Self-healing concrete repairs cracks, maintains strength

The white lines on this specimen of bendable concrete show where the material has healed itself by forming $CaCO_3$. This specimen has undergone deliberately introduced damage and succeeding self healing numerous times, illustrating the resiliency necessary for field structures that may undergo multiple overloads during their lifetime. Photo by Nicole Casal Moore, University of Michigan News Service.

Researchers at the University of Michigan (U-M) (Ann Arbor) have developed a fiber-reinforced cementitious composite that can automatically heal itself when it cracks and still be able to maintain its load strength. The researchers note that this new composite could make infrastructure safer and more durable, and by mitigating the corrosion process, reduce the cost and environmental impacts of building new structures. The new concrete material requires only water and air for self repair, and researchers say a handful of rainy days would be enough to mend a damaged bridge made of this new substance.

In addition to negatively affecting the mechanical performance and durability of concrete structures, cracking also reduces a structure's load capacity and stiffness. Concrete structures are usually reinforced with steel bars to keep cracks as small as possible, the researchers say, but these cracks are too large for self healing, and water and deicing salts are able to migrate through the cracked concrete and corrode the reinforcing bars. This causes the concrete to spall and further weaken the structure. The self-healing concrete composite developed by the U-M researchers is able to bend, and any cracks caused by strain are extremely narrow.

According to the material's inventors, Victor Li, the E. Benjamin Wylie Collegiate Professor of Civil Engineering and a professor of materials science and engineering at U-M, and En-Hua Yang,[1] the self-healing mechanism in concrete is caused by the formation of calcium carbonate ($CaCO_3$), a strong compound found naturally in seashells, resulting from the reaction between unhydrated cement and carbon dioxide (CO_2) dissolved in water. Concrete is unique in that it inherently contains micro-reservoirs of widely dispersed unhydrated cement particles that are available for self healing. In most concrete, and particularly in those with a low water/cement ratio, the amount of unhydrated cement particles is expected to be as much as 25% or higher. When concrete cracks, the unhydrated cement particles are exposed to the water and CO_2 present in the environment and combine with them to form a thin white healing scar of $CaCO_3$. Li explains there have been observations of the autogenous repair of cracks in old concrete structures that resulted in a gradual reduction of the crack's permeability over time and a decrease in the rate of water flow.

"The difference between what is created in the laboratory and regular concrete is the degree of robustness in self healing; we want to make sure that this type of self healing takes place all the time, every time," says Li. Controlled self healing is possible because the new fiber-reinforced cementitious composite, an improvement on an earlier generation of the bendable, engineered cement composite (ECC) that U-M scientists have been developing for the last 15 years, is engineered to bend and crack in narrow hairline fissures rather than break and split in wide gaps like traditional concrete.

"We've created a material with such tiny crack widths that it takes care of the healing by itself. Even if you overload it, the cracks stay small," Li explains. In the research lab, self-healed composite specimens recovered most if not all of their original strength after researchers subjected them to a tensile strain of 3%, which means stretching the specimens to 3% beyond their initial size. It's the equivalent of stretching a 100-ft (30-m) piece of composite an extra 3 ft (0.9 m)—enough strain to severely deform metal or catastrophically fracture traditional concrete. The average crack width in the researchers' self-healing composite is below 60 μm, about half the width of a human hair. For most practical service conditions the material strains are substantially less than 1% and microcracks, which can be as small as 10 to 20 μm, will heal effectively, Li says.

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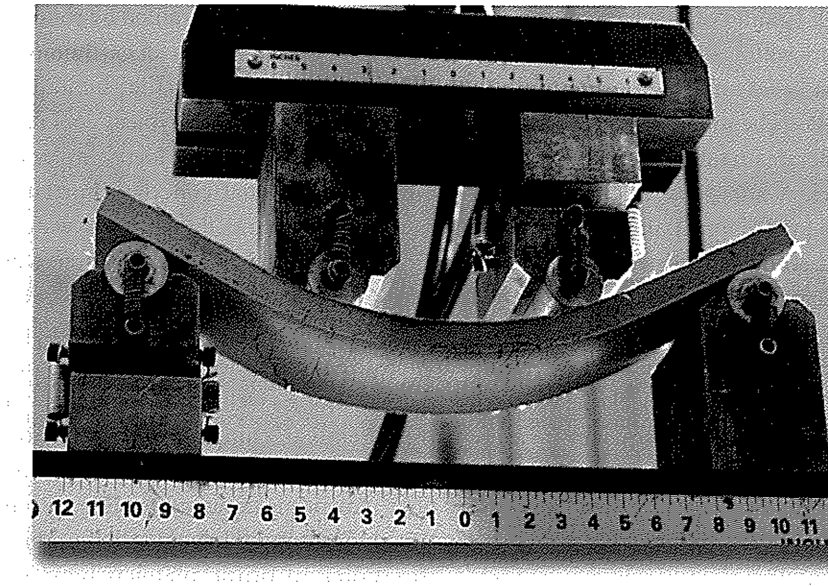

The self-healing composite works because it can bend. When it's strained, many microcracks form instead of one large crack that would cause it to fail. Here, a specimen is bending as a force causing 5% tensile strain is being applied. Traditional concrete would fail at 0.01% tensile strain. Photo by Nicole Casal Moore, University of Michigan News Service.

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"Self healing of crack damage recovered any stiffness lost when the material was damaged and returned it to its pristine state. The material can be damaged and still remain safe to load," Li says. The researchers found that when the composite was loaded again after healing, it exhibited stiffness and strength similar to undamaged composite. To test samples of the self-healed composite, which required between one and five cycles of wetting and drying to heal, the researchers utilized resonant frequency measurements, using sound waves, to determine the material's integrity before and after inducing crack damage, and after self healing.

