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Can this invasive exotic pest make better materials for industry and medicine?

May 4 2018, by Alison Gillespie

Although unappetizing in this lab shot, these creatures are already used for many other purposes, including as an ingredient in Asian cuisine. Credit: Johan Foster

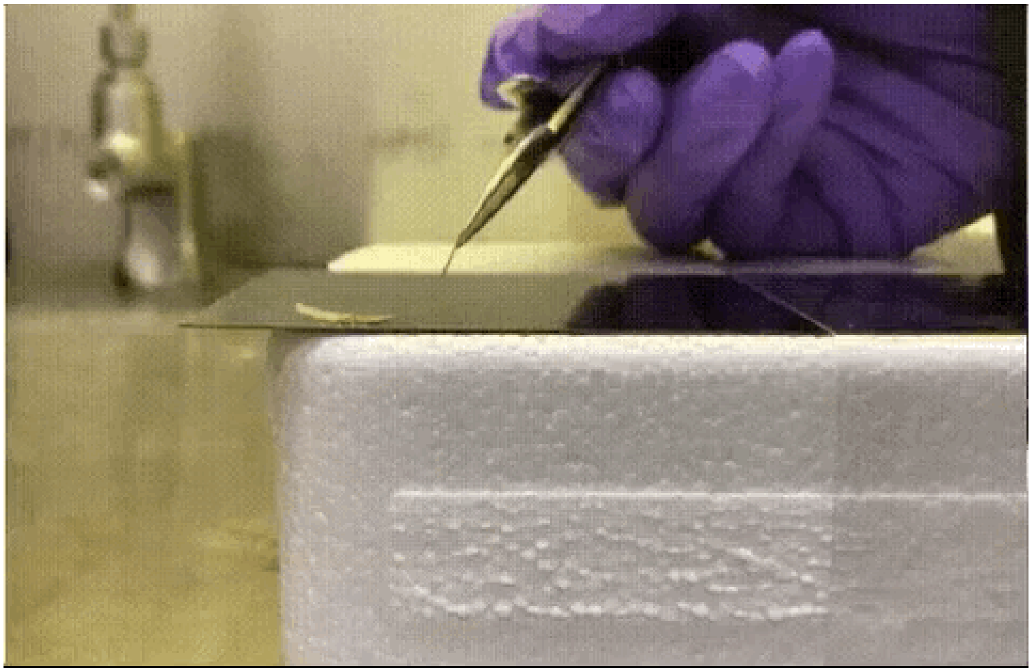
Researchers at the National Institute of Standards and Technology (NIST) have combined derivatives of two surplus materials—wood pulp and dried-up pieces of an invasive exotic pest—to form a new composite material that is flexible, sustainable, nontoxic and UV light-reflective. The material, described in a new paper published in *Advanced Functional Materials*, could soon be used in a wide variety of applications, including food packaging, biomedical devices, building construction and the design of cars, trucks and boats.

The key to this unlikely marriage of wood and pests is a motif called the "Bouligand structure," in which molecules stack up in a twisted shape, similar to tiny spiral staircases. Scientists have learned that the Bouligand structure provides a certain kind of resilience to cracking; the force of an impact is guided by those tiny, nanosized, staircase-like twists and turns through a series of detours. Rather than cracking straight through, the energy of a bump or crash is thus deflected through a kind of tortuous path, leaving the overall material intact and functional.

While wood does not have a natural Bouligand structure, it has attracted scientists for decades, in part because there is an ample supply of material left over after the processing of paper and commercial lumber.

"The idea of making useful products out of wood pulp has long intrigued a lot of people in many different industries," says Jeff Gilman, who leads the composites project team at NIST.

By washing that pulp with acid to remove its lignin and amorphous cellulose, scientists discovered several years ago that they could create a milky solution that ultimately dried to form a new material with a Bouligand structure. The key component of this solution was tiny crystalline rods of cellulose, known as cellulose nanocrystals or nanocellulose. However, on their own, the pulp-derived Bouligand films are brittle and won't hold much weight.



