Triple threat polymer captures and releases

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Karen L. Wooley (left) WUSTL James S. McDonnell Distinguished University Professor in Arts & Sciences, chemistry doctoral student Brooke Van Horn, and chemistry postdoctoral researcher Jinqi Xu, Ph.D., examine polymer samples in Wooley's McMillan Hall office. Wooley and her collaborators have mixed two normally incompatible polymers and have come up with nanoparticles that make a perfect host to serve guest molecules. David Kilper/WUSTL Photo

A chemist at Washington University in St. Louis has developed a remarkable nanostructured material that can repel pests, sweeten the air, and some day might even be used as a timed drug delivery system — as a nasal spray, for instance.

Karen L. Wooley, Ph.D., Washington University James S. McDonnell Distinguished University Professor in Arts & Sciences, has taken the same materials that she developed more than four years ago as marine

"antifouling" coatings that inhibit marine organisms such as barnacles from attaching to ship hulls to now capture fragrance molecules and release them at room temperature.

Wooley mixes two normally incompatible polymers — a hyperbranched fluoropolymer and a linear polyethylene glycol — and lets them phase-separate into distinct domains, one interspersed in the other. A chemical process called crosslinking then solidifies the mixture, thus creating a heterogeneous coating that, upon close examination, reveals treacherous nanometer-sized terrain composed of mountains and valleys, ranging from hard to soft, hydrophilic to hydrophobic. The complex surface that is created makes it difficult for marine organisms to establish a toehold. Her laboratory has produced these novel materials and they are being used around the world

Wooley and her collaborators were intrigued by the surface of these nanostructured materials and began to wonder what was beneath the surface. They found that their materials made a perfect host to serve guest molecules.

"We looked at the roughness and complexity of the surface and thought that the surface might provide interesting entrance and exit ports for small molecule guests," Wooley explained. "So, our material would be a host that would act like a sponge, because we have this complex subsurface morphology, and we thought of it as being domains that might be like holes in sponges and other domains that might be like sponge material."

Be my guest

The subsurface composition and properties might thereby allow the guests to partition off into one domain and then another guest partition into another domain.

"We have these channels to serve as capillaries to take in guest molecules and hold them inside the material," said Wooley, a member of Washington University's Center for Materials Innovation, (CMI) which enables collaborators from across the Washington University campus to make basic and applied advances in materials research, touching many aspects of daily life.

She and her group received a research grant from Imperial Chemical Industries/National Starch to continue their study, with a goal of taking the guest molecules in and holding them. Using the technology of thermogravimetric analysis (TGA), Gerald O. Brown, Ph.D., a postdoctoral research associate in Wooley's group, began analyzing the release of these guests — fragrance molecules — as gaseous small molecules from the polymer across the network of the host material.

"We found that the temperatures at which the guests left the material were dependent on the composition of the host, and when the release of the small guest molecules was monitored from just an empty TGA pan, there was a slight difference versus those guests in the presence of either the hyperbranched fluoropolymer or the polyethylene glycol," she said. "There is a slight depression of temperature at which the small molecule fragrance volatilizes and becomes a gas."

However, when they looked at the complex materials — the ones designed to be anti-fouling materials — they found a progression of decreasing temperature as they went with different amounts of poly (ethylene glycol) relative to hyperbranched fluoropolymer in the composite material.

"What's amazing is that there is a 55 degree temperature reduction at which this small molecule leaves the host material versus it leaving an empty pan," she said. "Then we thought that this material could be very useful as something to promote the release of a volatile agent — maybe

for some kind of nasal inhalation-based delivery of drugs. Or maybe something as simple as a room-temperature release of a fragrance."

Sponge analogy

Wooley said that they don't know where the guest molecules are residing in the host material, and her group is now inserting stable isotopes into the host and guest molecules and with the help of her colleague Jacob Schaefer, Ph.D., Washington University Charles Allen Thomas Professor of Chemistry, will measure the difference between those stable isotopes to help find where the guests are located relative to the host.

"We want to know where they reside because that should tell us why this material is providing a favorable environment at room temperature but at elevated temperature for some reason everything is being expelled rapidly," she said. "We don't know if there is some reorganization of the morphology of the material or whether the guests partition to different domains at different temperatures."

Wooley says that the results of her research with the polymers — the promoted release, the anti-fouling application — are "strange, if not weird, but there is so much going on here, we want to explore it all."

That weirdness suggests equally weird mechanical properties. Wooley and her post doctoral researcher Jinqi Xu, Ph.D., are exploring those properties and one essential irony — the material, similar to a hydrogel because it takes in water, oddly becomes stronger when water absorbs into it. Think of a soggy diaper as a hydrogel. If you liken Wooley's materials to a diaper, that wet one becomes nearly petrified. That's known as an increased modulus value — a measure of stress versus strain.

"When you pull on a sponge, the water comes back out," she said. "But in our case, because our sponge and the channels within it are essentially nanoscopic, the water cannot get out, at least not fast enough to allow for a reorganization of the material, and therefore it just rigidifies the material."

Xu made a presentation on this research at the 2006 Spring Meeting of the American Chemical Society (ACS), held March 26-30 in Atlanta. Wooley and her collaborators published a communication on the research in the Journal of the *American Chemical Society*, 2005, 127, 11238-11239.

Source: Washington University in St. Louis