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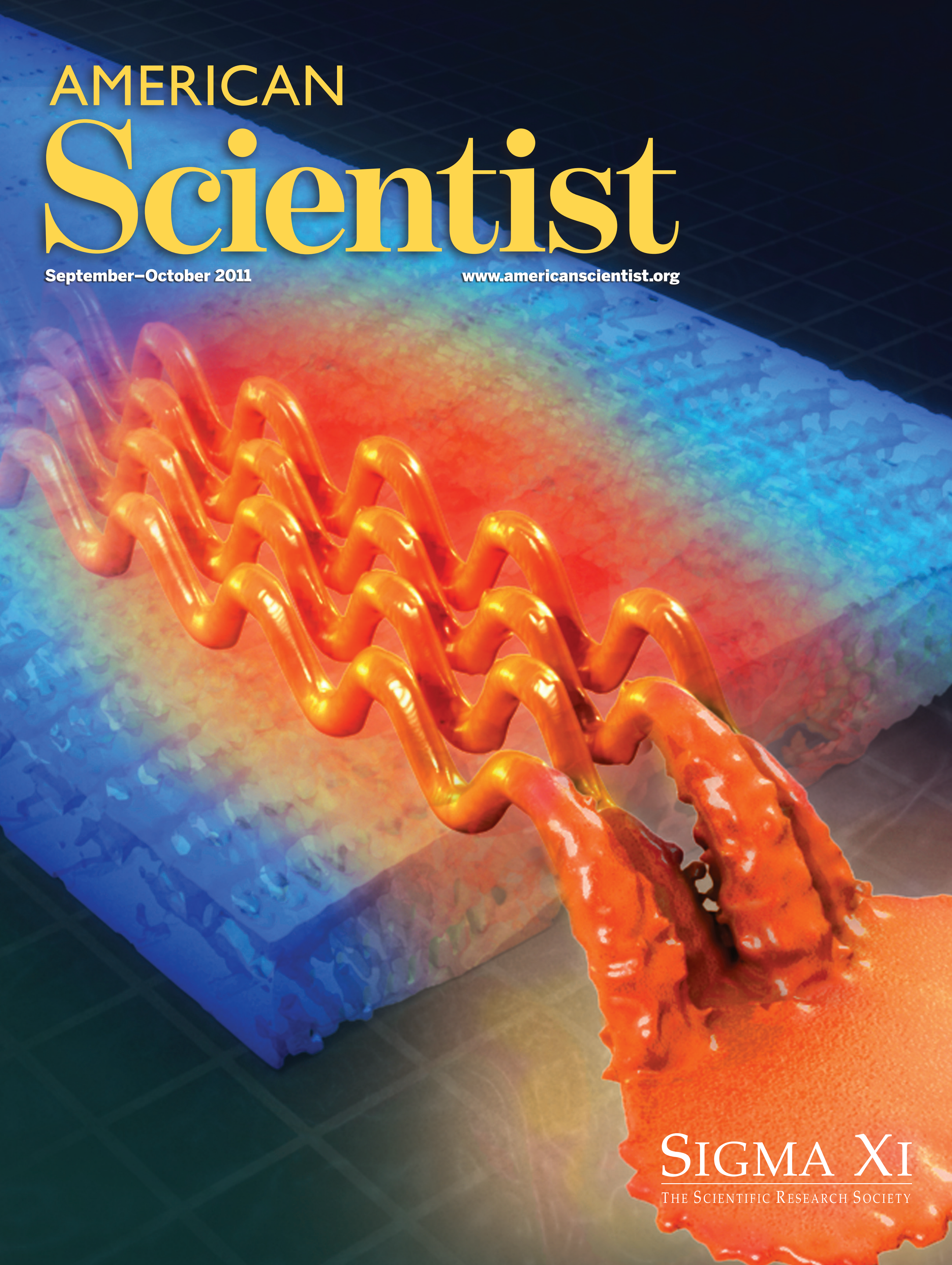

SIGMA XI
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Self-healing Polymers and Composites

Capsules, circulatory systems and chemistry allow materials to fix themselves

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Nothing lasts forever. Any human-made material, used in anything from toys to bridges, will eventually fail, if not maintained and repaired. Traditionally, this problem has been addressed through extensive inspection and expensive replacement of damaged parts. Biological systems, however, have evolved to include alternative ways to repair internal and external damage via healing mechanisms. Materials researchers worldwide, including those in our group, have been working on methods to mimic these healing abilities in polymers, composites and other synthetic materials. Such self-healing materials, when triggered by a crack or tear, can repair themselves and recover their original functionality using only the materials that are inherently available to them. They offer a new means to achieve safer and longer-lasting products and components, and signal a shift in the traditional paradigms of material design and engineering.

The guiding principles for synthetic self-healing are seen in biological systems. Damage that causes injury triggers the first response, inflammation and blood clotting. This initiating step is followed by cell proliferation at the site of injury, which deposits a matrix for the repair. The final stage of healing, *matrix remodeling,* is the regrowth of new tissue to fill in the wound. This process can take place over a longer period, months to possibly years, depending on the severity of the injury.

In synthetic systems, there is a similar cascade of events, but it is more simplistic and takes place at a faster rate. At first, damage actuates the start of the process, then new materials are transported to the site rapidly, and healing occurs as the material reacts to form an adhesive bond with the damaged area. Most often the healing agent is made of two types of liquid materials that solidify when mixed. Finally comes a chemical repair process, analogous to matrix remodeling; its timescale varies depending on the type of healing mechanism, but it occurs in the range of hours to several days at most. The goal of self-healing is to match the rate of repair with that of the damage, thereby achieving a state of stasis in the material. The rate of damage is largely controlled by external factors, such as the material's strain rate, how frequently it experiences loading and the magnitude of the loading. However, the healing rate can be adjusted by, for example, varying temperature or chemical-reaction rates through control of raw-material types and concentrations.

Research on self-healing materials is relatively new, with most of the progress coming within the last decade. Although in theory any material can self-heal, the results for polymers and fiber-reinforced composites are relatively more mature in comparison with efforts in ceramics, metals and other materials. Whatever the class of material, self-healing mechanisms can be broadly classified into three groups: *capsule-based, vascular* and *intrinsic*. Each group differs by the method used to sequester the material's healing functionality until it is triggered by damage. The groups also vary by the different amounts of damaged volume that they can heal, as well as the repeatability of healing in the same location and the rate of healing. Thus each approach has its own challenges and advantages.

