

# LEARNING FROM SPIDER SILK

Science draws on the wispy material's properties to make new types of **FUNCTIONAL MATERIALS**

MITCH JACOBY, C&EN CHICAGO

**SINCE TIME IMMEMORIAL**, spiders have been weaving webs that are resilient and tough enough to snag bugs that haplessly soar full speed into a web's sticky grip. But only recently have researchers begun figuring out what makes these webs work so well.

"Spiderwebs are quite remarkable," says Ali Dhinojwala, a professor of polymer science at the University of Akron. When people accidentally walk into a web, they often have to spend quite a bit of time peeling the slinky threads from their hair, skin, and clothing. That familiar and bothersome experience highlights some of spider silk's most noteworthy features, Dhinojwala says. The micrometer-thin fibers are almost invisible, yet they are sufficiently strong, stretchy, and sticky to catch and hold insects—and cling to people.

Dhinojwala's focus on spider silk stems from his group's interest in discovering the molecular basis of natural materials' outstanding properties and learning how to mimic them synthetically. Several years ago his group made news by developing a carbon nanotube-based adhesive tape inspired by microscopic structures found on the pads of gecko feet. These days he's caught up in adhesives found in spider silk.

The Akron researcher isn't alone in his fascination with spider silk properties. Earlier this month, a sampling of scientists who share a fascination with the fibers spun by the eight-legged critters presented their latest work at the American Physical Society (APS) meeting in Boston. Those scientists, along with others who didn't make it to

the conference, are working to uncover the chemical and physical basis of spider silk's toughness, which on a per-weight basis exceeds that of steel. They are also studying the nature of the material's elasticity and other properties, and devising ways to replicate them in the laboratory. Other researchers are developing techniques for chemically functionalizing natural spider silk. The groups aim to make novel materials with unique properties suitable for numerous applications ranging from medical products to electronic devices to musical instruments.

Spider silk's famed stickiness plays a key role in ensuring that insects that happen upon a

spiderweb stick around long enough for the spider to enjoy them for lunch. Common orb-weaving spiders, which produce a spiral or wheel-shaped web, deposit micrometer-sized glue droplets composed of an aqueous coat of salts that surround nodules of sticky polymeric glycoproteins on web fibers designed to catch prey ("capture" fibers, not the structurally supportive draglines, which are the biopolymeric threads that form the spokes and outer rim of webs). Although some details of the adhesive's chemical identity have been known for years, the mechanism through which the web adhesive helps the spider's entrée stay put has remained a mystery.

To address those secrets, Dhinojwala, graduate student Vasav Sahni, and Todd A. Blackledge, an Akron biologist, teamed

up about two years ago to design an experiment that examined individual spider glue droplets. The group's members repeatedly brought a probe tip in contact with a glue droplet and backed it away while imaging the point of contact and monitoring the speed of the probe, the rate at which the procedure was conducted, and the forces applied to drive and withdraw the probe. They adjusted those parameters over a range of conditions including ones that simulated the forces of a bug quickly flying into a web and coming to a rather abrupt stop and slowly trying to free itself over an extended period.

They found that the glycoproteins' elasticity—and not other factors such as capillary forces—deserves most of the credit for the web glue's prey-trapping abilities (*Nat. Commun.*, DOI: 10.1038/ncomms1019). "When a flying insect hits a web at high velocity," Sahni explains, "large forces are needed to catch it. But after the prey has been there a while, smaller but consistent forces are needed to hold it there." As Dhinojwala points out, that adhesive profile is exactly

## CATCHY MATERIAL

Tough, sticky, and stretchy, even when coated with dew droplets, spider silk exhibits a unique combination of qualities that draws researchers to try to mimic the material synthetically.

VASAV SAHNI/UNIVERSITY OF AKRON



the one presented by spiderweb glue because, similar to a wad of chewing gum, it behaves like a viscoelastic solid. Viscoelastic liquids, in contrast, lose their elasticity and sticking power quickly, he says.

More recently, the team compared the effects of humidity on the properties of glues of orb weavers to those of their evolutionary descendants, cobweb weavers, which build irregular, three-dimensional webs. The researchers found that cobweb glue's elasticity and adhesion remain rather constant with variation in humidity. In contrast, the glues of orb-weaving spiders respond strongly to humidity. Those glues expand dramatically and lose elasticity with increasing humidity, and they exhibit maximum adhesion at intermediate levels of humidity (*Sci. Rep.*, DOI: 10.1038/srep00041).

