Self-help for ailing structures

by Paula Gould

The notion of structures that mend themselves sounds more like an idea from science fiction than a topic for scientific investigation. Not so, say the researchers who are drawing inspiration from biological healing processes to create new composites with a built-in tool kit. This approach to materials maintenance is attracting considerable interest from the aerospace industry, given the potential value for self-repairing airplanes and spacecraft. But first, the self-help concept needs to be proven outside of the laboratory in tests that mimic likely wear and tear scenarios in the real world.

Image above is an optical micrograph of a self-healing polymer. Microcapsules containing a red healing agent are beginning to rupture as a crack progresses through the material. (Courtesy of Eric Brown, University of Illinois.)

It is relatively easy to illustrate the concept of a self-repairing system using familiar examples. Remember what happened when you tripped on a sidewalk as a child and grazed your knee or the last time you cut your finger. Almost at once, blood rushes to the site of the injury, leaking out where the skin has been punctured. But wait a while, and the blood oozing slowly from superficial cuts and scratches begins to clot. The clot formation slows, the bleeding stops, and, after a while, a scab forms over the damaged surface. Eventually, the scab falls off revealing a new patch of skin. Your body has healed itself, having responded instantaneously and subconsciously to the initial injury.

Talk to investigators working on any of the new self-healing materials currently under development, and you are likely to hear the same analogy drawn between the biological healing process and their own solution to self-repair. It is a handy comparison. The idea that synthetic materials could mimic the super-smart functionality of living tissue has a certain futuristic appeal. Yet, while the project goals can be described in simple terms, generating a self-healing mechanism in engineering materials is not quite so straightforward.

Scott R. White and Nancy R. Sottos from the University of Illinois at Urbana-Champaign (UIUC), together with colleagues Jeffrey S. Moore and Philippe H. Geubelle, have been working on such materials since the mid-1990s. Inspired by the human body's ability to repair minor cuts and grazes, they set out to devise a synthetic material with a similar

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in-built autonomic healing system. The new material, they hoped, would tackle signs of fatigue at an early stage, so preventing or delaying structural failure. If successful, this would rid the structural engineering community of a long-standing headache related to the sudden failure of materials subjected to repeated stresses and strains.

Materials fatigue is characterized as the propagation of multiple tiny cracks, often starting from minuscule defect sites. Repetitive loading causes the hairline cracks to grow, little by little, until eventually they join together to form a large, potentially problematic, crack. "Then you can get catastrophic failure," explains White, professor of aeronautical and astronautical engineering at UIUC. "So what we wanted to do was develop a material that could really get to the heart of the problem, which is those tiny cracks, and to do something about them."

White and Sottos quickly focused their attention on microcapsules as a means of storing and delivering an *in situ* 'glue' to stem the spread of cracks. With this method, a microencapsulated healing agent and a catalyst known to trigger polymerization in the chosen agent would be embedded in a composite matrix. Rupture of any microcapsules by an approaching crack defect would release the healing agent into the crack plane by capillary action. When the released healing agent comes in contact with the catalyst, the resulting polymerization would bond the crack face closed, stopping the defect in its tracks (Figs. 1-3).

The proposed approach has several points in its favor: technology for embedding microcapsules in polymers already

