Tinkering with Glass and Ceramic Structures

Advances in the venerable technique of sol-gel processing are producing new materials with previously unobtainable properties

THE WIZARDS OF MATERIALS SCIENCE have come up with many surprises lately. Take the advances they have been making in sol-gel technology, a time-honored way of producing glasses and ceramics. For more than 100 years, the materials made by this technology have found a wide variety of applications. They have been used, for example, for making insulating seals for electronic and aerospace equipment and as antireflection coatings for the windows of the Bauhaus-style "glass box" office buildings that dominate city skylines.

But the potential of the old technology is far from exhausted. Material scientists have recently used it to produce brand-new glasses and ceramics that cannot be made otherwise. These range from the aryl-gels, a type of glass that can be made so porous that 1 gram can have as much surface area as three tennis courts, to "nanocomposites," whose extremely small dimensions give them new properties, such as increased hardness, not seen in the more usual formulations.

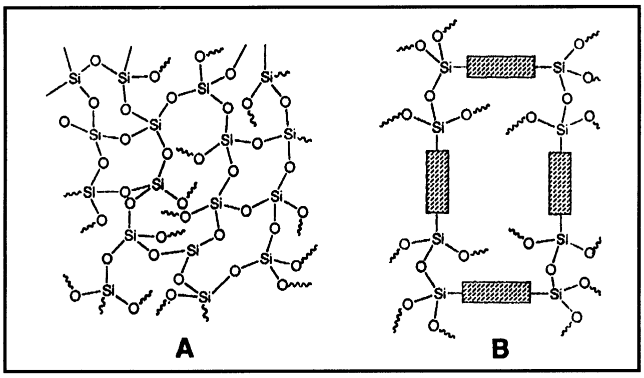
And this isn't just alchemy for its own sake. The new materials may help solve our toxic waste problems, prove invaluable to the petrochemical industry, and provide ultrapure, high strength advanced materials for the aerospace industry.

The aryl-gels are among the most advanced of these new materials. They are being developed in the laboratories of materials scientist Owen Webster of the Du Pont Company in Wilmington, Delaware, and his cross-country collaborators, chemists Kenneth Shea and Douglas Loy at the University of California, Irvine.

Regular glass is made of plain silica, with the silicon and oxygen atoms irregularly arranged to produce an amorphous solid. But the Irvine and Du Pont workers came up with the idea of introducing organic spacers, particularly aromatic rings (aryl groups) such as phenylene, at regular intervals between the silicate molecules. Loy compares the resulting aryl-gels to molecular Tinkertoys, "because a variety of aryl spacers of different lengths can be used to build new materials."

Shea, Loy, and Webster begin by joining organic silicate compounds called silanes to a desired aryl group by means of a Grignard reaction, a standard condensation reaction of organic chemistry. This produces a monomer, the simple building block that will next be polymerized to make the gels themselves. When one of the monomer materials is dissolved in the solvent ethanol and treated with aqueous acid or base, it polymerizes, Loy explains. Within a few hours, the solution gels, giving it a consistency similar to that of the familiar dessert, Jello. "At this stage, the aryl-gels behave more like glass, even ringing when lightly tapped," Loy says. After aging for 48 hours, the aryl-gels are dried under a vacuum to remove the solvent, leaving behind a porous network that resembles lightweight, brittle glass.

And the aryl spacers—the rods of the Tinkertoy—make the glasses very porous indeed. Just one gram of an aryl-gel can have a total surface area of 9000 square feet—more than that of three tennis courts. Moreover, the researchers have a degree of control over the pore size, which depends partly on the spacers used. Longer spacers tend to create larger pores in the aryl-gels and short spacers smaller pores, allowing pore diameters to be tailored to a specified molecular size, although the drying time also influences pore size. If aryl-gels are dried quickly, the pores shrink, causing the gels to lose as much as 70 to 90% of their volume.