Capsule-based materials incorporate a healing agent that is held and protected in discrete spherical shells, which are ruptured by damage. The self-healing mechanism is activated by the release and reaction of the healing agent at the damage site. However, after release, the healing agent is depleted, so it only works for a single local healing.

Vascular materials carry the healing agent in a network of capillaries or hollow channels, which may be single tubes, discrete planes of interconnected tubes, or three-dimensional networks of channels. When damage ruptures the vasculature and delivers the healing agent, the network can be refilled (either from an external source or from undamaged, connected channels), so it can support multiple local-healing events.

Intrinsic materials instead have a latent self-healing ability, usually built into the chemical network of the polymer material, rather than a separate, sequestered healing agent. They rely on repairs made through molecular-scale mechanisms, such as hydrogen bonding, ionic interactions or polymer-chain mobility and entanglement. Each of these mechanisms is reversible, making multiple healings possible.

Raw Materials

For capsule-based materials, there are a number of techniques for creating polymer shell walls that protect the reactive materials inside them. The most common methods involve forming a shell at the interface of droplets in an oil-in-water emulsion. In this case, the resulting shell will be thin and brittle, like that of an egg, and it will rupture when force is applied. Another procedure involves emulsifying a melted polymer so that it forms droplets, which are then solidified by a temperature change or by the removal of a solvent, creating a thick protective sphere around the core.

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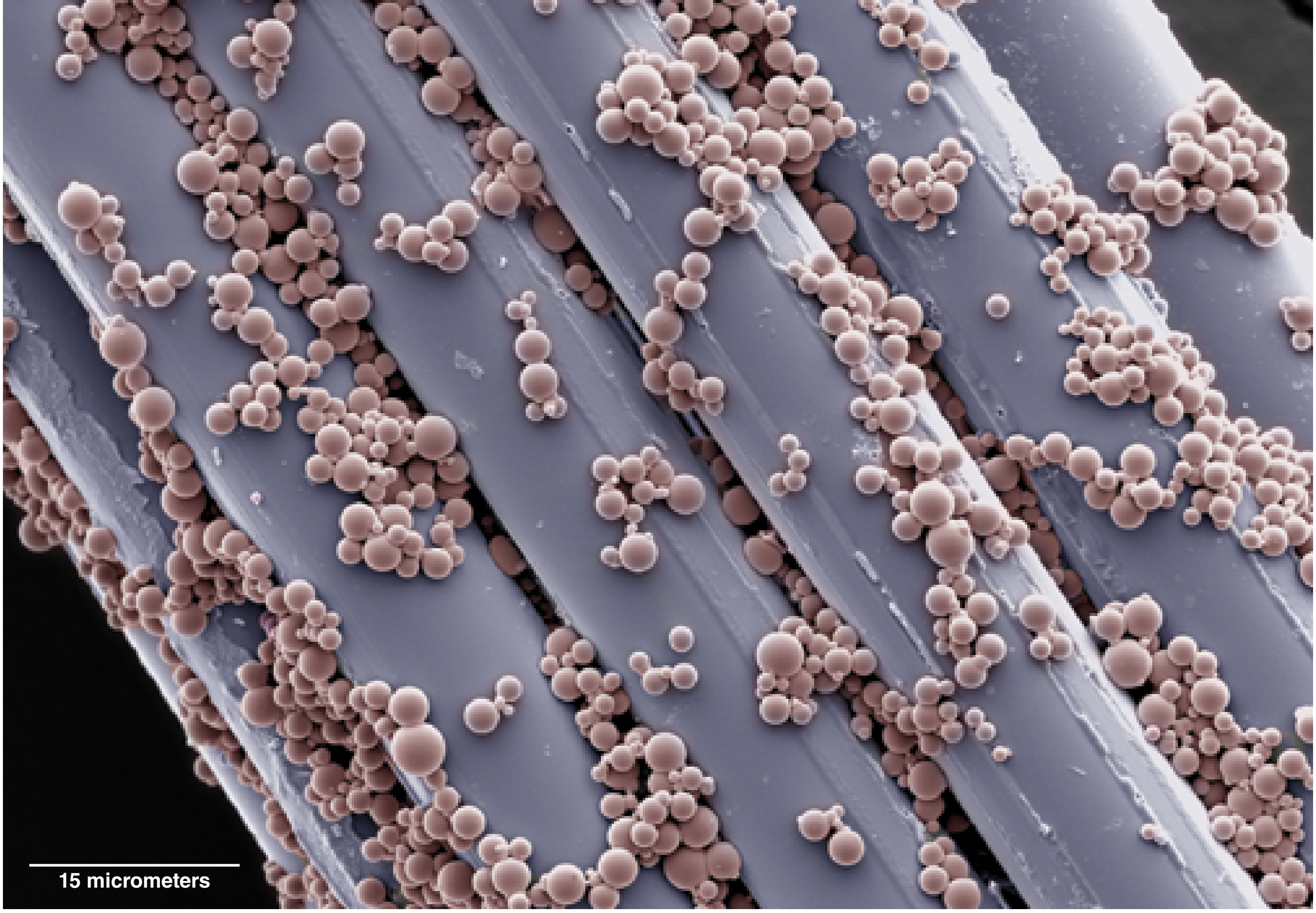


Figure 1. Fibers destined to reinforce a composite material are coated with capsules that act as a repair system. The glass fibers, about 15 micrometers wide, are smaller than the diameter of a human hair, and the capsules are about 10 times smaller. The capsules are filled with a liquid healing agent that spills out when a crack ruptures them. Such self-healing agents can also be delivered by networks of channels, or they can be built directly into the chemistry of the material. (Image reprinted from B. Blaiszik et al., *Advanced Functional Materials* 20:3547, with permission of John Wiley and Sons.)

Once the healing agent is protected inside capsules, the next step is to incorporate them into a polymer. In practice, capsules have been shown to survive shear forces, temperature changes and other processing conditions encountered during mixing with various matrices, or body materials, at multiple scales. After the capsules are integrated, the composite material can be characterized, as the capsules can affect the mechanical properties of the material, such as its strength, fracture toughness and elasticity. The effectiveness of the triggering mechanism and healing performance can be validated after the fact using a number of imaging methods, such as optical microscopy, infrared or x-ray spectroscopy, or scanning electron microscopy.

