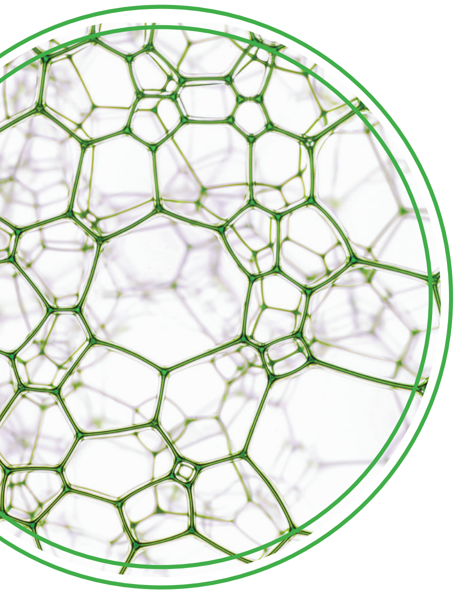


TAPPI INTERNATIONAL CONFERENCE ON NANOTECHNOLOGY

# Uncovering green gold in Grenoble

The Technical Association of the Paper and Pulp Industry (TAPPI) hosted its international conference on nanotechnology in Grenoble in June, where it highlighted mind-blowing innovation from around the world. TAPPSA chairman **Iain Kerr** filed this report on his return from the conference in France.

Imagine a future in which a family member suffers a spinal injury causing paralysis to the legs, and a brain implant made of nanocellulose gives them back their movement .... Or perhaps that degraded knee cartilage could be remedied by the use of biocompsites of nanocellulose and a synthetic polymer.

These are two of many materials that have already been developed by researchers for use in the human body, and the beauty of it is that these substances are all derived from wood. And you thought paper was the best product you could make from trees!

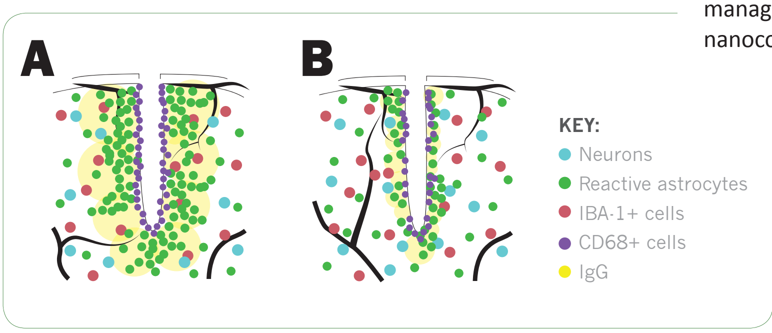
The conference heard that in addition to pure extractions and manipulations of cellulose from wood-based biomaterials, natural sources like sugar cane, hemp and algae can be combined with bio and oil-derived polymers to create novel new biocomposites.

## Be bio-inspired

Christoph Weder, an executive director and professor of polymer chemistry and materials at Switzerland's Adolphe Merkle Research Institute, has been working to produce natural or what he refers to as 'bio-inspired' materials. An example he used was the replication of the danger response mechanisms of the sea cucumber to induce movement in limbs following injuries to the spinal cord.

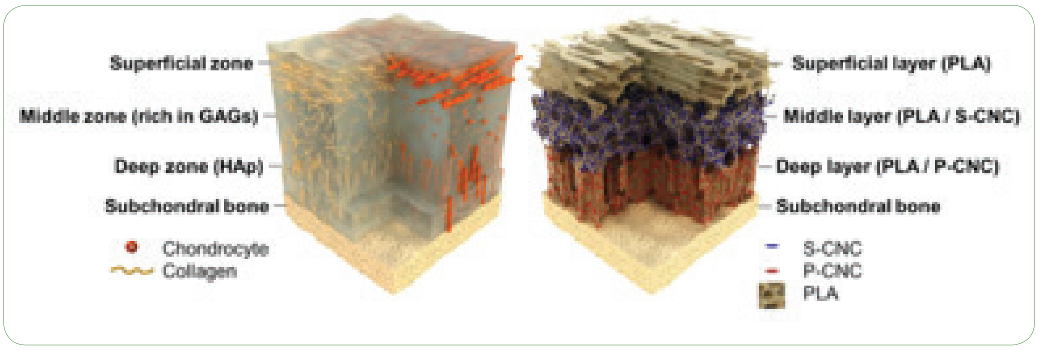
The sea cucumber can change its skin from soft and pliable to rigid and hard, a characteristic considered useful in devices like brain implants. These implants are used to transfer electric signals from the brain to other parts of the body to induce movement in the case of spinal cord injuries.