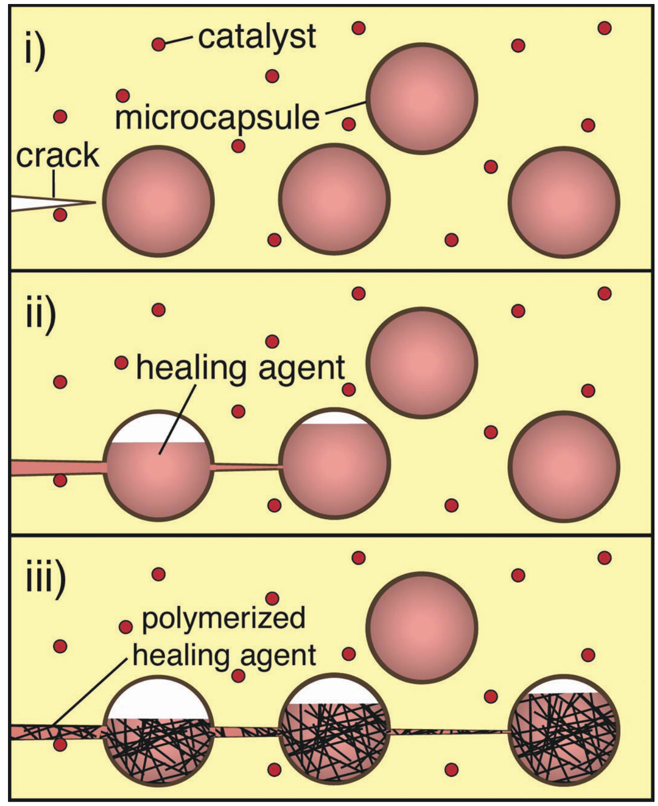

Fig. 1 The self-healing concept. A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent. (i) Cracks form in the matrix wherever damage occurs. (ii) The crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action. (iii) The healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed[1]. (© 2001 Nature Publishing Group.)

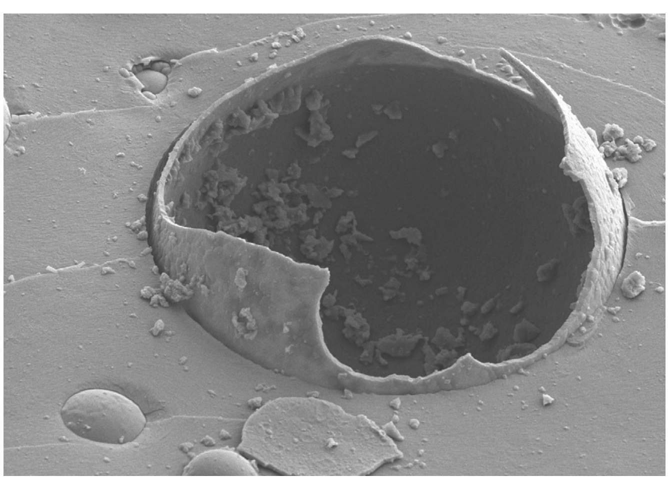

Fig. 2 A scanning electron micrograph shows the fracture plane of a self-healing epoxy with a ruptured urea-formaldehyde microcapsule in the center of the image. (Courtesy of Michael Kessler, University of Illinois.)

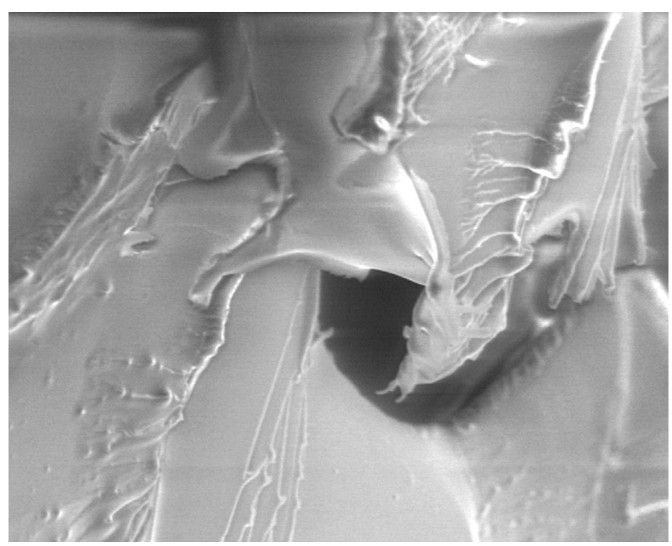

Fig. 3 A scanning electron micrograph shows the fracture plane of a self-healing epoxy and the polymerized healing agent coating the original fracture plane. A broken (emptied) microcapsule appears in the background. (Courtesy of Michael Kessler, University of Illinois.)

exists and is widely used in the paints industry; the capsules could be produced relatively easily using standard processing techniques; and the insertion of small, spherical particles into a brittle matrix is known not to weaken the material's mechanical properties. This latter point is particularly important, according to Sottos, professor of applied mechanics at UIUC. "If you're adding something to a material, then you're adding functionality, and you really don't want to degrade the inherent properties of the material you start with," she says.