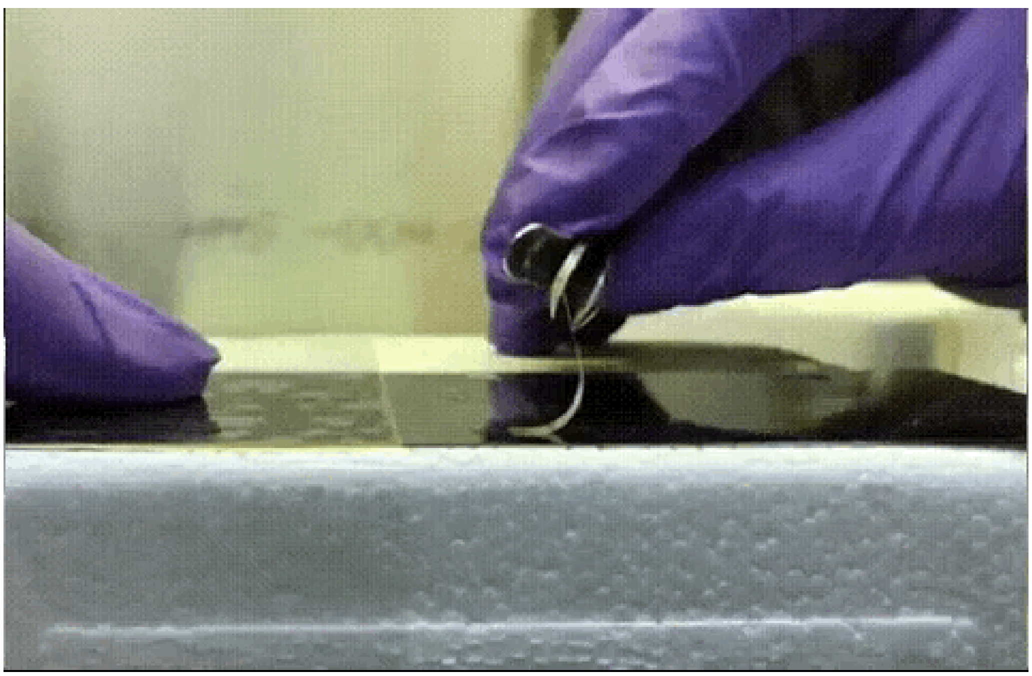
Researchers demonstrate bending wood pulp with no tunicate added. Credit: B. Natarajan/NIST

The NIST team hypothesized that combining the short wood-derived nanocellulose rods with another natural material with longer crystalline rods would result in something new that would be incredibly strong and flexible. With appropriate additives, this new material could be used to create films that could slow down the diffusion of water and oxygen.

"The right product, if developed, could be used in everything from aerospace composites to packaging that would keep food fresh," Gilman said.

One option for the new composite material: the carcasses of a dried-up aquatic creature called a tunicate that is considered a pest in some countries and a delicious treat in others.

In many parts of Asia, the brown aquatic creatures (*Styela clava*) are often cooked and served in spicy sauces. But without natural predators present to eat them in new environments, their populations begin to grow into super-abundant numbers that eventually clog boat engines and fishing gear, outcompete native fish, reduce healthy plankton populations and foul and ruin productive shellfish beds. Some environmental managers think that finding a way to remove and use them as a resource could serve a beneficial purpose. Harvesting them is one option. Like an oyster, the inside of a tunicate is considered the tasty bit. The outside is usually just thrown away, meaning there could be a ready source for this material in areas where they are often cooked.