Each healing event requires at least two materials: the healing agent and a *polymerizer*, which makes it solidify. With capsules, several arrangements can be used to ensure that the materials don't come into contact until healing is needed. In all cases, the healing agent is placed in capsules, but there are different methods for incorporating the polymerizer. For instance, the catalyst simply can be distributed freely through the bulk of the main material. Several types of materials, including epoxies and fiber-reinforced composites, have been tried with this arrangement, and our group has found that the resulting materials have high healing efficiencies and have extended lifespans when subjected to fatigue loading. A variation on this method is to enclose the polymerizer in wax spheres that protect the relatively sensitive chemical from the harsh matrix environment.

Another approach is to sequester both the healing agent and the polymerizer in separate capsules. This method proves particularly useful when there are more than two materials required in order to make a repair. The capsules for the different substances don't have to be of the same type, as some components may react differently with the shell wall. Some of our work on this multicapsule method has been used for corrosion inhibition, where a separately encapsulated resin healing agent and a tin-based catalyst were incorporated into an epoxy coating. The same approach has been applied in a self-sealing laminated composite. Other research groups have developed similar strategies with different agents and polymerizers.

It is also possible to incorporate the polymerizer as a latent ability in the matrix itself, as either a residual part of the matrix polymerization reaction, or one that results from an environmental stimulus. One example we have researched is adding an excess of organic compounds called amines to an epoxy matrix, which initiate polymerization when the healing agent is delivered. Other research relies on environmental stimuli to produce a reaction, such as oxidation or evaporation. And finally, one of the agents may be phase-separated, or dispersed as small, insoluble droplets within the bulk material, providing a latent reactivity for healing.

More Dimensions

Encapsulated healing agents have great potential but come with a significant limitation: They are finite in volume and allow only one local healing event. This restriction has led researchers to develop vascular self-healing materials, drawing inspiration from the robust distributed vascular networks in biological systems. In the synthetic approach, one network of capillaries or hollow channels holds the healing

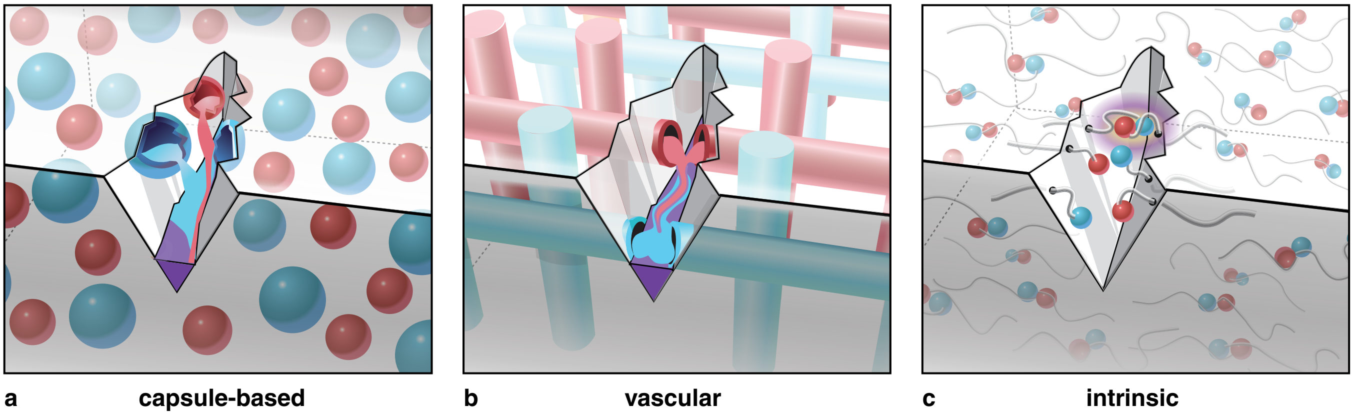


Figure 2. Self-healing systems are divided into three major categories. Capsule-based systems *(a)* sequester healing agents *(blue),* and polymerizers *(red),* in shells throughout the material. Vascular systems *(b)* use a network of refillable channels to deliver both healing agent and polymerizer. Intrinsic systems *(c)* utilize the reversible nature of certain chemical bonds to incorporate healing abilities directly into the material.

agent, while an interspersed but unconnected second network holds the polymerizer. The network's size, its wall stiffness, its bonding with the matrix, its fraction of the material's overall volume, and the channel distribution and uniformity all affect the mechanical properties of the material. Many of the design challenges are the same as for capsule systems—researchers must work out the effect on mechanical properties, efficiency of triggering, and quality of healing performance. However, the challenges of fabrication and integration with the bulk matrix material are where the two systems diverge.

Unlike capsule-based systems, vascular networks receive the healing agent after the network is in place, usually by applying a vacuum. So the choice of healing agents must account for properties such as surface wettability, viscosity and chemical reactivity. If an agent has a high viscosity or a low ability to wet (or adhere to) a surface, it may not be able to efficiently fill a network—and it might not be released or transported well to damage sites. Obviously, if it's chemically incompatible with the vasculature, the long-term stability of the system is questionable.

Perhaps the simplest technique to assemble a vascular network is to use hollow glass fibers as channels. The fibers are easily made with existing technology, they are compatible with many standard polymer materials, and the glass does not react with many popular self-healing agents, such as two-part

