A material fix

Richard P. Wool

The idea of materials that can mend themselves seems far-fetched. But a system that allows composite materials to 'self-heal' has been devised and has passed some early tests.

Everyone has had minor scratches or abrasions that have healed, the damaged skin becoming as good as new. In contrast to that, we are now so used to products of all sorts breaking or wearing out that we fully accept planned obsolescence, disposable or busted materials, and mountains of rubbish looking for a landfill site. Materials are bound to become fatigued and weakened, however, and self-healing in which the material is made as good as new would seem to be the stuff of fantasy. Not so, say White and co-workers on page 794 of this issue[1], in a paper entitled "Autonomic healing of polymer composites".

Polymer composites are advanced materials that consist of two components — a reinforcing fibre (such as carbon, glass, Kevlar, flax, hemp or jute) and a liquid moulding resin (epoxy, unsaturated polyester, vinyl ester or urethane). Typically, the fibres are first placed in a mould. The resin, which has a viscosity similar to that of olive oil, is poured or injected into the mould. The resin hardens, and out comes the finished item. We use these composite materials in all manner of products, for all manner of applications. The market is huge: some 20 million tonnes of composites are used annually in civil engineering, aerospace and defence-related projects, offshore oil exploration, electronics and biomedicine.

So, how are materials repaired — and why do they fail in the first place? Biological healing processes are exceedingly complex and involve events that occur both simultaneously and sequentially, and are affected by a host of external variables (temperature, humidity and pressure, as well as electrical, ultrasonic and magnetic fields). Healing of materials is similarly complex and involves several stages which together act to eliminate damage induced by mechanical, chemical or thermal means. The damage may involve bond rupture, the formation of microvoids, debonding of the fibres from the resin, or various other events at the molecular and microscopic levels that collectively weaken the material and perhaps put its user at risk. The most common route to failure is fatigue — the formation of microvoids incurred by mechanical stress through repeated usage. The microvoids enlarge and coalesce to form microcracks in the material; in turn the microcracks can grow to catastrophic proportions and cause total failure of the product.

