A renewable bioplastic made from squid proteins

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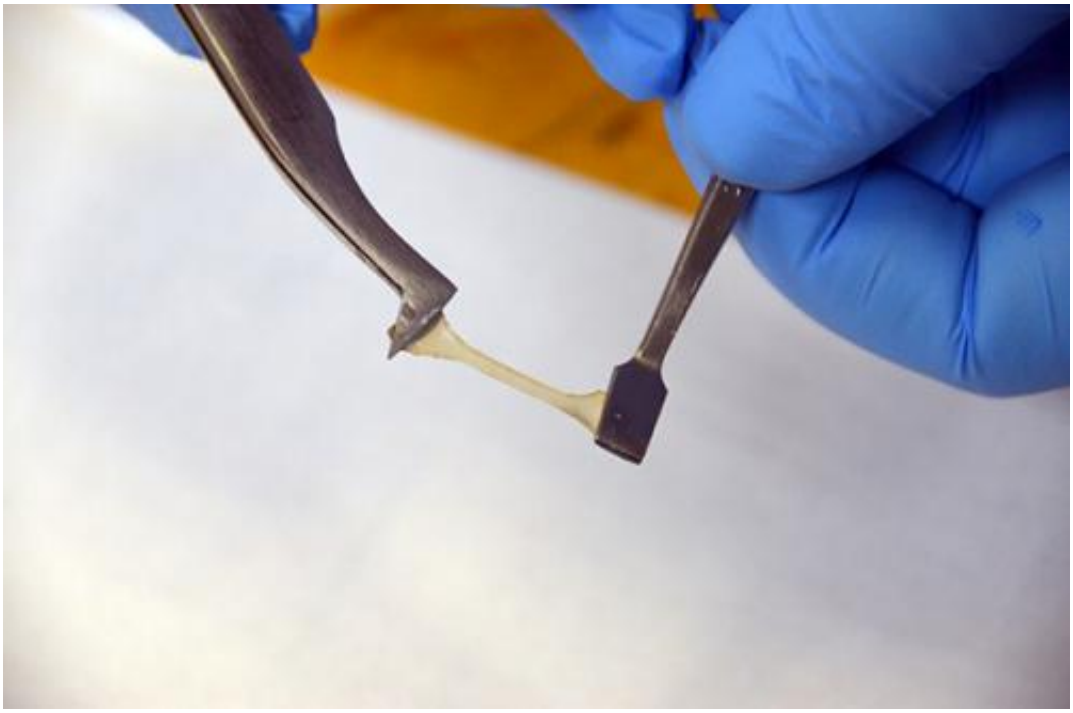


A thermoplastic made of squid protein can be stretched up to 300%. Credit: Penn State

In the central Northern Pacific is an area that may be the size of Texas called the Great Pacific Garbage Patch. Made up of tons of floating plastic debris, the patch is killing seabirds and poisoning marine life in the North Pacific Ocean and in other oceans where converging currents, called gyres, concentrate the floating plastic. Over time, plastic bottles and fishing lines from coastal locations and seagoing vessels break down

into nearly invisible pieces small enough to enter the food chain where some of the chemicals may eventually be ingested by human beings.

At Penn State, a group led by Melik Demirel, professor of engineering science and mechanics, is designing a biodegradable plastic from structural proteins that could help clean up the world's oceans and solve an interesting set of other problems along the way.

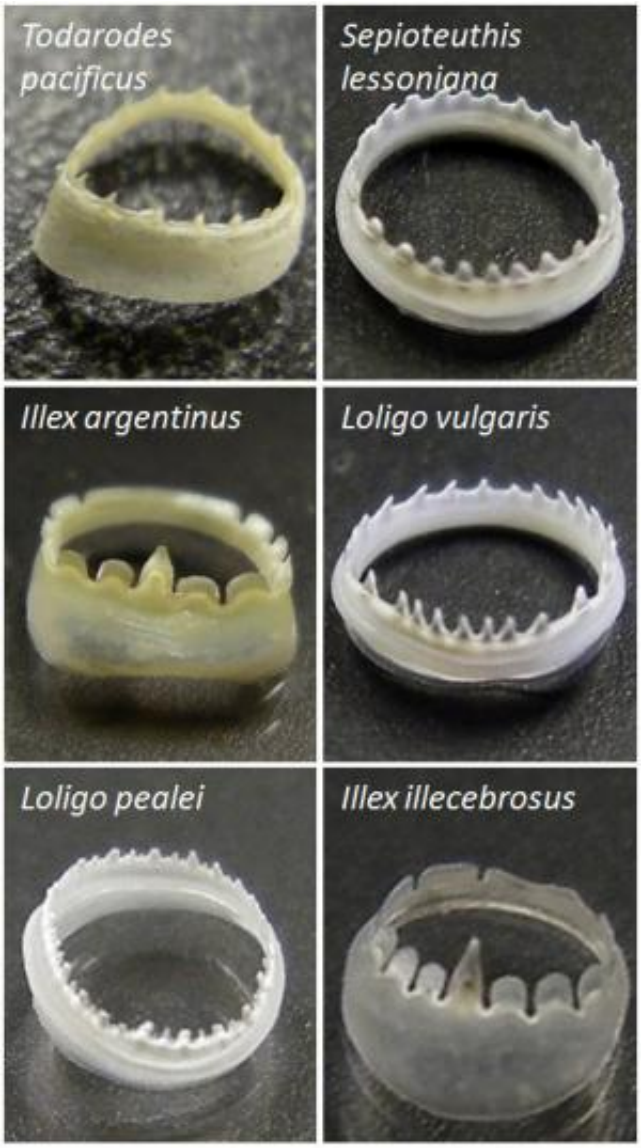
Demirel and his students have gathered squids from around the world, from the Atlantic coast, the coast of Spain, from Korea, and later this year, from Argentina. From these specimens, his lab has extracted the squid ring teeth (SRT) from their tentacles, and re-engineered their proteins in ways that go beyond nature. He plans to find ways to biosynthesize the engineered protein in bacteria through fermentation on an industrial scale. And though that may be a few years down the road, it is entirely feasible, he believes. "Structural proteins are eco-friendly materials with remarkable mechanical properties," he says. "It's a material that looks a lot like silk, except that it is thermoplastic, which means that it can be melted and reshaped into different forms without losing its properties. Like silk, SRT is lightweight and strong, which is why the Army is interested in the material for textiles."