Results of fracture experiments on the trial polymer have proved encouraging, yielding a 75% recovery in toughness after self-healing. Three separate control samples, containing neither catalyst particles, nor microspheres, nor additional components, were unable to halt crack propagation or repair fracture defects. As an added bonus, insertion of the hollow microcapsules increases the polymer's toughness by 120%[1].

Since completion of these initial tests, researchers at the UIUC labs have worked on refining the system. Small changes to the capsule contents and catalyst concentration, for instance, have helped improve overall efficiency. Recovery of 90% toughness in the polymer following fracture and subsequent self-healing is now common. This could well be as good as it needs to be, according to White. "We're talking about healing a fatigue crack, and we can do that with very good bonding," he says. "The next crack that opens up is probably going to be somewhere else at some other defect, so I don't think that pushing performance to 100% at individual sites is really the most important thing to be doing right now."

Ian Bond, lecturer in aerospace materials at the University of Bristol, UK, is adopting a similar strategy to autonomic repair, though with a subtle twist that brings his system even closer to healing as nature intended. While the Illinois team is storing their healing agent in spherical capsules, researchers at Bristol are using a series of hollow glass fibers to deliver their crack-stopping liquid remedy. "The fibers are acting as blood vessels in some respects," says Bond.

His approach is designed to counteract impact damage in brittle glass fiber reinforced plastics. Hollow fibers, filled either with epoxy hardener or uncured resin, are arranged in alternate layers. If a sudden impact to the composite causes at least two of the layers to rupture, the released components mix and polymerize to form a standard epoxy that shores up the damage. While this does not make the material as good as new, the spontaneous repair does at least mitigate some of the damage immediately, Bond explains. "Most of the damage when you impact a composite is invisible. It's not necessarily on the surface, but inside at the different ply layers," he says. "So what we're hoping is that we can get this resin to seep out into the cracks and start to hold the material together a bit longer."

High flyers

Both groups regard the aerospace industry as a key potential beneficiary of the technology. Indeed, the UIUC research has been part-funded by the US Air Force. Spotting and stopping fatigue and identifying possible crack formation is a crucial part of routine aircraft maintenance. Yet, this is often far easier said than done. Materials capable of performing midair first aid should unseen scratches and dents escalate in severity, is clearly an attractive prospect when you are flying at many hundreds of miles per hour, several thousand feet above the ground.

"If things break in a car, it's generally not catastrophic, and you just pull up at the side of the road. In an aircraft, if it's the wing, you really don't want any failures," says Bond. "General wear and tear can start to initiate problems by creating small sites of damage, and this won't necessarily get picked up until the next inspection period."

Ironically, a significant proportion of damage occurs during the maintenance checks themselves, he says. Dropped tools, bumps from maintenance vehicles, and shortcuts over the aircraft shell can all weaken the structure. Outside the maintenance hanger, runway debris and bad weather – such as hailstorms – may also contribute to early failure of aircraft parts. And to make matters worse, engineers may not even see any internal damage that has occurred since the last inspection. Bond's proposed self-healing system, consequently, includes an aid to visual inspection. The uncured resin is mixed with a fluorescent dye before being sealed within the hollow glass fibers. If the structure is damaged and fibers break to release the epoxy-forming ingredients, the dye will be discharged too. This internal dye leakage can then be identified by ground engineers shining a UV light over the aircraft's surface, explains Bond (Fig. 4).

What works well for aircraft may also prove valuable in space, where structural materials must withstand greater extremes of temperature, pressure, and acceleration, as well as unexpected impacts from orbiting debris. Discussion of the

