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FEATURE ARTICLE

Self-healing Polymers and Composites

Capsules, circulatory systems and chemistry allow materials to fix themselves

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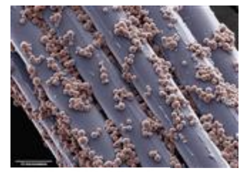
Nothing lasts forever. Any humanmade material, used in anything from toys to bridges, will eventually fail, if not maintained and repaired. Traditionally, this problem has been addressed through extensive inspection and expensive replacement of damaged parts. Biological systems, however, have evolved 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.



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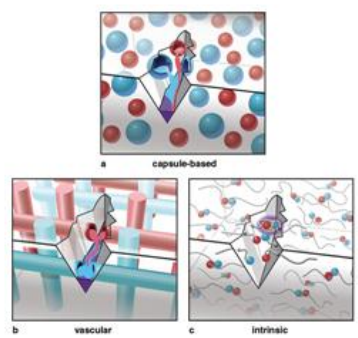
The guiding principles for synthetic self-healing are seen in biological systems. Damage that causes injury triggers the first response, inflammation and blood clotting. This initiating step is followed by cell proliferation at the site of injury, which deposits a matrix for the repair. The final stage 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.



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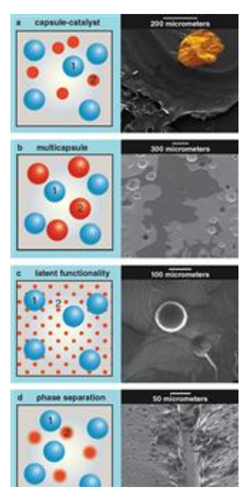
Capsule-based materials incorporate a healing agent that is held and protected in discrete spherical shells, which are ruptured by damage. The self-healing mechanism is activated by the release and reaction of the healing agent at the damage site. However, after release, the healing agent is depleted,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