In a study published earlier this year, the Akron researchers mimicked a web-building tactic of orb-weaving spiders to produce synthetic fibers that look and function similar to natural ones (*Langmuir*, DOI: 10.1021/la203275x). Specifically, as a result of the manner in which these spiders deposit glue droplets along the length of

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To watch "coiling instability" cause strings of viscous liquids to form loops and patterns, visit [cenm.ag/coiling](http://cenm.ag/coiling).

capture fibers, those threads take on a beads-on-a-string morphology that resembles some kinds of necklaces.

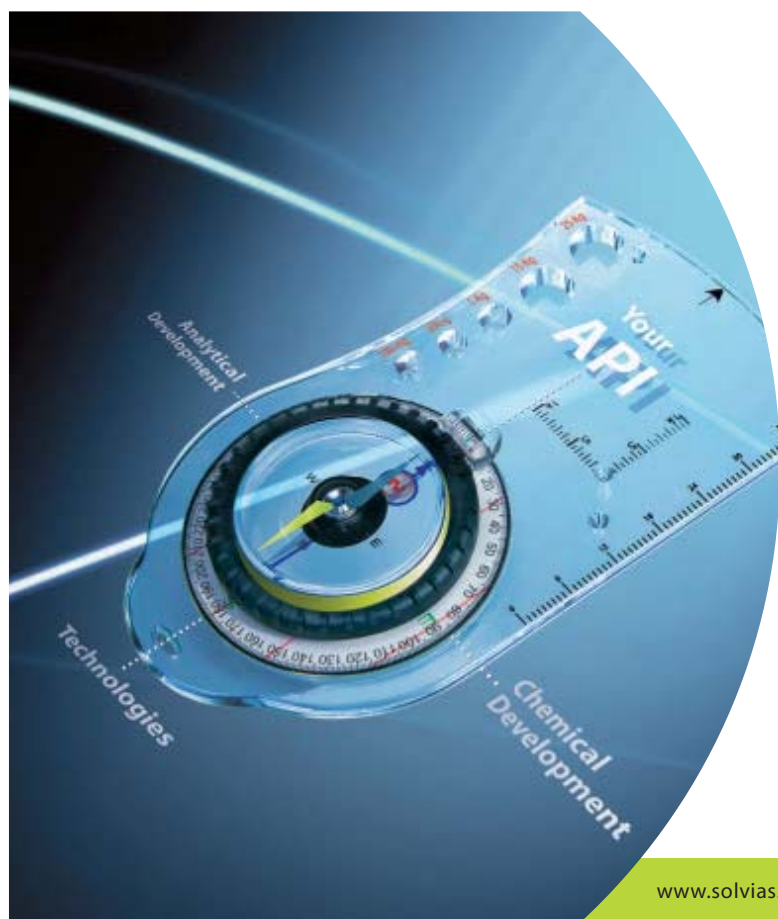
Dhinojwala, Sahni, and a coworker made similar structures in their lab by withdrawing 30- $\mu\text{m}$ -diameter nylon fibers vertically from a reservoir containing a polydimethylsiloxane (PDMS) solution. The initially uniform cylindrical PDMS coating spontaneously breaks up into an array of droplets. By controlling the solution's viscosity and surface tension and the rate at which the fiber is withdrawn, the team is able to tailor the diameter and spacing of the droplets—the beads on the string.

**ARMED WITH A SIMPLE** technique for mimicking the shape of orb-web capture threads, the researchers investigated the relation between this unique morphology and adhesion under conditions that simulate an insect's collision and separation from a web. They found that compared with a uniform cylindrical glue coating, the

characteristic glue-bead shape enhances adhesion by increasing the contact area between a probe (or an insect) and the glue. That shape also increases the energy that must be expended to free the probe (or unlucky bug).

