MEETING BRIEFS

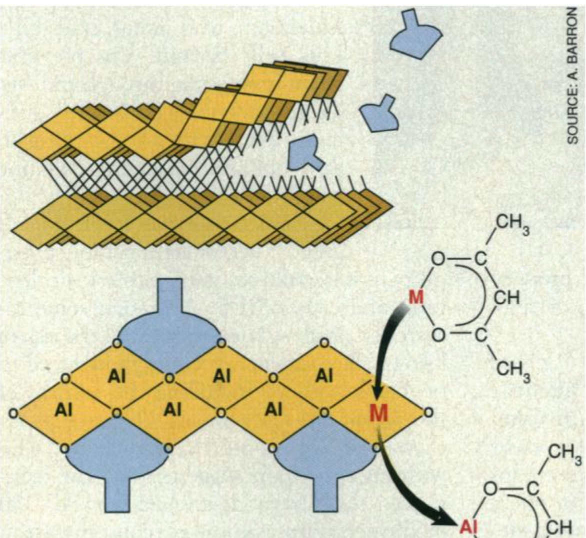
Chemists Clean Ceramics and Coat Enzymes in Plastic

NEW ORLEANS—Southern hospitality welcomed nearly 13,000 scientists here from 24 to 28 March for the 210th national meeting of the American Chemical Society (ACS). In return, researchers shared their ideas on topics that included ways to take toxic chemicals out of the ceramics production line, push up the catalytic activity of enzyme-plastic hybrids in organic solvents, and drive up student interest in chemistry.

Cleaning Up Ceramics

Nothing looks cleaner than a smooth, white ceramic, but they can be messy in the making. Aluminum-oxide ceramics, found in everything from lightweight ceramic engine parts to bathroom sinks and even lasers, start out as an inoffensive powder of aluminum oxide particles. But knitting the precursors together into ceramics with particular forms commonly requires hazardous organic compounds and strong acids. Millions of liters of these solvents and acids must then be safely disposed of every year, and ceramics researchers have longed for a way to clean up their act.

In New Orleans, they got one. Andrew R. Barron, an inorganic chemist at Rice University in Houston, and his colleagues C. Jeff Harlan and Rhonda L. Callender reported that by breaking down the aluminum-oxide particles, they produced even smaller subunits that easily dissolve in nontoxic, nonhazardous water. "It's hot stuff," says Richard Wells, a professor of chemistry at Duke University in Durham, North Carolina. The material can be put back together as either bulk ceramics like those used for engine parts, or thin films that form protective coatings for carbon fibers and other materials used in high-strength composites. Georgia Tech chemist William Rees, however, does add a note of caution. "I think it has a lot of potential," he says. "But I don't see it changing the way toilet bowls are made this year," as the process still must prove that it can match the high-quality ceramics currently made by industry without driving up costs.



Just add water. Boehmite, a ceramic precursor, is broken down by carboxylic acid *(purple)* into small fragments that dissolve in water, eliminating toxic solvents. Then compounds called acacs swap aluminum atoms in these fragments for other metal atoms (M), forming a variety of ceramics.

Typically, companies have made bulk ceramics by dissolving a powder of aluminum oxide in organic solvents and then adding organic binders to give the material some body. Next they pour their slurry into a mold, evaporate much of the solvent, allow the material to set, then fire the ceramic at temperatures around 1000 degrees Celsius. To make more complex ceramics, ceramic-makers simply mix in other metal oxides such as yttrium-oxide with the aluminum-oxide powder. Turning ceramic mixtures into coatings and films requires a different technique, called sol-gel processing, which relies on caustic acids and other compounds that are expensive.

Researchers searching for environmentally friendly alternatives have been stymied because other techniques for doing away with solvents required prohibitively expensive compounds. Water, Barron's group knew, is cheap and safe, but the aluminum-oxide particles don't dissolve in it. They're too big and heavy. So the researchers decided to break them down.