By copolymerising CNC obtained from marine invertebrates (tunicate CNC) with ethylene oxide-epichlorohydrin (EO-EPI) to form a nanocomposite, the research team managed to achieve just this effect: a bio-inspired adaptive nanocomposite.




**(LEFT) FIGURE 1:** Schematic representation of the tissue response around stiff (A) and compliant (B) implants. Stiff implants induce increased gliosis, BBB permeation, and neurodegeneration in comparison with compliant materials.

**(RIGHT) FIGURE 2:** Architecture of mature articular cartilage and the multi-layer polymer nanocomposite scaffolds studied **(Camarero et al, 2016)**



When no water is present, the copolymer is in the rigid state with polymer molecules tightly bound to each other by hydrogen bonds. In water, the hydrogen bonding between the polymer molecules is 'turned off' due to the presence of competing water molecules (relaxed state). They successfully manufactured mechanically-adaptive nanocomposites, which change their mechanical properties from a rigid to a compliant state in less than five minutes after implantation (http://europepmc.org/articles/pmc4175058 ).

Tests performed on the cortex of rats using this novel material indicated that there was considerably reduced immune response in the area surrounding the implant as compared with other materials that had previously been tested (http://europepmc.org/articles/pmc4175058 ).

## Captivated by cartilage

Weder's team has also been active in the development of materials to aid injured or deteriorating cartilages, such as those found in the human knee. Human cartilage is constructed of three distinct layers as shown in Fig 2 and reported by Camarero. To mimic this bio-material, poly (D,L-lactide) (PLA) on its own and PLA copolymerised with different forms of CNC, phosphate CNC (P-CNC) and sulphated CNC (S-CNC) was used to develop the three layers (Fig 2.). P-CNC is CNC produced by hydrolysis with sulphuric acid, the most commonly accepted means of producing CNC, while P-CNC is produced by hydrolysis using phosphoric acid. Each of these forms of CNC exhibits different properties.

The phosphate groups attached to the P-CNC were considered necessary to aid in the formation hydroxyapatite, which plays a role in bonding the cartilage to the bone.

There are countless examples of the nanocellulosic application in the medical and health sciences field but these two struck a chord in me. With some lateral thinking we can and will find uses and applications for cellulose in all of its forms.

## Should we leave oil before it leaves us?

Bernard de Galembert, innovation and bioeconomy director of the Confederation of European Paper Industries (Cepi), discussed the concept of a non-fossil-based economy, describing the paper industry as a potential front runner of the bioeconomy - an economy that uses renewable resources from land and sea, including crops, forests, fish and animals for the production of food, materials and energy.

With Europe setting course for a resource-efficient and sustainable economy, a balance needs to be struck between a more innovative and low-emissions economy; the demands for sustainable agriculture and fisheries, food security; the sustainable use of renewable biological resources for industrial purposes; and the protection of biodiversity and the environment.

He posed a number of interesting questions relating to bioeconomic boundaries. How do they compare in terms of burning wood for heat or for use as a building material

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## Back to **basics**

The language of nanotechnology is a minefield of acronyms covering the various forms of cellulose - NCC, MFC, CNF, MCC and more. Confused yet? We're only just getting started. Here are the meanings and definitions of some of the more important nanocellulosic substances.

