Long Live the Polymer!

A new class of polymer that self-heals when exposed to ultraviolet light has been developed. Could this be the dawn of a technological future with self-healing materials?

You have accidentally dropped your cell phone, and now the screen is cracked beyond repair... or is it? What if the screen could self-heal, before your very eyes, in a matter of seconds? This is the future scenario that many material scientists yearn for, most likely inspired by the intriguing and fascinating ability of living organisms to self-heal upon getting wounded. A new approach to *mending damage* in polymers through exposure to ultraviolet light takes us a step further towards a technological future with self-healing materials. This was developed by researchers at the Case Western Reserve University (Cleveland, Ohio, USA), at the Aberdeen Proving Ground (Aberdeen, Maryland, USA), and at the University of Fribourg (Switzerland).

Self-healing materials belong to a class of so called *smart materials*: materials whose physical properties can be controlled by an external signal, such as temperature, stress, or light. Take progressive lenses, also known as polarized lenses, for instance. A perfect example of a *smart material*, they boast the rather *chameleonic* ability to become darker when exposed to sunlight. Likewise, *self-healing materials* incorporate the ability to repair cracks and other microscopic damages resulting from usage, which means that their performance remains unaffected by the passage of time.

How can we create a self-healing material? Polymers are a good starting point due to their structural properties: They are large chains of smaller molecules, or monomers (as their fundamental building blocks are called), held together by strong chemical bonds. Moreover, polymers play a ubiquitous role in our everyday life, making up many important natural and synthetic materials, such as rubber, plastics, and even proteins and DNA.

In a damaged polymer some of these bonds are broken, so repairing the damage could be as easy as soldering some — or many — of these bonds back together. A simple enough idea to contemplate, somewhat more challenging, perhaps, to implement. "Most approaches to self-healing polymers are still in the research or development stage," points out Christoph Weder at the University of Fribourg. "Several concepts for making such materials have been reported by various research groups in the past ten years. The first approach is a simple engineering approach, where liquid monomers (think of them as glue) are encapsulated into microcapsules embedded within a polymer. When a crack into the polymer reaches one of these microcapsules, the capsule breaks and the monomer bleeds into the crack, where it can polymerize and mend the damage."

More advanced approaches rely on mending the damaged polymer, for example by exploiting the structural properties of *supramolecular polymers*. In many ways, these polymers are exactly like standard, solid polymers, although their fundamental blocks are held together by chemical bonds that are weaker than those of conventional polymers — as a result, they are not one big molecule, but rather an assembly of many molecules bound tightly together. As Weder explains, these polymers "are composed of smaller molecules with *sticky-end groups* that like to stick to one another and that assemble the building blocks into longer, polymer-like chains. The end groups serve as a kind of *molecular glue*." If an external stimulus is applied, the sticky-end groups can disassemble: the originally solid material transforms into a *liquid* that can easily flow and fill any cut or crack. Eventually, when the stimulus is removed, the fundamental blocks reassemble, and the material is restored to its original state, before the damage.

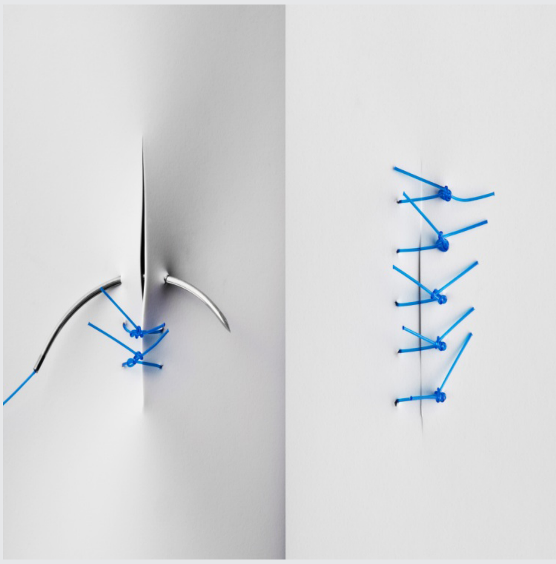

Figure 1: Artistic view of a self-healing material at work. Novel materials attempt to mimic the unique ability of biological tissues to self-heal after receiving a wound. The new results show how the combination of supramolecular polymers with a light-heat conversion scheme is a particularly effective approach when it comes to making healable materials. Picture courtesy: Dominique Bersier and Gina Fiore.

In their study, Weder and colleagues propose a new supramolecular polymer that responds to intense ultraviolet light, instead of to more conventional stimuli such as exposure to heat or to a solvent. "Ultraviolet light is absorbed by the sticky-end groups of our new supramolecular polymers, converted into heat, and the supramolecular structures disassemble into the small building blocks from which they were made," explains Weder. The use of light offers more control over this process than the direct use of heat or of a solvent: light, in fact, can be applied in the very proximity of a defect. The damaged portion can be healed then, leaving the rest of the material untouched to continue serving its function. "This is probably the most significant aspect of our work," says Weder, and he adds: "Light-heat conversion is a general process. We therefore expect that the method will work well also for other supramolecular polymers, as long as light can be efficiently converted to heat."

While self-healing polymers could have countless applications, as Weder says, "we are still far from any commercial product, but the new concept may be useful for the development of automotive paints, varnishes for floors and furniture, and many other applications where it would be wonderful if damages could be easily fixed." In the words of Marek Urban, at the University of Southern Mississippi (Mississippi, USA), what this study definitely leaves clear yet again, is that "a clever combination of known polymers with inorganic chemistry can provide endless opportunities for innovative materials design." And he adds: "There are many applications that may spin off from this approach, just like from elastomeric thermoplastic polymers that offer numerous applications, ranging from membrane technologies to biomimetics or footwear, wire insulation, adhesives, and others. The impact may be tremendous, and the key advantage will be materials sustainability."

Giorgio Volpe

Mark Burnworth, Liming Tang, Justin R. Kumpfer, Andrew J. Duncan, Frederick L. Beyer, Gina L. Fiore, Stuart J. Rowan & Christoph Weder, **Optically healable supramolecular polymers**, Nature (2011) **472**, 334–337.