The convergence of materials and life sciences

In the Demirel lab, graduate student Abdon Pena-Francesch removes the protein from the suction cups on the squid's tentacle using a toothpick. He then processes the protein into a viscous melt at a temperature above its softening temperature, around body temperature in water. The melt could be used in a number of industrial processes, such as electrospinning, extrusion, molding, or by coating onto a surface. A new and potentially dramatic way to use the protein melt is in 3D printing.

"The squid protein Abdon is working with can be melted and solidified

over and over without losing its mechanical properties, which include high toughness (how much energy it can absorb), high strength (the load that can be borne before failure, around one gigapascal), and its extensibility (how far can it be stretched before breaking), which can be engineered up to 300%," Demirel says. In addition, this fibrous protein can be chemically functionalized and can be controlled so as to biodegrade in anywhere from hours to years. This makes squid protein a good prospect for packaging, such as plastic bottles, or timed-release drug delivery.



Squid ring teeth proteins can be mixed across species to engineer the required properties. Credit: Penn State

With so many potential advantages to using a safe, recyclable, biodegradable, composite material, there is still a big roadblock, says Demirel. That is the processing of the tiny rings is slow and expensive and there are not enough squids in the ocean for an industrial scale material. In order to compete with plastics that are a byproduct of relatively cheap oil extraction, a better method for producing these proteins is required.

This is where materials science and life sciences begin to converge, Demirel says. Genes coding squid proteins were read by sequencing instruments in the Genomics Facility at Penn State. Once Demirel's team obtained the genomic data, they had to find out which portions of the data actually contain the code for protein formation. For this they took their data to the Proteomics and Mass Spectrometry Facility at Penn State. Both facilities are operated by the Huck Institutes of the Life Sciences.

"At the Proteomics Facility, we read the sequence of the protein. The problem is the mass spectrometer can only read a small portion of the sequence at a time. That's when bioinformatics people step in, such as Dr. Istvan Albert and his Bioinformatics Consulting Center in the Dept. of Biochemistry and Molecular Biology," Demirel says. "They start building the whole map, put it into bacteria and express it."

There are multiple systems for biologically synthesizing the squid proteins into a plant or animal system. These include bacteria, yeast, mammal, plant, or insect systems. Demirel currently works with Wayne

Curtis, professor of chemical engineering, to express the protein in bacteria. Bacteria are already in use to make high-end products such as pharmaceuticals and cosmetics.

There are several proteins in squid tentacles, some of which show thermoplastic properties and others elastic properties. The ratio of these proteins is distributed differently in each of the species. This gives his group a large canvas of properties to work with.

"Now we can go beyond nature, because we can take each of these proteins and mix them as we wish. We can mix within species or we can mix across species. We know by theory that depending on their molecular weight they will either be all thermoplastic or all thermoelastic. By mixing the molecular weight you get something in between," says Demirel. His group is already producing on the order of 100s of grams of protein. Their goal is to produce kilograms by the end of this year, and then, in the next couple of years, tons. Eventually with Wayne Curtis' expertise, he proposes to make a thermoplastic elastomer that is competitive with synthetic oil-based plastic.

In the lab, Pena-Francesch coats a glass slide with a squid protein and sets a second glass slide on top of it. The two slides bond, and it takes a powerful pressure to pull them apart. The adhesive is stable underwater for at least six months and could be used for a marine coating or for bandages for wound healing. The fibrous protein can be reformed several times and retains its elasticity or stiffness in wet or dry conditions.

Next, he stretches a small strand of elastomer protein with small pliers until it finally snaps. To demonstrate the material's self-healing property, Pena-Francesch heats the broken strands above its softening temperature and rejoins the ends seamlessly.

"We are in the process of taking something from nature, reproducing it, and mimicking it using gene sequences to get properties that materials scientists are interested in, such as specific physical properties including surface, mechanical, and barrier properties," Demirel says.

Provided by Pennsylvania State University