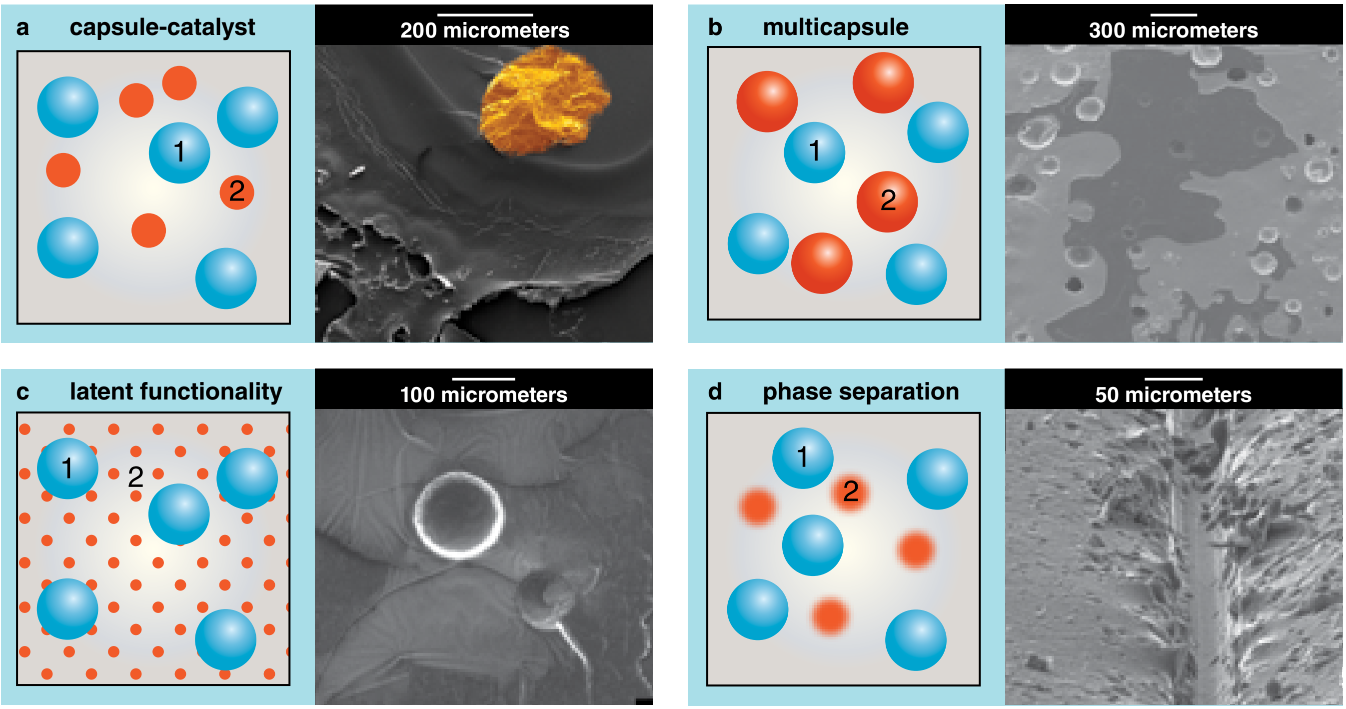


Figure 3. Capsule-based healing methods differ in the ways that they sequester the polymerizer *(2)* that reacts with the healing agent *(1).* Capsule-catalyst systems *(a)* incorporate the polymerizer directly into the material *(yellow).* Multicapsule systems *(b)* have separate capsule types for both polymerizer and healing agent. It is also possible to incorporate the polymerizer as a latent functionality in the matrix itself *(c)* to react with a released healing agent. Finally, the polymerizer can also be phase separated *(d),* dispersed as insoluble droplets within the material. (Image in *a* reprinted from E. N. Brown et al., *Experimental Mechanics* 42:372, with permission from Springer. Image in *b* reprinted from M. W. Keller et al., *Advanced Functional Materials* 17:2399, in *c* from M. M. Caruso et al., *Advanced Functional Materials* 18: 1898, and in *d* from S. H. Cho et al., *Advanced Materials* 21:645, all with permission from John Wiley and Sons.)

epoxy resins. Also, these hollow fibers can be interwoven with the glass and carbon-fiber reinforcements used in composites, as they are of similar size and shape. In the first experimental systems, channels were made of fibers a millimeter in diameter, but fibers 15 micrometers in diameter are now available. However, one big drawback to using hollow glass fibers is that they are restricted to one-dimensional connections; they cannot be made into more complex vascular networks.

Additional connectivity, in two- or three-dimensional networks of channels, gives vascular systems numerous performance advantages. Each point in these networks has multiple connections, so the system has greater reliability in case of blockages, as well as access to a larger reservoir of healing agents, which means it not only can fix larger areas of damage but also can more easily be refilled for repeated use. Two-dimensional networks are particularly useful in composite materials that are assembled essentially by stacking layers, because the 2D network can be sandwiched in at the interfaces between layers without significant impact on the mechanical strength of the final composite.

In the technique most commonly used for building 2D and 3D connected networks, *direct-ink writing*, a scaffold is first formed inside a mold, which is then filled with a polymer precursor. After the polymer solidifies, the scaffold is chemically dissolved, leaving behind a network of hollow channels in the polymer. This approach offers a great deal of control over the shape of the network, but the choice of matrix materials is limited to ones that can be formed around the scaffold.

A recent advancement by our group overcomes many of the limitations of direct-ink writing. *Sacrificial fibers* are interwoven into a composite material, then evaporate at temperatures of 200 to 240 degrees celsius. The fibers remain structural up to 180 degrees so they can be integrated with standard fibers. A 3D weaving process creates a woven preform, which is then infiltrated with a polymer matrix and heated to cure. Places where the sacrificial fibers cross in the weave create connections between channels in the finished material. Unlike direct-ink writing, which is difficult to scale up to commercial production, the sacrificial-fiber method uses conventional manufacturing techniques. We have created channels up to 1 meter long and with considerable vascular complexity.

Various members of our research group have had increasing success with the development of multi-dimensional networks. To understand how to efficiently design 3D networks, we utilized a modeling scheme based on genetic algorithms to optimize properties such as reliability, network volume and channel diameter. Other work used direct-ink writing to mimic the structure and functionality of epidermal tissue. In this case, a brittle epoxy coating containing a polymerizer was deposited on a flexible epoxy substrate with a 3D grid of channels about 200 micrometers in diameter. Surface cracks in the coating released healing agent from the underlying vasculature. The network could be refilled and we found that the samples could be healed up to seven times. To increase the number of healing cycles, members of our group next placed healing agents and polymerizers in two isolated networks, which extended the number of healings to 16. By refining direct-ink writing methods to create complex, isolated but interpenetrating networks, we have achieved more than 30 repeated healing cycles in a coating. The most recent advances in multi-dimensional vascular design also allow for repeatable healing of damage to the bulk of the matrix material.