Kenneth Shea and Douglas Loy

Molecular Tinkertoy. *Aryl-gels (B) have organic spacers (bars) that make them much more porous than ordinary glass (B).*

Rapid drying can also cause the gels to fragment. This may sound disastrous, but it isn't. Fragment the gels and you have a powder, perfect for some applications, for use as starting materials for making other ceramics, for example. And then there's chromatography.

The beauty of these Tinkertoys is that their high porosity makes them extremely well suited for use as "molecular sieves," chromatographic adsorbents that separate mixtures of molecules by size. And the ability to control the pore size means that they can be custom-designed according to the specifications that a researcher wants. For this application, the gels have to be ground to a powder anyway.

In addition to their high molecular surface area and microporosity, the new materials have yet another advantage as chromatographic adsorbents: they are stable at temperatures of up to 500°C. That property has caught the eye of the oil industry, as none of the chromatographic adsorbents it currently uses can withstand temperatures that high. "We've had several calls from the oil industry asking about their potential uses in gas purification," Loy says.

And the aryl-gels, thanks to their organic spacers, can fluoresce—absorb light at 1 wavelength and emit it at another. This may make them ideal for another application, as laser dyes. Current lasers cannot emit light at all desired wavelengths. Although this problem can be solved by incorporating appropriate liquid dyes into the laser setup, aryl-gels may have several advantages over liquids. The gels are easier to transport and store and may also last longer than liquids. In addition, they should simplify laser design by eliminating the pumps needed to circulate liquid dyes.

So why aren't aryl-gels sweeping the marketplace? Their major limitation is their production cost, which currently runs several times higher than the cost of making traditional glasses and ceramics. The latter are often produced from cheap and readily available starting materials, such as sand, whereas the starting materials for the aryl-gels have to be made synthetically. The Irvine and Du Pont team is confident, however, that it can develop economical ways of producing the large quantities of aryl-gels needed for industrial application.

Meanwhile, researchers at other labs are making their own advances in sol-gel technology. For example, chemist Jeff Brinker and his colleagues at Sandia National Laboratory in Albuquerque, New Mexico, have developed a way to use sol-gel technology to make thin films at room temperature. The method is applicable, Brinker says, "to anything that you can make glass with." That includes the aryl-gels, although the Sandia team hasn't used them so far, as well as commonplace starting materials such as silica and alumina. The advantage of the thin films is that they don't shrink and crack the way the gels are likely to do when made in bulk.

To make a thin film, Brinker first dissolves an inorganic polymer in a solvent and concentrates the solution. Then the item to be coated, which can be made of plastic, glass, metal, ceramic, or other material, is dipped into the solution and slowly withdrawn at a constant rate. Maintaining the constant rate is important because otherwise the film will be uneven. Typical coatings at Sandia have been between 100 and 500 nanometers thick and up to 10 feet long, but, Brinker says, "They can be scaled to any length you want."

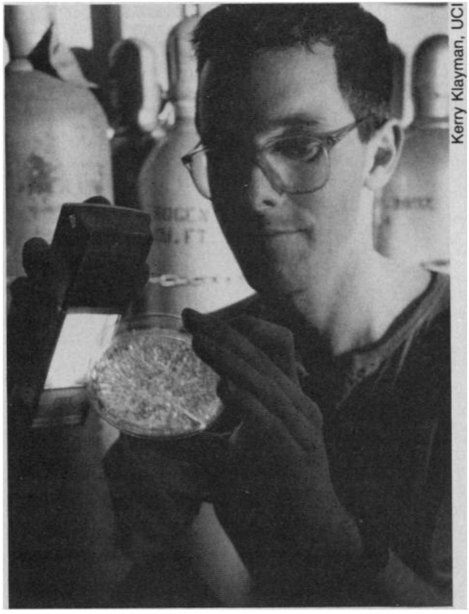
One of the main benefits of making thin films by Sandia's sol-gel method is that the films can be layered, one on top of another. "At the molecular level, the thin films resemble tumbleweeds," Brinker explains. "They each have highly porous interiors but cannot penetrate each other. They pile up rather like tumbleweeds pile up against a fence." The total thickness of all the layers can be no greater than about 500 nanometers, however, because around that point the materials begin to crack.