At the outset of the study, it seemed counterintuitive to the team that these spiders would have adopted the beads-on-a-string tactic because it compromises the invisibility of the web. The results, however, show that the invisibility-adhesion trade-off favors the spider by helping it get a grip on its next meal. The Akron team is now studying ways of applying its findings to design new types of adhesives for water-resistant bandages, in-body sutures, underwater sealants, and other applications.

Frédéric P. Gosselin, a mechanical engineering professor at Polytechnique Montreal, also seeks to make new types of advanced materials by drawing on lessons learned from spider silk. He's focusing on the silk's extreme toughness, which



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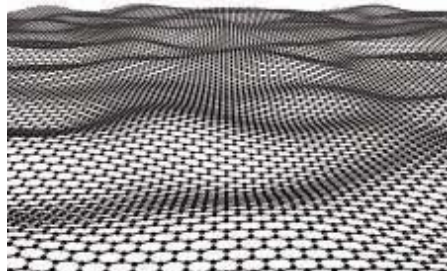
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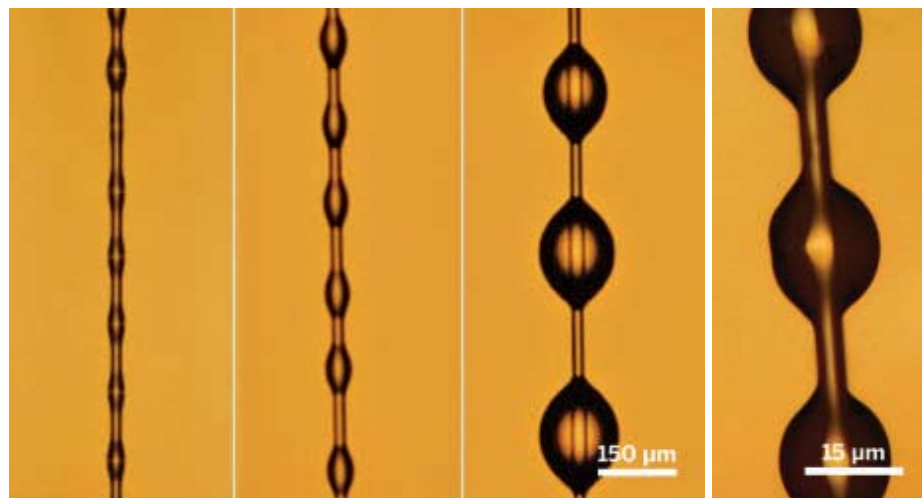
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is partly attributed to hydrogen bonds between coiled sections of the fibers' protein chains. Previously, researchers had shown that pulling on the fibers extends their length by breaking sacrificial hydrogen bonds and uncoiling the nanometer-sized springlike chains—as opposed to snapping them. As Gosselin reported at the APS meeting, he's just begun developing methods for mimicking that molecular chain process with macroscopic coiled polymer fibers.

To control fiber coiling, Gosselin is exploiting a curious phenomenon known as liquid rope-coiling instability, which can cause viscous liquids such as honey to spontaneously form springlike coils when dripped onto a surface from a long, continuous string of the liquid. Honey coils quickly turn into a shapeless puddle. But coils in threads of polylactic acid-dichloromethane solution retain their shape as the solvent evaporates and the fibers solidify, as Gosselin showed in videos of the polymer being dispensed from micrometer-diameter needles onto a moving platform. Data from stress-strain tests conducted on the fibers bear the signature of uncoiling events, he reported, but the fibers' toughness—which varies with the rate at which the solution is dispensed and the solvent evaporates—and other parameters have not yet been optimized.

Tufts University researchers are also making new materials inspired by spider silk properties, specifically those attributable to sequences of amino acids in the dragline silk of the commonly studied orb-weaving spider *Nephila clavipes*. Peggy

**LOOK-ALIKE** The beads-on-a-string structure of sticky spiderweb threads (SEM image at right) can be reproduced with synthetic materials (other images) via a method that affords control over bead sizes and spacings.

Cebe and David L. Kaplan, professors of physics and biomedical engineering, respectively, and graduate students Wenwen Huang and Sreevidhya Krishnaji have synthesized a new family of block copolymers in which the blocks are

composed of amino acid sequences related to two key regions of silk fibers. One sequence, found in crystalline regions of the silk and rich in alanine groups, gives spider silk its strength and toughness. The other sequence is glycine-rich and credited with imparting elasticity to the fibers.