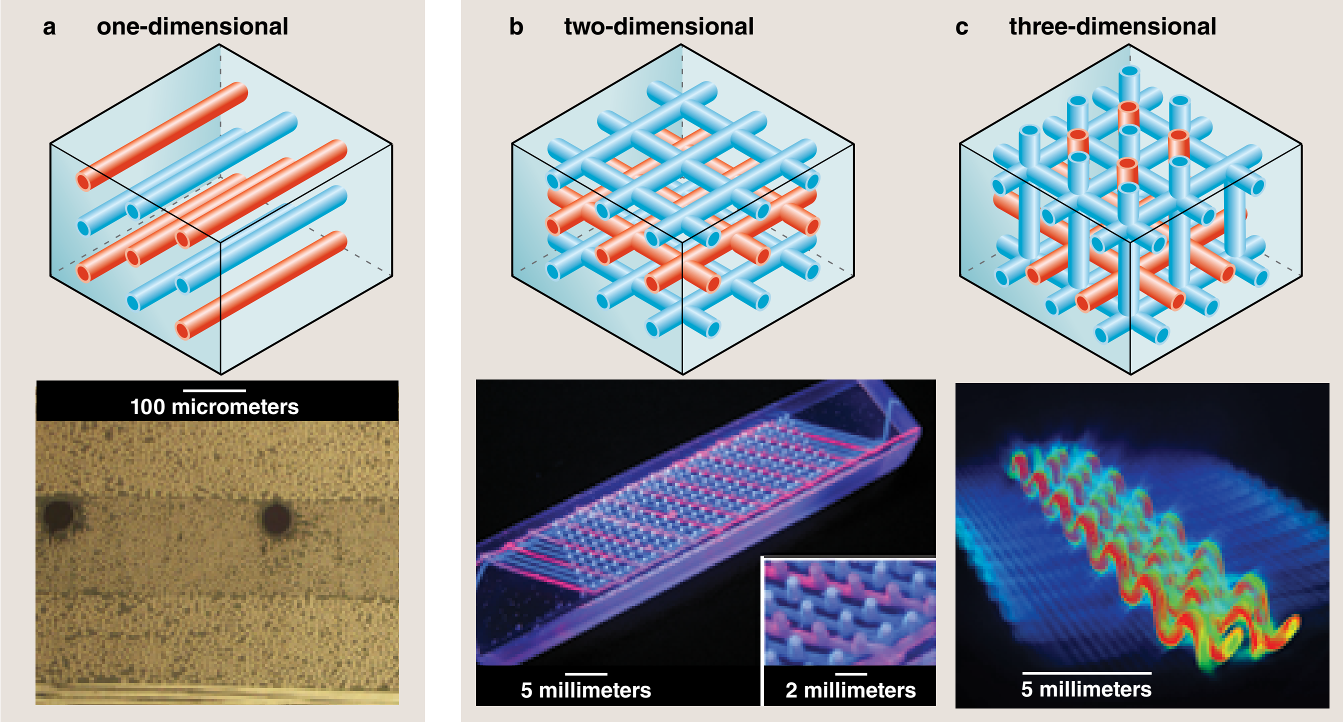
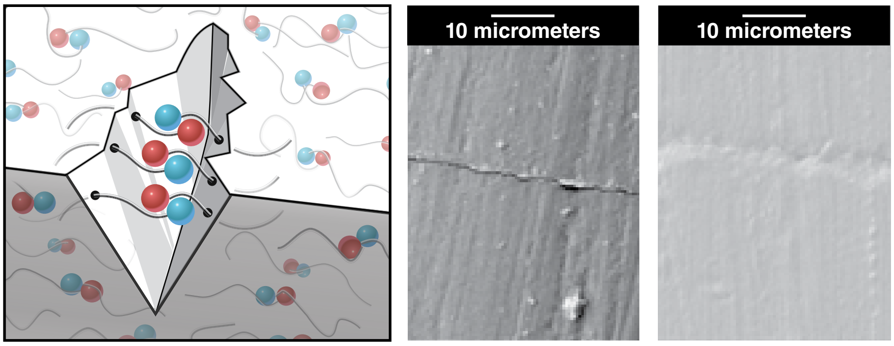
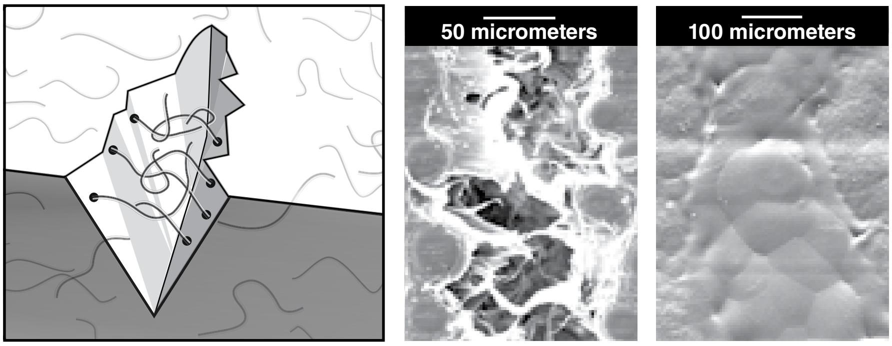


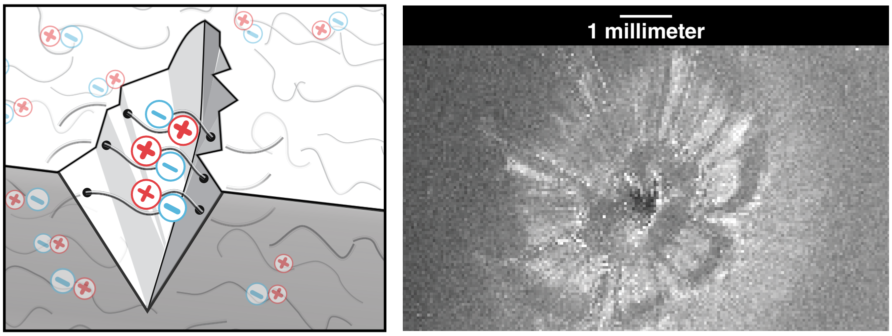
Figure 4. Vascular self-healing networks keep healing agents *(blue)* and polymerizers *(red)* in separate channels. One-dimensional networks *(a)* can be made from hollow glass fibers, an end view of which is shown in a scanning electron micrograph *(a, bottom)*. Two-dimensional *(b)* and three-dimensional *(c)* networks can be made by direct-ink writing a scaffold *(b, bottom)* or by interweaving sacrificial fibers with standard composite fibers *(c, bottom)*. (Image in *a* is reprinted from G. Williams et al., *Composites Part A* 38:1525, with permission from Elsevier. Image in *b* is reprinted from C. J. Hansen et al., *Advanced Materials* 21:4143, and in *c* from *Advanced Materials* 23(32), both with permission from John Wiley and Sons.)



a **reversible bonding**



b **chain reentanglement**



c **noncovalent healing**

Figure 5. Intrinsic self-healing networks use three main schemes. Reversible bonding *(a)* takes advantage of a polymer's ability to revert back to its simpler components and then rebuild bonds. The mobility of materials at crack faces can be utilized to entangle polymer chains that span the damage *(b)*. Noncovalent healing *(c)* relies on reversible hydrogen bonding or ionic clustering, which manifests as reversible cross-links in polymers. Scanning electron micrographs of damage and healing by each method are shown at right. (Images in *a* are reprinted from E. B. Murphy et al., *Macromolecules* 41:5203, and in *b* from X. Luo et al., *Applied Materials and Interfaces* 1(3):612, both with permission of the American Chemical Society. Image in *c* reprinted from R. J. Varley et al., *Acta Materialia* 56:5737, with permission from Elsevier.)