They started with a cheap aluminum-oxide powder known as boehmite. Each boehmite crystal is made up of sheets of aluminum atoms surrounded by oxygens, which are stitched together with an array of weak hydrogen bonds. The researchers added a mild, noncaustic acid, such as carboxylic acid, which essentially unzips the hydrogen bonds between aluminum-oxide layers and breaks some of the sheets into tiny rodlike fragments known as alumoxanes. Each of these fragments is surrounded by carboxylic acid groups which—advantageously—have long, oxygen-rich tails that readily bind to water molecules. As a result, the alumoxanes readily dissolve in water.

The solution itself isn't concentrated enough to be turned into a bulk ceramic. So the researchers add additional boehmite powder; because there aren't enough carboxylic acids to go around, most of these newly introduced particles remain intact but in solution. The result is a claylike substance that can be molded and fired.

Barron and his colleagues also showed they can make a wide variety of ceramics by adding in other organic compounds known as acetylacetenoates (acacs), which can hold metal atoms such as yttrium, manganese, or erbium. In the mix, the metal atoms on the acacs trade places with aluminum atoms in the alumoxanes. Researchers don't completely understand the reasons for the trade, but they're quite willing to take advantage of it to incorporate other metals into the ceramic. "It's so simple, my grandmother could do it," says Barron.

The Rice team recently formed a collaboration with TDA, a ceramics development company in Wheat Ridge, Colorado, to test the cost of industrial-scale alumoxane production. The group is also pursuing scientific questions, such as exactly how the metal exchange reaction works. In the end, they hope to have a clean resolution to a messy problem.

Plastic Enzymes

Enzymes are the movers and shakers of the biochemical world, and plastics have become bulwarks of the material one. Researchers would like to bring these two stalwarts together, combining plastics with enzymes that could, say, keep the inside of a plastic fuel hose clean by breaking down deposits of organic compounds. But such unions have been hindered, because most enzymes are at home only in water. The organic solvents needed to make polymers typically can't dissolve enzymes—and even if the enzymes did dissolve, they would lose their normal activity. In New Orleans, however, self-cleaning pipes moved closer to reality.

At the meeting, Jonathan Dordick and his colleagues at the University of Iowa, Iowa City, along with Doug Clark at the University of California, Berkeley, showed that by linking enzymes to molecules called surfactants, they could dissolve the enzymes in solvents and incorporate them in a variety of plastics, from polystyrene to polymethylmethacrylate, the tough plastic in Plexiglas. Alan Russell, a chemist at the University of Pittsburgh, says "The idea is very powerful, because you're not limited by the polymer you can make." And it's even more powerful, says Russell, because once linked to the surfactants, their enzymes retain their activity in organic solvents, broadening the range of settings in which the enzyme-laden polymers could be used. Other such hybrids have been formed before, he points out. But these typically show strong enzymatic activity only in water.

When Dordick and his colleagues began this work several years ago, they weren't thinking about enzymes and plastics at all. Instead, says Dordick, "we were working on how to dissolve proteins into organic solvents" in order to study their behavior and perhaps understand why solvents curtail enzymatic activity, says Dordick. Two years ago, the researchers got the proteins into solution by linking them to two-part surfactants. One part, the head group, has a negative charge that binds to positively charged lysine groups on proteins. The other part, a hydrocarbon tail, flees from water and prefers to associate with similar hydrocarbons in organic solvents. When the tail rises into the solvent, it pulls the bound protein along for the ride.

Not only did the enzymes dissolve; they also retained their activity. Enzymes contain numerous chemical groups with positive and negative charges, which would cause neighboring proteins to bind together, altering their conformation and hampering their activity, if these charges weren't blocked, or "passivated." Water is well suited to doing so, because it is highly polar, meaning that water molecules have negatively and positively charged sides. But hydrocarbons in organic solvents can't fulfill this role because they are not polar. Dordick suggests that the surfactant molecules can fill in for the water by binding to the positively charged groups on the proteins. "The protein is therefore able to resist being forced into an incorrect conformation, and thus the activity of the enzyme tends to be higher," he says. While this explanation is still speculative, Russell says it's reasonable.

Last year Dordick realized that the technique could be adapted to embed enzymes in plastics. The idea was to add plastic building blocks—which are also hydrocarbons—to the solvent. In the presence of a pair of common polymerizing compounds, the building blocks, known as monomers, would then come together and form long polymer chains which then entangle themselves in a complex network. Dordick thought that creating this network in the enzyme-doped solvent would trap the enzymes, which are too large to escape through the tiny pores in the network. Using that strategy, researchers embedded a well-characterized enzyme known as chymotrypsin, which breaks down other proteins, in polymethylmethacrylate. They showed that even when trapped within a plastic, 75% to 80% of the enzymes remain active.