By tuning the composition of the copolymers, the Tufts team can control the crystallinity and morphology of the products and has used that approach to make a variety of materials including disordered films, fibrils, and micelles, some of which are hollow and roughly 50 μm in diameter. It's unclear why these micelles form, Cebe acknowledges. To help discover the reason, the group's members are currently working to map the copolymer's phase diagram. They are also exploring the potential for using the micelles as drug delivery vehicles in human disease therapies.

**RATHER THAN MIMICKING** spider silk properties in synthetic materials, Florida State University (FSU) physicist James S. Brooks, graduate student Eden Steven, and coworkers functionalize the natural stuff to make it electrically conducting and use it in applications for electronics. Motivated by a need to make new types of microscopic wires and electrical connectors, the group has tried a number of strategies for modifying spider silk.

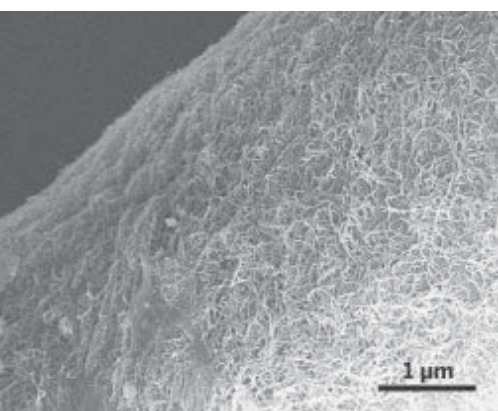
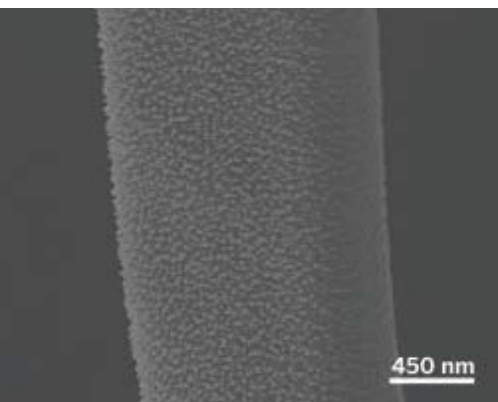


## “Spiderwebs are quite remarkable.”

In one test, the FSU team showed that pyrolyzed, iodine-doped silk is conductive enough to be used as a lightbulb filament. In another test, they sputtered deposited gold onto silk fibers and found that the metallized silk remains elastic over a wide temperature range and is robust enough to be wired into a test device for measuring electrical properties of tiny organic crystals. They also coated silk with carbon nanotubes and showed that the resulting fibers can be fashioned into a strain-sensing heart pulse monitor (*Sci. Tech. Adv. Mater.*, DOI: 10.1088/1468-6996/12/5/055002).

Iowa State University mechanical engineer Xinwei Wang also has electronics in mind. His team reported just days ago that dragline silk fibers of *N. clavipes* are far better thermal conductors than most materials. The team found that after the fibers are stretched, their thermal conductivity exceeds that of copper. They also determined that in contrast to most materials, the thermal conductivity of these fibers increases under strain, a finding that may lead to novel heat-controlling polymers for flexible electronics applications (*Adv. Mater.*, DOI: 10.1002/adma.201104668).

EDEN STEVEN/FSU



**FUNCTIONAL** The spider silk fibers shown in these SEM images were coated with gold (top) and carbon nanotubes (bottom) to render the micrometer-sized threads conductive and useful for electronics applications.

On an entirely different note, Shigeyoshi Osaki of Japan's Nara Medical University made violin strings by twisting together thousands of spider silk fibers. Twisting changes the filaments' cross-sectional shapes from circular to polygonal, Osaki says, which in turn alters their packing geometry and leads to strings that produce “a soft and profound timbre.” A report on the work has just been accepted for publication in *Physical Review Letters*.

Spiders have had eons to capitalize on natural phenomena that endow their silk with unique and useful properties. Researchers are trying to learn from the little critters' ways by probing the secrets of their webs' slender strands, sticky glues, and performance characteristics to make new types of advanced materials. The eight-legged weavers have had a significant head start, but science is starting to catch up. ■

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