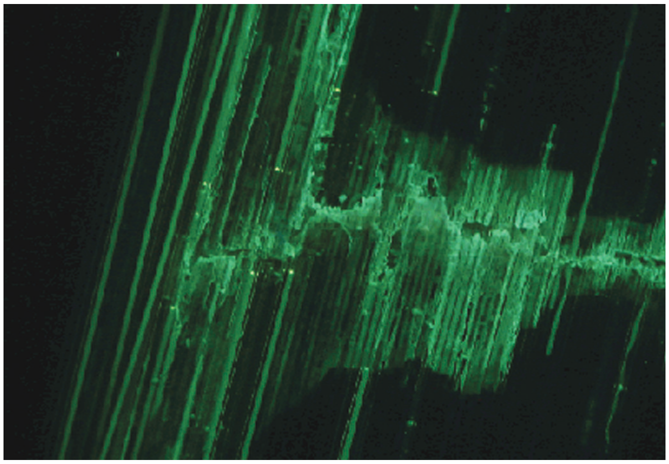

Fig. 4 Damaged hollow fiber composite material viewed under UV light shows 'bleeding' of the fluorescent dye mixed with the healing resin. (Courtesy of Ian Bond, University of Bristol, UK.)

possible benefits of autonomic repair systems to manned spacecraft has become all too topical. NASA investigators have yet to establish exactly what caused the tragic break up of the space shuttle Columbia upon reentry to the Earth's atmosphere earlier this year. However, much attention has focused on an incident during Columbia's launch, when a chunk of foam hit the shuttle's side. This may have generated a point of weakness in the external shell that eventually compromised the shuttle's structural integrity.

The extent to which a self-healing composite could stop minor damage from escalating to critical levels during the stresses and strains of space flight is clearly debatable. But it is an avenue that NASA, for one, deems worthy of further exploration. Even before Columbia had left the launch pad, NASA officials had signed-off funding for research into synthetic materials with biological self-healing functionality.

Ilhan Aksay, professor of chemical engineering at Princeton University, is leading the project under the auspices of NASA's new Institute for Biologically Inspired Materials. Formally inaugurated in September 2002, the virtual institute comprises a consortium of scientists and engineers from Princeton, Northwestern University, the University of California at Santa Barbara, and the University of North Carolina at Chapel Hill, plus researchers from NASA's labs at Langley. The team members, who can expect to receive a total of $30 million from NASA over the next ten years, will be combining their expertise to study a range of features exhibited by materials in the natural world. "Our main aim is to come up with new types of materials that will mimic the functions of biological materials," Aksay says. "They won't be based on biological systems; they will actually function like biological materials."

Simulation of the natural repair mechanisms seen in plants and animals is a key part of this overarching investigation. At Princeton, Aksay and his colleague Dudley Saville are focusing on the classic blood clot scenario, using a principle based on electrohydrodynamic (EHD) flow to replicate the same functionality in a synthetic material[2]. He describes a test system in which a suspension of colloidal particles is enclosed between the walls of a double-walled cylinder (Fig. 5). The cylindrical walls are coated with a thin conducting layer, followed by an insulating film, and are then attached to an electrical power source. This forms a double-wall electrode

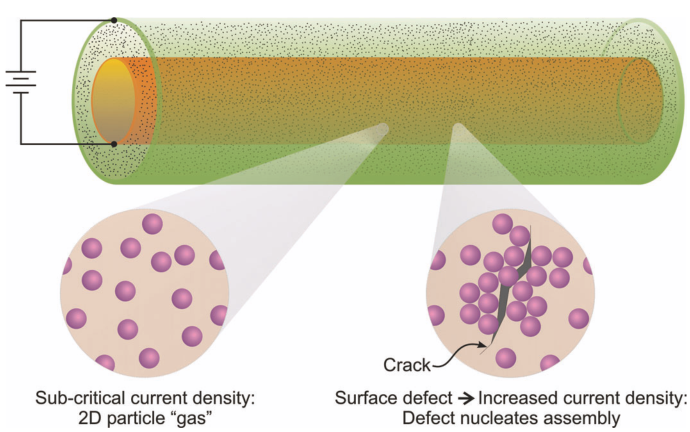

Fig. 5 Electrohydrodynamic aggregation of particles. (Courtesy of Ilhan Aksay, Princeton University.)