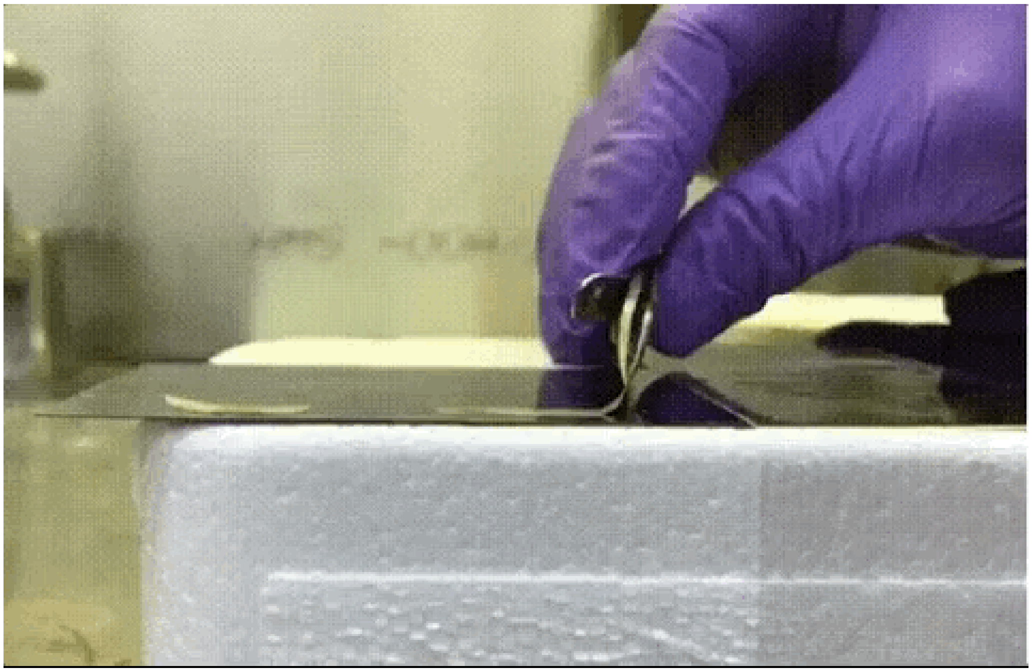
Researchers demonstrate bending wood pulp with 5% tunicate added. Credit: B. Natarajan/NIST

What specifically intrigued the NIST researchers, however, was the tunicate's inner structure, which was made of very long, highly crystalline nanocellulose. These were different from the shorter crystals found in wood.

"Tunicates have stuck out as the gold standard for their physical properties," said Johan Foster from Virginia Tech University, who is one of only a handful of teams working on tunicate harvest and research around the globe. Foster gathered and supplied the tunicates for the NIST project from a dock in Western France, where the animals are considered a nuisance species.

Some scientists had assumed that a composite made entirely out of long crystalline tunicate nanocellulose would be incredibly strong and tough. However, by testing dried mixed tunicate/wood composite materials, lead author Bharath Natarajan was able to identify the exact point of greatest toughness.

"If you put a little tunicate into the wood pulp composite, it makes it a little stiffer, and it doesn't break as quickly and becomes more flexible," Natarajan said. "Put in 10 percent and it's twice as strong. If your mixture is 30 percent tunicate and 70 percent wood pulp, the resulting composite is 15-20 times tougher. But after that, you really don't see an improvement in strength, and there is a reduction in toughness."



Researchers demonstrate bending wood pulp with 30% tunicate added. Credit: B. Natarajan/NIST

Tunicates are plentiful, but remain expensive to process, so knowing exactly how much to add is key to scaling up their use in the future, and for keeping any resulting products affordable.

Adding the tunicates also caused the nanocrystals to twist in a different way and accelerated the structure formation in the wood pulp. It also formed a pattern that was tighter and denser, making the new composite material UV-reflective.

"Many materials begin to degrade if they are exposed to the sun for a long time," said Gilman. "This material could potentially be used as a coating on other surfaces in order to reflect light and extend durability."

In the coming years, Natarajan and his team will continue to test ways their new tunicate-wood pulp mixture could be used to manufacture resilient, flexible and UV-reflective composites for use in the manufacture of sustainable, lightweight automobiles and aerospace vehicles, among other products.

More information: Bharath Natarajan et al, Binary Cellulose Nanocrystal Blends for Bioinspired Damage Tolerant Photonic Films, *Advanced Functional Materials* (2018). DOI: 10.1002/adfm.201800032

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