- **MCC** = Micro crystalline cellulose

- **CNF/MFC** = Cellulose nanofibres or microfibrillated cellulose. CNF/MFC is a material composed of nanosized cellulose fibrils with a high aspect ratio (length to width ratio). Typical lateral dimensions are 5–20 nanometers (nm) and longitudinal dimension is in a wide range, of several micrometers (µm). It is pseudo-plastic and exhibits the property of certain gels or fluids that are thick (viscous) under normal conditions, but flow (become thin, less viscous) over time when shaken, agitated, or otherwise stressed. This property is known as thixotropy. When the shearing forces are removed the gel regains much of its original state. The fibrils are isolated from any cellulose containing source including wood-based fibres (pulp fibres) through high-pressure, high temperature and high velocity impact homogenisation, grinding or microfluidisation (https://en.wikipedia.org/wiki/Nanocellulose)

- **CNC OR NCC** = Crystalline nanocellulose or nano-crystalline cellulose. Nanocellulose can be obtained from native fibres by acid hydrolysis, giving rise to highly crystalline and rigid nanoparticles (often referred to as CNC or nanowhiskers) which are shorter (100 to 1 000 nanometers) than the nanofibrils obtained through the homogenisation, microfluidisation or grinding routes. The resulting material is known as nanocrystalline cellulose (NCC)(Peng et al., 2011).

- **CNF** = cellulose nanofibrils. MFC materials may be composed of (1) nanofibrils, (2) fibrillar fines, (3) fibre fragments and (4) fibres. This implies that MFC is not necessarily synonymous with nanofibrils, microfibrils or any other cellulose nano-structure. However, properly produced MFC materials contain nano-structures as a main component, i.e. nanofibrils (http://nanoscalereslett.springeropen.com/articles/10.1186/1556-276X-6-417)

In addition to the above pure extractions and manipulations of the cellulose from biomaterials such as wood, non-wood plants such as sugar cane or hemp, and algae, there are ways in which the cellulose can be combined with polymers (either biopolymers or oil derived polymers) to create new and novel biocomposites.

in comparison with converting the same resource into chemicals and pharmaceuticals? He also made the point that there was a need for policy and direction within the paper industry and that European leadership needs to double available bioresources in terms of crops, residues and the use of byproducts and waste collection.

## Biodegradable technology?

Another revealing fact that arose from the presentation is the use of nanotechnology in meeting the needs and aspirations of an aspirant bioeconomy. Developed nonmaterials are demonstrating exceptional properties in respect of stiffness, strength and weight against conventional alternatives.

A mind-boggling example of changes to be brought about is an iPad that is fully biodegradable in about 10 years' time. The aim should be to produce a bio-based product that is better than its fossil based equivalent in terms of environmental and climate benefits made of feeedstocks of sustainable origin in a resource efficient, cost efficient and cost competitive way and which are renewable, biodegradable, recyclable and compostable.

## Extracting maximum value from wood

One of the key revelations of the conference and its discussions was that wood-based products are being produced at a greater rate than the existence of current applications.

In his presentation on the 'Quantitative Analysis of Market Data and Trends for Cellulose Nanomaterials', University of Maine's Michael Bilodeau made the point that paper manufacturers are missing huge commercial opportunities by not deriving the maximum benefits from their raw material.

Saleable products such as bioethanol, lignin, cellulose and nanocellulose are just a small proportion of the products which can be extracted from their predominant feedsource.

A RISI study suggests that there will be a 15kt per annum demand for CNF by 2017. The demand for CNF is growing faster than for CNC, since CNC is more costly to produce.

A significant determination was that forest products represent one of the best ways of reducing the global reliance on fossil fuels, underlining the maxim from Innventia's 2015 Annual Report, that everything that can be made from fossils can, in future, also be made from wood.

We are entering a new and exciting era in the forest products industry. To me, the production of 'green gold' is the best way, if not the only way, out of our total reliance on fossil fuels. If this is to be, then the future is bright in this industry. ■

## **The value** of cellulose

### Characteristics and applications of cellulose

**Light, yet strong**
Automotive parts can be made by moulding cellulose nanofibres with resins and rubbers.

**Ultra-fine fibres**

**Large specific surface area**
Filters made from nanofibres with a large specific surface area can control small dust particles.

**Low thermal expansion**

**High gas barrier properties**
Can be used in gas barrier films. Films through which air cannot easily pass are effective in maintaining freshness in food.

**Environmentally-friendly biomass material**

**Exhibits characteristic viscosity in water**
Can be used in cosmetics, food, coating mixtures etc, as it imparts viscosity in water and can distribute particles.

Referenced from http://www.nipponpapergroup.com/

*The conference covered many papers on nanocellulose and its applications. These can be found on www.tappinano.org and the papers are available from TAPPI.*