Alternately, the researchers have found that they can bind proteins directly into the polymer strands. They chemically bind polymerizable compounds, such as acrylate groups, to the enzyme before adding the surfactants. Once the proteins and surfactants form ion pairs, the whole web can be pulled together into a polymer network when the acrylate groups link up.

Because the polymerization techniques used by the Iowa researchers form plastics without high temperatures, there is no danger of denaturing the proteins. To shape their plastics into films, the researchers simply carry out their polymerization reactions between a pair of glass sheets and then peel the plastic off.

Dordick thinks such films, equipped with enzymes known as peroxidases, could be used to line fuel pipes, making them able to clean themselves by breaking down organic compounds such as tars. Another possibility, he adds, is to create catalytic membranes that can carry out reactions that are critical in drug synthesis. But before these hybrids go to work in industry, the researchers must still show that the enzymes remain active and stable in the polymer matrix for long periods of time. If they can accomplish that, enzyme-plastic hybrids may trigger a bit of a reaction of their own.

Driving Up Interest In Chemistry

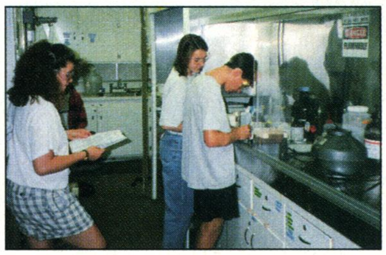
Consider it a chemist's bookmobile. Instead of carrying shelves of books, however, the 18-meter-long tractor trailer driving the country roads of upstate New York is stocked with mass spectrometers, gas chromatographs, and other high-tech analytical chemistry equipment. It's a mobile chemistry lab, known as the Sidney Science Express, and it's providing rural high school students with training that most students don't receive until they're near the end of college.

The lab is the brain child of Sidney (New York) High School chemistry teacher David Pysnik, who was honored in New Orleans with the ACS annual high school teachers award for taking his chemistry show on the road. Programs like Pysnik's "really increase the enthusiasm by the students for science quite a bit," says Don Jones, a program officer at the National Science Foundation in Arlington, Virginia, who oversees funding for similar mobile labs. About 20 such labs are currently driving up interest in science around the country, nearly all of which are operated by universities.

Pysnik says he got the idea for the mobile lab a few years ago, when a colleague told him the pharmaceutical company Ciba-Geigy had recently finished using a mobile lab on a promotional tour for a new product. After a string of pitches from Pysnik, Ciba-Geigy offered to sell their lab for $1. Pysnik then rounded up other contributions: Perkin-Elmer, the scientific equipment manufacturer, donated $70,000 worth of analytical equipment, and the New York City–based Dreyfus Foundation chipped in an extra $20,000 to pay for the development of lab courses and manuals.

The lab, which is in its second year on the road, travels to high schools within an 80-kilometer radius of its home at Pysnik's school and remains at each school for one month. Each summer, Pysnik parks the lab in nearby Ithaca, and he and his students run through the workings of the instruments with teachers and students from schools that the lab is scheduled to visit over the next year. Later, when the lab makes its rounds, these teachers and students take a quick refresher course and then become the instructors, in turn putting other students through the paces of measuring everything from trace contaminants in water samples to the amount of caffeine in different soft drinks. Thus far, says Pysnik, hundreds of kids have participated in the project.

PHOTOS BY D. PYSNIK



Road show. High school students in rural New York state learn chemistry in a mobile lab *(above)*.

"It's been a great opportunity to see a new side of chemistry," says Ann Margrave, a Sidney High School senior and mobile lab instructor, who adds that she's particularly enjoyed the chance to teach analytical chemistry techniques to other high school teachers. "You're used to having teachers telling you what to do," she says. But the teachers who participated in the mobile chemistry project "were very willing to learn." So are students: Over 80% of those who help Pysnik in the program have gone on either to study science in college or work in a science-related field.

–Robert F. Service