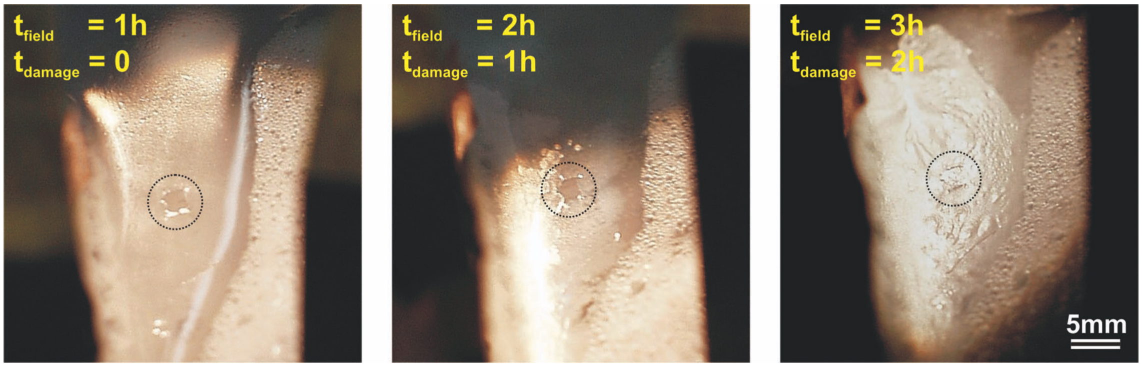

Fig. 6 Healing under an electric field. Initial damage in a film of ~2 mm^2 (at t_{field} = 1 h) under an applied field (-1.5 V, 100 mA) healed within ten minutes. After the film was damaged again (t_{field} = 2 h, 10 min), healing was apparent at the edges of the damaged region after one hour and the damaged area had 'scabbed over' after two hours under the applied field. There was no discernable healing in the control sample during the same period. (Courtesy of Ilhan Aksay, Princeton University.)

system that can be activated if the insulating film fails. If the structure is damaged in any way, leading to crack formation in the insulating film, the colloidal particles aggregate (similar to blood coagulation) at the defect site by EHD flow and trigger the first stage of self-healing, he explains (Fig. 6).

The system's dependence on a continuous electric field is analogous to biological materials, which rely on a continual sensing mechanism provided by nerve endings, Aksay says. This, he suggests, is far closer to the natural healing process than self-repair systems involving the puncture of liquid reservoirs containing a healing agent. "The way a biological system works is that you first feel pain, so you know you have scarred or damaged something," he says. "The electrical field in our system brings in that active mode, so these particles immediately go and coagulate at the site. We have already demonstrated that this can be done."

Down to Earth

Aksay acknowledges that the project is still at a very early stage. Having illustrated the principle of electrically induced coagulation in a sealed tube, the Princeton researchers must now demonstrate their system's efficacy in the walls of a specially designed cellular structure. This open design will have the additional advantage of being lightweight, another requirement of engineering materials for the aerospace industry. A parallel research project is also under way to mimic the next step in natural healing, where skin reforms beneath the scab. "We are starting with self-assembling organic matter, but this will not survive in space, so we will eventually convert it into ceramics," Aksay says.

The teams working on sealed capsule/tube models for self-repair also have a considerable way to go before commercial applications become viable. Bond estimates that it will be another two to three years before his hollow glass fiber system looks anything like a marketable product. Lab scale trials might have proved that the composite is capable of performing remedial first aid, but further experimentation is needed to develop a more sophisticated self-healing system.

White and Sottos are still working to devise evermore sophisticated tests to demonstrate that their new polymer system matches the criteria required by everyday engineering materials. "What we're moving towards now is healing damage that is more realistic to what actually happens," says Sottos. "So we're doing fatigue tests, rather than healing a giant crack that has been put in the material on purpose. We're also trying to look at new chemistries in terms of materials that can withstand higher and lower temperatures. This has a lot of relevance for space applications where temperatures cycle between very high and very low extremes."

Yet, no matter how convincing the eventual experimental results, persuading an aircraft manufacturer or defense department to adopt novel materials is going to be another matter altogether. "It's really difficult to get a new material certified," White says. "Even if you're only talking about a small variation in an aluminum alloy, it might take ten years to get all the approvals done. Here we're talking about a whole revolutionary change in the materials themselves."