Built-in Repair

One of the major disadvantages of both capsule-based and vascular systems is that they require that additional materials (and volume) be integrated into a material. A more elegant approach is to incorporate healing ability directly into the basic nature of the material—an intrinsic healing system. Materials using such systems achieve repair through the inherent reversibility of chemical bonds within the matrix polymer. Mechanisms include thermally reversible reactions, hydrogen bonding, coupling of ionomers, phase change of dispersed, meltable thermoplastic, or molecular diffusion.

Design of such materials can be less complex than for capsule or vascular systems, because healing agents don't have to be sequestered or integrated, and there are no problems with compatibility. However, the main challenge associated with intrinsic self-healing materials is that they need to have the required mechanical, chemical and optical bulk properties for the final product's desired use. In addition, intrinsic self-healing tends to work best when the damaged area is small, as rebonding requires close proximity of the cracked surfaces, which limits repair in cases of extensive damage.

A polymer material is made from the linking of simpler components, called monomers. The material's inherent ability to reversibly transform from monomers to cross-linked polymers, through the addition of external energy, is one way to effect intrinsic self-healing. For instance, if a damaged area of polymer is subjected to intense heat or light, that may trigger an increase in the mobility of material in the damage region so that it can rebuild bonds and mend the polymer. A number of groups have characterized polymers and composites that have achieved multiple thermal mending cycles.

Another approach is to incorporate a meltable thermoplastic additive. When this material liquefies, it disperses into cracks and mechanically interlocks with the surrounding matrix material. Some additives also expand in volume when they are heated, filling in damage. Such reactions can occur multiple times, and the materials have been shown to sustain loads in post-repair tests.

In some cases, segments of the polymer can be made to have an electric charge, and these pieces are called ionomers. Clusters of such ionic segments can act as reversible cross-links, interweaving across a crack, when activated by such external stimuli as heat or ultraviolet radiation. Several groups have looked at how such ionomeric materials fared when punctured with projectiles, and have shown that the heat generated by the projectile traveling through the material is sufficient to trigger self-healing. The rate at which the hole is sealed is virtually the same as that of the ballistic damage *(see Figure 8)*.

Polymers can also be designed so that they form strong associations at either end groups or side groups along their long chains, via multiple reversible hydrogen bonds. Such rubbery materials have been shown to reform hydrogen bonds in areas of damage when the broken pieces are brought back into close contact. Similarly, materials may achieve intrinsic self-healing through enhanced molecular diffusion, which promotes polymer movement and entanglement across a fracture. This method has also been shown to inhibit corrosion of aluminum and zinc: The increased pH levels that accompany cathodic corrosion induce increased mobility of compounds in a coating, thus triggering self-healing.

Taking Stock

Optimally, a self-healing material will recover at the same rate at which damage occurs, maintaining material stasis. The vast majority of self-healing materials have yet to reach this milestone (although a few do accomplish it under some circumstances). Healing efficiency can be calculated as a ratio of the healed material properties to the original material properties. The goal of any system is 100 percent healing efficiency, and each approach to self-healing has at least one such successful example. Reported efficiencies for various materials range from 20 percent to more than 100 percent, in cases where repaired areas were actually tougher than the original material.

The number of ways that a polymer or composite can be damaged is extensive. The list includes impact, fatigue, fracture, puncture and corrosion, and each of these types includes more specific modes. For instance, impact can induce surface cracking, subsurface delamination, polymer matrix cracking or transverse ply cracking (in which new cracks develop to span between existing cracks). These damage modes affect not only the material's mechanical properties but also its ability to act as a barrier. Researchers have studied not only the restoration of fracture properties but also the recovery of a material's ability to prevent the leakage of a gas or liquid, or to protect a substrate from corrosion.

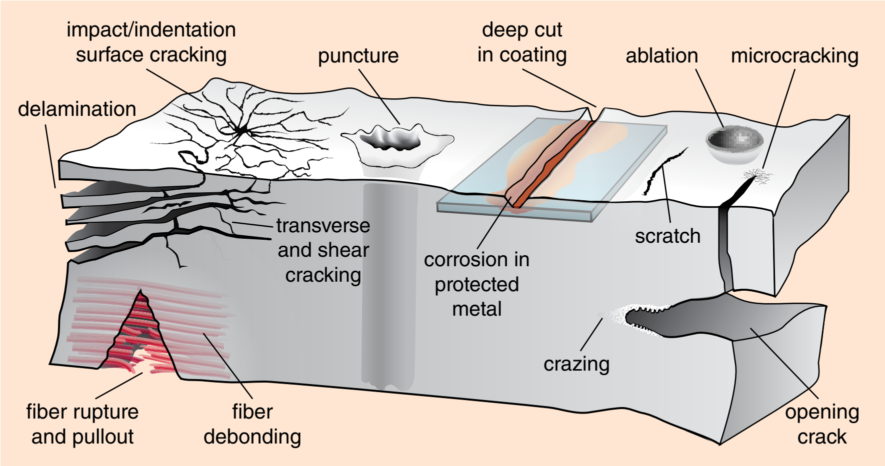


Figure 6. Various forms of damage may require different systems, or even a combination of systems, to achieve optimal healing. Indentation, impact, exposure to corrosive environments, ballistic punctures, surface scratching and fatigue can lead to these various damage modes. When broken, the type of composite, the polymer matrix, and the rate and extent of loading all influence the form and extent of damage that requires healing.

In order to test for recovery from fractures under controlled conditions, samples of materials are subjected to all kinds of impacting, bending, pulling and tearing. In 2001 our group demonstrated the first successful autonomic self-healing in an epoxy with a capsule-based healing system, which after healing recovered 75 percent of its original material properties. We also found that microcapsules could increase the toughness of undamaged epoxy, because the spheres absorb the energy of growing cracks, preventing their expansion.

