it. To that end, it will continue to engage with the Purdue researchers, who are now conducting large-scale testing. ■

Project

Cellulose nanoparticles as rheology modifiers for complex fluids (No. 16/04514-7); **Grant Mechanism** Regular Research Grant; **Principal Investigator** Juliana da Silva Bernardes (CNPEM); **Investment** R$115,773.36.

INFOGRAPHIC ANA PAULA CAMPOS **ILLUSTRATION** BARBARA MALAGOLI

Research in Brazil

Several research groups are studying the production and functionality of cellulose nanocrystals

Several research groups at Brazilian institutes and universities are studying ways to extract and purify cellulose nanocrystals, along with the applications of this material. Two recent studies have focused on light reflection, a feature of nanocrystals. One of these studies was the cover story of *Advanced Materials*, a scientific journal in the field of materials. "The innovation was in placing liquid crystals onto cellulose nanocrystals to produce iridescent films that absorb light and reflect only a few colors," says Antônio Figueiredo Neto, a professor at the USP Physics Institute. He heads the group that is partnered with researchers from Portuguese institutions. "With cellulose, we obtained greater color versatility than we can with films made from synthetic material," Figueiredo reports.

A project by a group of researchers from the Federal University of Minas Gerais (UFMG) in Belo Horizonte and the Federal University of Jequitinhonha and Mucuri Valleys (UFVJM) in Diamantina demonstrated that cellulose nanocrystals can be precursors for carbon nanomaterials known as carbon dots. They can be used as a substitute for quantum dots made from semiconductor materials in nanometric dimensions. Possible applications include solar cells, medical image-capturing devices and displays. Quantum dots are currently found in TVs that use this material to improve visibility and resolution on LED screens—known as QLED TVs.

"We developed a way to pyrolyze cellulose nanocrystals that result in spherical carbon dots from 4 nm to 8 nm in circumference, which show photoluminescence in green and blue. Carbon dots have been a known entity since 2004, and in this paper, we demonstrated that they can be made from cellulose—an abundant renewal source," explains chemist Fabiano Pereira, a professor at UFMG."Another advantage of carbon dots is the fact that they present no toxicity."

Project

Optical and structural properties of elastomers and complex fluids of biological interest (No. 11/13616-4); **Grant Mechanism** Thematic Project; **Principal Investigator** Antônio Martins Figueiredo Neto (USP); **Investment** R$2,519,727.73.