Sottos notes that the smart self-repairing mechanism could also be applied to more low-tech applications, such as

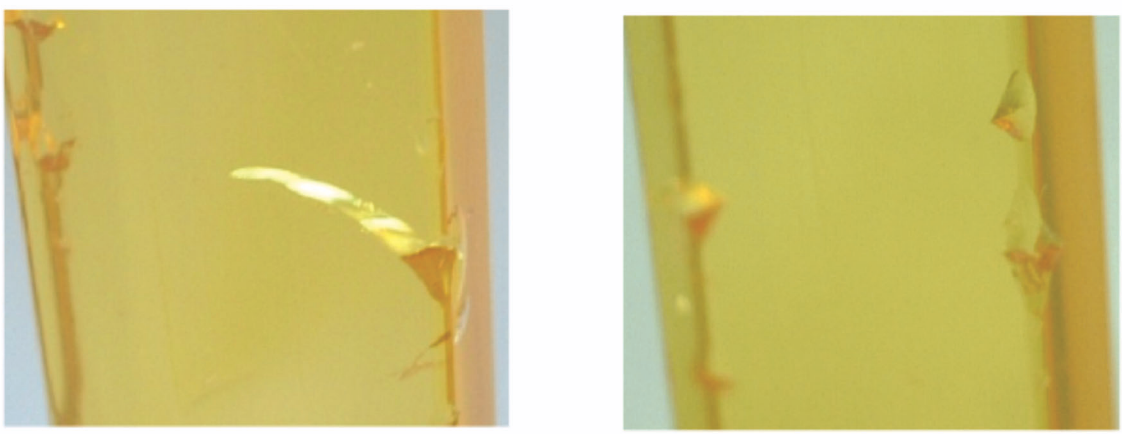

Fig. 7. Left: polymer with shiny crack. Right: crack disappears after thermal healing at 120°C. (Courtesy of Xiangxu Chen, University of California, Los Angeles. Originally published in the New York Times, 5 March 2002)

the development of improved two-part adhesives or improvements to manufacturing techniques where joints need to be re-healed. The high cost of system components, particularly the catalyst, currently prohibits this move into the low-tech market. Issues of shelf life and environmental stability will also need to be tackled if such a self-healing system is to succeed as a low cost, mass-manufactured product.

Fred Wudl, director of the Exotic Materials Institute at the University of California in Los Angeles, is skeptical about the ability of high-tech, self-repair chemistry to make it in the real world. "This sophisticated, purely autonomous mending is far too complex to become an engineering material," he says. "They are very clever approaches but, nonetheless, at this stage, they are really academic."

Eschewing all analogies with biological self-healing systems, Wudl and his team went back to the basics of polymer chemistry to create an alternative type of self-mending material. The UCLA researchers initially intended to develop a synthetic polymer with the strength of diamond, a project they are still working towards. To gain maximum strength from the polymer, they opted for a structure built up from multiple, reversible steps, to keep the material's thermodynamic energy to a minimum. Their finished product consequently contained a large number of weak covalent bonds that broke when the material cracked, but easily polymerized again on the application of heat (Fig. 7). The reformed material retains 60% of its original strength, far surpassing the 15-20% strength recovery expected from alternative polymer mending methods, such as hot plate welding[3].

Given the material's reliance on a thermal input of around 120°C to trigger mending, the 'self-healing' tag is perhaps debatable. Yet Wudl points to applications such as the glass in car headlights or heated windshields where a heat source is readily available and the polymer could self-repair on its own. Indeed, several automobile manufacturers contacted the group immediately after publication of their results last year. The researchers have subsequently improved the material, ironing out some of its less commercially attractive properties, and are working on scaling-up production to generate samples for interested parties.

"The first generation polymer that we made had a problem in that it was yellow in color, because one of the monomers was yellow," Wudl says. "In the meantime, we have made colorless monomers, so now we have made beautiful, transparent, colorless – or maybe only slightly yellow – self-repairing polymers."

But no matter how good the chemistry, how simple the idea, how effective the *in situ* repair system, the ultimate success of self-healing materials may depend on manufacturers agreeing that longevity is back in fashion. "We're talking about extending the life of products," White says. "But not every company is interested in that in a throwaway society." MT

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