When we have tested fracture repair in fiber-reinforced composites, we have found that incorporating microcapsules that are larger than the reinforcing fibers thickens the regions where layers are laminated together, which results in an initial decrease in fracture toughness. But after 48 hours of healing at room temperature, previously fractured samples showed a healing efficiency of about 40 percent, and this value increased to as much as a 80 percent when samples were healed at an increased temperature of 80 degrees celsius. Full recovery of fracture toughness in such materials seems to be limited in cases where few fibers bridge the damaged area and where there is an uneven distribution of healing agents within the fracture plane. In a recent advancement, our group has patterned capsule-based systems directly onto the surface of the reinforcing glass fibers to specifically target and repair damage that affects the bond between the reinforcement and matrix. Initial testing has shown that as much as 50 percent recovery of the interfacial bond between a glass fiber and epoxy matrix can be achieved. Our colleagues at the University of California at Los Angeles tested carbon-fiber reinforced composites containing an intrinsic self-

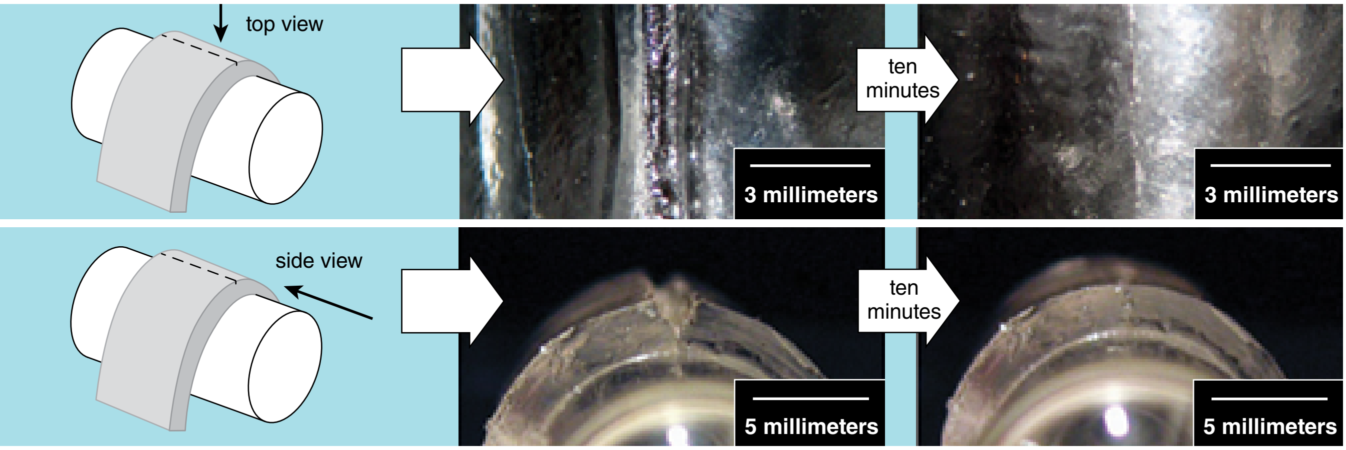


Figure 7. An intrinsic self-healing polymer is tested by cutting its surface and stretching it over a cylinder *(left)* in order to view the damage *(middle)* and healing. After 10 minutes, molecular diffusion and entanglement of dangling chains across the cut have healed the surface *(right)*. (Images reprinted from M. Yamaguchi et al., *Materials Letters* 61:1396, with permission of Elsevier.)

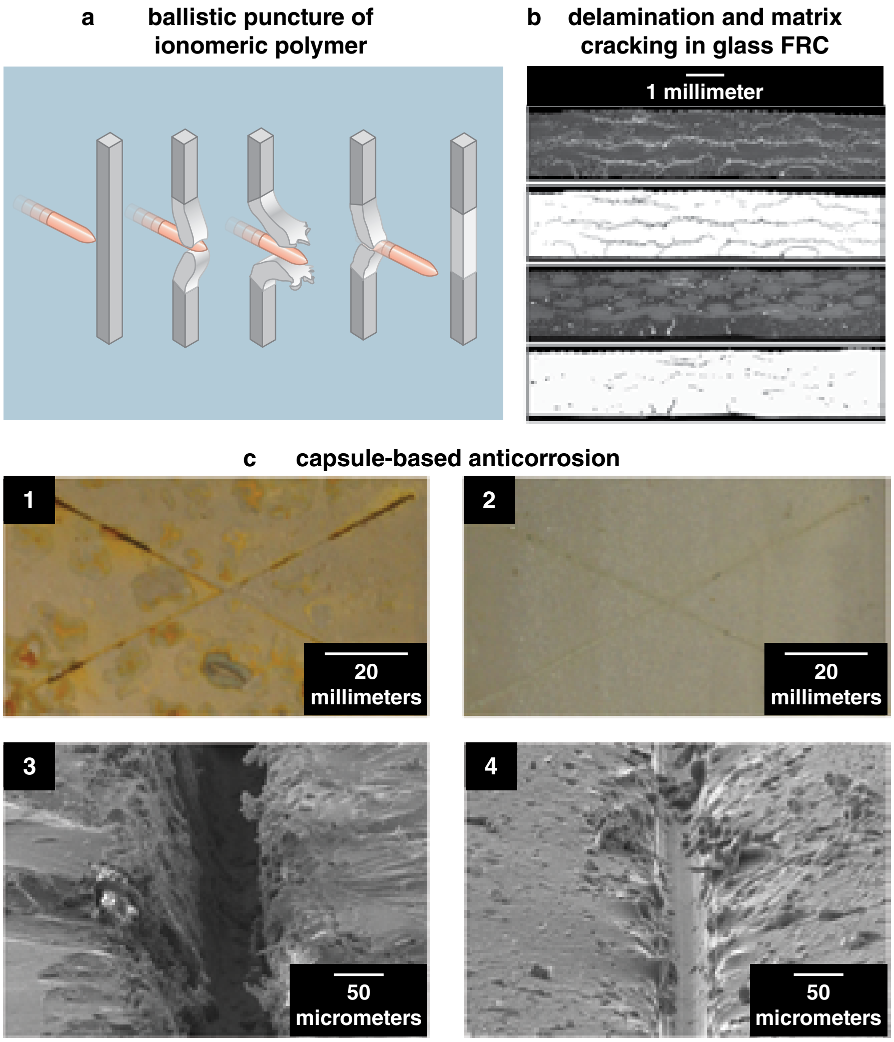


Figure 8. Self-healing materials are of particular interest for the recovery of barrier properties and enhanced corrosion resistance. When a projectile punctures a polymer that has an ionomeric intrinsic self-healing system *(a)*, the polymer, melted by the ballistic heat, elastically snaps back into place; viscous flow and interdiffusion of the molten surfaces seal the remaining cracks. A glass-fiber-reinforced composite (FRC) is damaged by indentation *(b)*; cracks in cross section of a control sample *(top)* are reduced via healing in a sample with a capsule-based system *(bottom)*. Steel coated with an epoxy *(c)* is scratched and then examined both optically *(top)* and in scanning electron micrographs *(bottom)*, showing corrosion in a control sample *(1 and 3)* and improved corrosion resistance in a self-healing sample *(2 and 4)*. (Images in *b* reprinted from J. L. Moll et al., *Journal of Composite Materials* 44:2573, with permission of Sage Publications. Images in *c* reprinted from S. H. Cho et al., *Advanced Materials* 21:645, with permission from John Wiley and Sons.)

healing matrix capable of thermally reversible reactions; they found that there was a 90 percent recovery for three healing cycles when microcracks they induced in the material were heated to 150 degrees for one minute.