According to Li, traditional concrete is brittle and rigid like a ceramic, typically fracturing when subjected to a tensile strain of 0.01%, and can suffer catastrophic failure when strained by routine overuse or events such as an earthquake. In comparison, the ductile, bendable ECC looks exactly like typical concrete and is comprised of ingredients similar to those in traditional concrete (Portland cement, water, sand, fly ash, and a water-reducing agent); but ECC concrete will bend under excessive strain because of a network of specially coated reinforcing microscale fibers distributed throughout the material, as well as careful control of the chemical composition, size, and amount of the various ingredients. The fiber network is designed to slide within the composite with behavior that mimics the sliding of brittle platelets between organic materials in nacre. The fibers, which comprise about 2% of the mixture's volume, are tailored to work with the mortar matrix to suppress fractures and, for optimal self healing, distribute strain and tension damage to the composite through highly controlled crack widths engineered to be <150 µm and preferably below 50 µm. Compared to traditional concrete, it is 40% lighter in weight, and more flexible—500 times more resistant to cracking—at tensile strains up to 5%.

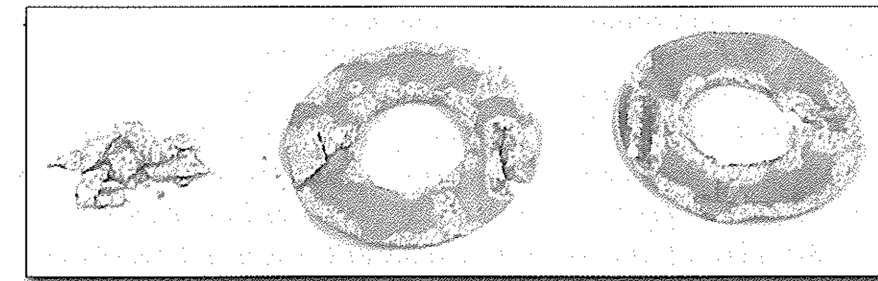
The University of Michigan holds four patents, with three pending, on ECC technologies and is seeking commercialization partners to help bring the technology to market.

Contact Victor Li, University of Michigan—e-mail: vcli@umich.edu.

Reference

1 Victor C. Li and En-Hua Yang, "Engineered Self Healing Cementitious Composites," U.S. Patent Application 20080261027, 2008. MP

Corrosion-resistant coatings incorporate metal oxide nanoparticles



An uncoated aluminum fin (left), aluminum fin coated with low cerium oxide (CeO_2) content (center), and aluminum fin coated with high CeO_2 content (right) after exposure in a wet/dry cycle fatigue test in brine. Image courtesy of Toshifumi Sugama.

Scientists with the U.S. Department of Energy's (DOE) Brookhaven National Laboratory (Upton, New York) have developed and patented a coating for metal surfaces—an ultrathin film containing rare-earth metal nanoparticles—that renders metal substrates corrosion resistant. According to the researchers, the coating is also highly economical and efficient because the method deposits such a thin coating of material on a substrate. The mechanism of the new coating mitigates the corrosion process in much the same way as a chromium-based coating.

Traditionally, hexavalent chromium compounds, a toxic form of chromium, provided the best corrosion resistance for metals for a wide range of applications. However, scientists looking to develop chromium-free alternatives had been unable to achieve the thin layers desirable for many applications, says chemist Toshifumi Sugama, a guest researcher at Brookhaven Lab. "Ultrathin coatings reduce the amount of material needed to provide corrosion resistance, thereby reducing the cost."

The scientists' new ultrathin coating achieves several goals—low toxicity and corrosion resistance in a film measuring <10-nm thick that can be applied to a wide array of metals, including aluminum, steel, nickel, zinc, copper, bronze, and brass. According to Sugama, the coating should be of specific interest to industries that produce coated valves, pumps, and other components, as well as the manufacturers of aluminum fins used in air-cooled condensers at geothermal power plants, where preventing brine-induced corrosion is a high priority.

The coating structure consists of two components, a siloxane-based polymeric matrix and nanoscale rare-earth metal oxides, Sugama explains. The rare-earth metals used by the scientists are commercially available cerium and samarium. To form the coating, the proper proportions of two starting reactants, organo-functional silens and rare-earth metal-linked acetate dopants, are incorporated into water to create precursor paint. The scientists' patented technology facilitates the creation of precursor paint with extreme wetting capabilities that allow it to flow into a uniform, ultrathin film when applied to the metal substrate. "This is particularly advantageous when the metal to be coated possesses fine structural detail," Sugama says, noting that the coating is able to permeate small shapes and flow into tiny crevices.

The precursor paint is applied to the substrate; and once the paint is dry, the substrate is heated to temperatures between 60 to 70 °C to trigger several chemical reactions that cross-link the two reactants to form a hydrophobic siloxane matrix containing nano-size rare-earth metal oxide particles, such as environmentally benign cerium- and samarium-based oxides.

The siloxane matrix displays good water repellency as well as superior adherence to metal substrates, Sugama says, adding that the rare-earth metal nanoparticles, which form adjacent to the metal surface in the ultrathin film, impede cathodic corrosion reactions and protect the metal from corrosion by trapping electrons and inhibiting corrosive ionic electrolyte attack. This process works much the same way as the corrosion-inhibiting mechanism of chromates, and the corrosion resistance of these coatings can be comparable or even superior to chromium-based coatings. In fact, he notes, these new coatings provide better surface coverage than chromium coatings.

The coating can be applied to small metal shapes or thin metal pieces by either a dip or spray method. In laboratory tests, Sugama says, the scientists dipped thin metal pieces into the coating, let them dry, and baked them in an oven for several hours to ensure the reaction process was complete.

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