The most obvious application for such thin films would be as protective coatings for microelectrical components and for metals subject to corrosion. But it is possible that their most valuable application will not be as a coating but in making chemical sensors and membranes for separating molecules of different sizes.

Layered films can be constructed so that the outer layer has very tiny pores that allow some molecules to enter the film while keeping larger molecules out. The pores of the inner layer can be much larger, big enough to incorporate ion exchange sites for holding on to any molecules that have entered the porous maze or for housing chemical reactants that could serve as detectors for the trapped molecules.

Such layered films might be used both to monitor and clean up the toxic pollutants in waste streams from chemical processes. The Sandia group has so far focused on membranes that can trap and analyze inorganic chemicals, such as the heavy metals in electroplating effluents, but it should ultimately be possible, Brinker says, to construct layered membranes that can sense virtually anything.

Rustum Roy, at Pennsylvania State University in University Park, is spearheading research into perhaps the most exotic phase of sol-gel technology: the making of the ultrathin films he calls nanocomposites. These nanocomposites vary in thickness from 1 to 100 nanometers, just thinner than the thinnest gels at Sandia. At nanometer dimensions, matter begins to take on new properties (also see *Science*, 5 January, p. 26). Metals may be harder than normal, for example, or ceramics more ductile.


Kerry Klayman, UCI

Fluorescent glass. *Chemist Douglas Loy examines one of his group's aryl-gels, which is glowing under fluorescent light.*

But thinness is not even the major distinction between Roy's films and those of other investigators. The Penn State researcher's advance is to combine two different compounds to produce heterogeneous materials, a breakthrough in sol-gel processing.

To make the heterogeneous composites, a noncrystalline clay mineral, such as thorium silicate, is ground to an exceedingly fine powder and hydrolyzed to form a gel. The gel is then seeded with very tiny crystals of a crystalline material, such as the mineral huttonite. As a result, the entire gel takes on a crystalline structure, in this case that of huttonite, as opposed to the amorphous structure it would have otherwise had.

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As a result, Roy says, ceramics, polymers, metals, and semiconductors can be mixed in any combination, thereby yielding a vast array of potential new materials. Moreover, nanocomposites can be processed at much lower temperatures than more conventional mixtures of the same bulk composition, and therefore can be produced at a lower cost.

Other benefits of nanocomposites include their strength, which increases fivefold as sizes decrease from 100 to 20 nanometers. "Some scientists have even reported nanocomposites that are harder than diamonds. They are made of crystalline diamonds in a semicrystalline diamond mixture, but the scientific community is still skeptical," Roy says.

The optical properties of nanocomposites may also change. For example, when chemists at the N.E.C. Corporation's Materials Development Center in Tokyo embedded a luminescent material in a nanocomposite, its light output was ten times brighter than normal. Already, Roy says, about 50 companies have applied for patents based upon nanocomposite technology in ceramic processing.

Additional nanocomposites are being investigated by Ilhan A. Aksay of the University of Washington in Seattle. He has produced a new form of mullite, a rare aluminum silicate. Mullite is extremely heat-resistant, retaining its chemical identity and physical shape when subjected to high temperatures. That makes it useful as engine components and for other high-temperature industrial applications, but also makes it difficult to process. Production of ordinary mullite requires temperatures as high as 1650°C, and the resulting material is not homogeneous, as it contains pockets of amorphous silica.

But Aksay's sol-gel method, which uses a controlled hydrolysis of tetraethoxysilane around particles of aluminum hydroxide to guide the mullite formation, deforms the silica portion of this mixture at 1250°C, causing it to become dense quickly and then to crystallize into a homogeneous, transparent material. That opens up a potential new application for the ceramic as lenses that are transparent to infrared light with wavelengths between 3 and 5 micrometers, a range for which good lenses had not previously been available.

The new advances in sol-gel processing are producing a wealth of novel materials with previously inaccessible applications. The technology should be good for another 100 years. ■ GAIL FINLAYSON-DUTTON

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