Another test of self-healing fractures is to physically cut the surface of a polymer sample and then optically evaluate both the scratch damage and crack closure. In several studies, polymers with intrinsic self-healing systems were cut with a razor blade and healed by realigning the pieces for 10 to 15 minutes at room temperature. The repaired samples were bent or deformed to check for reopening of the crack faces. Some samples were weaker than their undamaged counterparts, but many showed no breaks in the healed areas. Some of the same studies examined samples that were torn instead of cut, with similar results.

Fatigue is a common mode of failure in structural materials, and it presents unique challenges when designing self-healing materials. The load a material experiences from fatigue depends on an array of variables, including the frequency and amplitude of the applied stress. To date, only a few studies of self-healing systems have looked at fatigue damage. Our group and others have investigated the relationship between the damage rate, the healing rate and material life extension in these systems. When the damage rate is faster than the healing rate, damage accumulates and the material eventually fails. To counteract this result, faster chemistries or longer rest periods for the material may be required. However, when the damage rate and healing rate are balanced, significant life extension has been shown.

Impacts can also produce massive damage volume, and can take on various modes of failure, such as puncture, delamination or mixed-mode cracking. So far, the focus of testing has been on quantifying the restoration of compression strength after low-velocity impact. Our colleagues at the University of Bristol have tested carbon-fiber reinforced epoxy with a hollow-glass-fiber networks filled with healing agent, which was subjected to a range of impact energies up to 3 joules. They found that the hollow-fiber system absorbs significant energy as it fractures on impact, increasing compression strength by 13 percent. Elevated temperatures allowed significant healing of the damage, but the study also demonstrated the material's sensitivity to the uniformity of the channels distributed within the laminate.

Studies of impact damage on capsule-based healing have shown mixed results. Our colleagues at Zhongshan University in China tested woven-glass fiber-reinforced composites containing healing capsules. At impact energies ranging from 1.5 to 3.5 joules, they found close to 100 percent healing efficiencies for the 1.5-joule impacts, but only about 20 percent efficiency for the 3.5-joule impacts. However, when our group tested a similar material at impact energies of 13 to 45 joules, despite extensive cracking of the sample, healing efficiency was found to be nearly 100 percent for impacts up to 20 joules; this efficiency decreased as the damage volume increased at higher impact energies.

Testing with a milder form of impact, indentation, can lead to more controlled damage. The group at the University of Bristol has used this method extensively on epoxy composites with hollow glass fibers to assess the release and transport of healing agents, mechanical performance and environmental aging.

Besides bulk samples, our group has also tested the self-healing ability of polymer samples, such as thin bladders or composite sandwich panels, to act as barriers to gas and fluid flow. For example, we have looked at thin bladders where a microcapsule healing system was sandwiched between two epoxy-coated nylon layers. The bladders were punctured with hypodermic needles and then allowed to heal for 24 hours. The healing efficiency, measured by the effectiveness of sealing the holes, ranged from 40 to 100 percent, depending on microcapsule size and concentration.

Finally, there are corrosion-resistant coatings, critical protection for metal parts that operate in wet or salty environments. Barrier coatings lose their protective abilities once they are scratched or abraded, making them obvious targets for self-healing systems. Samples are tested by scoring the coating and then subjecting the material to salt water and, sometimes, to ultraviolet light. Recovery is determined by either visible corrosion in the cut or by the electrical conductance of the surface; an intact coating should have more impedance than bared metal.

Several groups have the tested corrosion resistance of capsule-based coating systems containing linseed oil, camphor oil and tung oil, among others. In our labs we have shown remarkable performance for epoxy and vinyl-based coatings with capsule systems, upon exposure to salt water. Intrinsic healing systems are particularly well suited for barrier protection, as they emphasize the healing of small defects, and several groups have reported complete corrosion suppression with such systems.

Increasing Longevity

The nascent field of self-healing materials research has made great strides over the past decade, but many technical challenges still exist. Continuing progress in the field will lead to new healing chemistries that possess greater stability, faster healing rates and higher reactivity. But how such materials will perform when subjected to long-term exposure in harsh environments remains an open question. The ultimate usefulness of self-healing systems will be in combating fatigue and periodic damage events, but the vast majority of research thus far has focused on performance in response to static fractures, not on the dynamic aspects of self-healing under fatigue conditions.

It is likely that large-scale applications will not incorporate fully distributed self-healing systems, but rather will employ targeted and locally patterned self-healing components, in order to optimize cost, efficiency and detrimental effects to the overall properties of the material. For the field to gain traction, it is critical to have a near-term successful commercial demonstration of self-healing. Most likely, this milestone will happen first for coatings, as they are prevalent across many industrial applications and they require only modest mechanical performance compared to structural components.

But there are other material properties besides mechanical ones that may be good targets for self-healing. For instance, restoring conductivity could be highly beneficial for applications in energy storage and microelectronics. Damaged computer chips might be able to repair themselves on site, instead of requiring replacement. Our group and others have synthesized organometallic polymers with semiconductor-level conductivity that can self-heal with applied heat, and we have recently demonstrated automatic restoration of conductivity via the delivery of highly conductive materials from microcapsules.

Restoration of optical properties may also be a fruitful path for self-healing research. Cracks have a different refractive index from the rest of a material, so they scatter light and disrupt transparency. The ability of a vascular or capsule-based system to deliver an index-matched polymer to a site of damage could enable autonomous mitigation of this problematic effect.

Wherever materials are used, there is hope that self-healing may lead to increased safety and utility, and decreased cost over the lifetime of the material. Safer self-healing batteries, self-repairing automobile coatings, resealing tires, fade-resistant fabrics and antitamper electronics are all potential applications. But could the possibilities extend beyond healing? Looking again to biological systems for a road map, materials such as bone regenerate and remodel in response to stress and other stimuli. It is possible that in the future, synthetic materials that currently can heal themselves in response to damage may also be able to respond in a more complex fashion, regenerating and remodeling themselves over their lifetimes.

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