

ORGANIC MATERIALS

Wood, trees and nanotechnology

The cellulose nanofibrils that are found in wood and other natural materials are similar to carbon nanotubes in many ways and could be used to strengthen composites for manufacturing.

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Although the prefix 'nano' has been added to almost every contemporary concept and device, it will probably come as a surprise to readers to learn that the second International Conference on Nanotechnology for the Forest Products Industry¹ took place in June. Nearly 200 researchers from the paper- and wood-products communities gathered at the conference to discuss ways of addressing the challenges facing these industries, including overcapacity and the need for national industries to remain competitive in an international environment. Having a history of seeking technological solutions to manufacturing problems, researchers are exploring nanotechnology to solve problems that limit efficiency and to seek new value streams from forest resources.

Wood has important advantages that match current needs. It is a renewable, sustainable and carbon-neutral resource that has the potential to displace part of our petroleum-based economy with a carbohydrate-based economy. Over two-thirds of the biomass in wood could be transformed by fermentation or gasification into liquid biofuels or monomers (most commercially used monomers are presently derived from unrenovable resources). The rest consists of domains of crystalline cellulose — a glucose-based polymer that is the most abundant organic polymer on earth. These domains are made of cellulose nanofibrils that are roughly 5–20 nm in diameter and hundreds of nanometres in length² (Fig. 1). This remaining third is more resistant to being broken down, but could prove to be a useful nanomaterial.

The most common theme at the conference, which took place at Knoxville, near the Oak Ridge National Laboratory in Tennessee, involved the incorporation of various types of cellulose nanofibrils — nanocrystals, cellulose whiskers and

[Figure deleted for copyright compliance]

Figure 1 The cellulose nanofibrils found in wood and other organic matter could be used to strengthen nanocomposites. This atomic force microscope image² of cellulose nanofibrils in maize measures $2 \times 2 \mu$

nanocellulose — into polymer matrices to produce reinforced composites for manufacturing. The stiffness (145 GPa) and tensile strength (7.5 GPa) of these nanofibrils approach those of the carbon nanotubes that are currently used to reinforce materials and should also, one expects, be much cheaper to produce.

Two steps must be mastered before cellulose nanofibrils are ready for real-world applications: isolation of the nanofibrils, and their dispersion in the material to be reinforced. Most research reported at the conference used nanofibrils that had been isolated by hydrolysis of the starting materials with strong acids — which does not appear to be an environmentally or economically friendly process — or ultrasonic disintegration, which achieved only partial success. Isolation of the nanofibrils therefore remains an important area for research and development. One possible approach, suggested by William Winters (State University of New York College of Environmental Science and Forestry)

during a brainstorming session, is the use of enzymes known as cellulases, perhaps genetically modified, to isolate the nanofibrils.

Cellulose nanofibrils have hydrophilic surfaces, so they disperse most readily in water-soluble polymers such as poly(vinyl alcohol) and poly(lactic acid). However, the composites produced from these starting materials are not suitable for many applications because they are water sensitive. In hydrophobic environments, such as polypropylene, cellulose nanofibrils prefer to agglomerate rather than disperse.

Perhaps the best example was reported by John Simonsen (Oregon State) who incorporated 10% cellulose nanofibrils in poly(vinyl alcohol) and crosslinked the matrix with poly(acrylic acid). The resulting film exhibited enhanced barrier properties towards the diffusion of hydrophobic molecules (trichloroethylene vapour in this 'proof-of-concept' demonstration) plus high tensile strength, toughness and thermal stability.

The increase in the strength of the nanocomposites is due to the formation of a percolating fibre network that spans the length of the material, as explained by Alain Dufresne (Ecole Française de Papeterie et des Industries Graphiques). Dufresne and others also reported that chemical modification of the cellulose surface can, in some cases, lead to better compatibility with the hydrophobic polymers that are widely used in engineering composites. Meanwhile, Jeffrey Catchmark (Penn State) used finite-element calculations to demonstrate that the rigidity of connections between fibrils greatly affects network strength.

The structure and organization of materials at the nanoscale was another common theme at the conference, with natural composites (for example, nacre, bone and wood) often providing the inspiration³. Benny Hallam (Imerys Minerals) described how the brightly coloured wings of some butterflies are not due to pigments but to optical

effects such as interference, which are caused by the wing surface having detailed structure on length scales of the order of the wavelength of visible light. Hallam suggested ways of organizing nanomaterials to mimic these effects and produce intense colours that are difficult to achieve with pigments⁴. This could lead to very thin opaque paper coatings that could be used in lightweight paper.

Optical properties of cellulose nanofibril films were extensively described by Maren Roman (Virginia Tech). Cellulose is chiral on molecular and supermolecular levels, so these condensed films behave like liquid crystals⁵, a property that could be exploited in security features, decorative coatings, automotive windows, information storage and laser optics.

The application of nanoscale materials depends on our ability to measure and characterize them, as is the case in most manufacturing, so it is essential to develop techniques and tools that work at the nanometre scale. Two sessions at the conference were devoted to measurement techniques, and the use of nanoindentation to measure hardness and stiffness was described by five different groups. Joseph Pickel (Oak Ridge National Laboratory) elaborated on the tools and services that are available at the Center for Nanophase Material Sciences at Oak Ridge, and Altaf Carim (Department of Energy) described the user facilities provided by the Department of Energy at five national laboratories, including Oak Ridge. For example, neutron scattering could be a valuable tool for determining the distribution of fibrils in polymers.

This conference was the third major event to promote nanotechnology for the forest products industry. The ball started rolling at a workshop held near Washington DC in October 2004, which resulted in a technology roadmap⁶. The first conference was held in Atlanta, Georgia, in April 2006, and the enthusiasm of the participants at the Knoxville conference — where 16% of the delegates were from outside the US — means that a fourth event will take place next year.

References

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