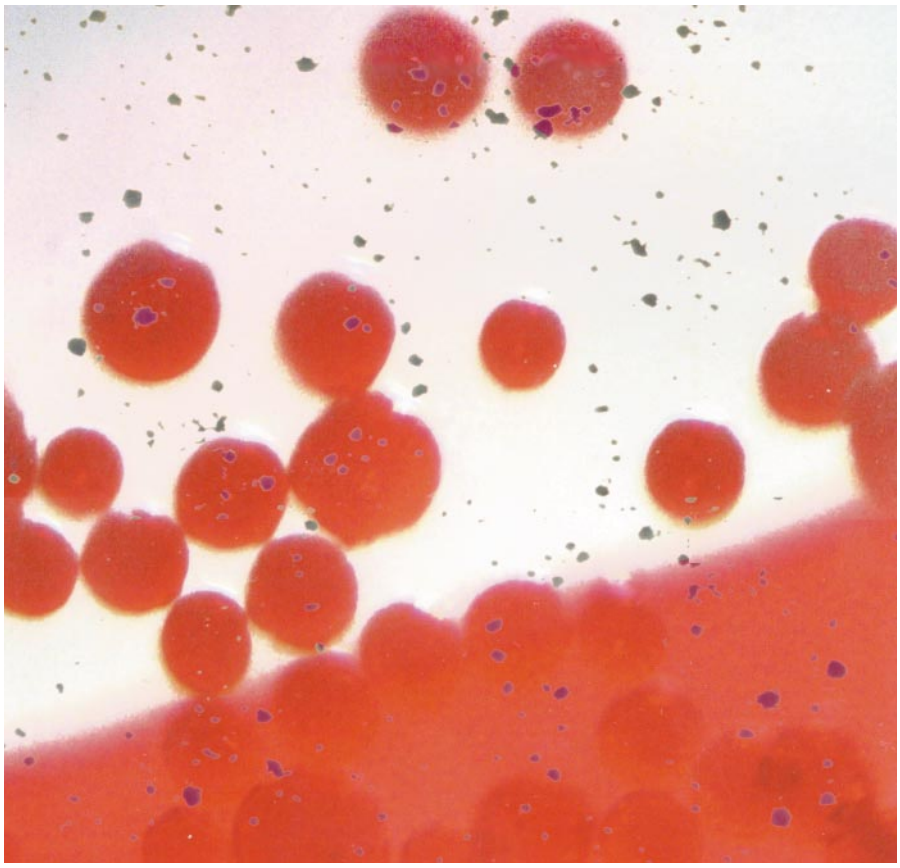

Figure 1 **Autonomic healing[1] in action. This image shows a crack in an epoxy polymer material, the crack plane running along the bottom of the picture. The red spheres are microcapsules, 200 micrometres in diameter, containing the red-dyed repair fluid. Following polymerization by Grubbs' catalyst, the fluid has filled part of the crack. The material being mended appears white. The black flakes are the Grubbs' catalyst, embedded in the material's matrix. (Picture courtesy of S. R. White *et al.*)**

As I have described elsewhere[2], various workers have studied crack repair in polymers using thermal or solvent processes. In these processes, the polymer is softened by heating or with a solvent, and the cracks weld themselves in several stages. But applying the same treatment to a large composite structure is not very practical.

The challenge for White *et al.*[1] was to design a self-repairing composite to satisfy the following wish list. It has to contain a self-repair system that does not affect the material's overall properties or performance. It must also be able to sense damage, and then be able to react to that damage and initiate healing. Finally, it must restore the material's original properties (strength and stiffness, for example).

This is a formidable array of requirements, which is probably why White *et al.* are the first to claim success in meeting them. Their system is ingenious and involves adding several low-volume components to the composite. It is outlined diagrammatically in their Fig. 1 on page 794.

Microcapsules are first filled with a repair fluid (dicyclopentadiene, or DCPD). This fluid can polymerize in the presence of a catalyst (patented by R. Grubbs, and known as the Grubbs' catalyst) to form a very tough polymer. The catalyst and the fluid must not meet until they are needed in the damaged zone, which is the function of the microcapsule membrane. The catalyst is distributed first in the epoxy resin, followed by the microcapsules filled with the DCPD fluid. This modified resin is added to the fibres,

the epoxy hardens, and the composite is moulded into its final shape.

Testing the system involved mechanically loading the composite, causing microcracks to form in the matrix of the epoxy polymer. What is especially clever is that, for stress field reasons, the microcracks migrate towards the soft, fluid-filled microcapsules and rupture them, releasing the repair fluid. The fluid travels down the microcracks by capillary action and encounters the Grubbs' catalyst, which initiates the polymerization reaction. The polymerized fluid fills the microcracks and repairs them (Fig. 1), largely restoring the composite material to its original strength and stiffness.

The concept of self-healing composites cuts against the grain of current material-design principles, but has far-reaching consequences for improving product safety and reliability. The approach should prove especially useful where it is not possible, or practical, to repair the material once it has been put into use. Components of vehicles used in deep-space exploration, satellites, rocket motors and prosthetic organs are prime candidates for such treatment. So too are the space stations of the present and future, and engineering innovations such as bridges constructed from composite materials. ■

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1. White, S. R. *et al. Nature* **409,** 794–797 (2001).
2. Wool, R. P. *Polymer Interfaces: Structure and Strength* (Hanser/Gardner, Munich, 1995).

Quantum physics

Count them all

Philippe Grangier

Direct experimental evidence to resolve the conflict between classical and quantum physics has been a long-awaited goal. As the last loophole closes, it seems that quantum mechanics was right all along.

Certain features of quantum mechanics are undeniably strange, and it has taken a long time for physicists to understand them — a necessary step before being able to accept them. The predictions of quantum physics often seem to contradict the intuitive, and seemingly reasonable, assumptions about how the world should behave that can be deduced from classical physics. Not surprisingly, many experiments have been done to explore these differences, and the results have tended to support quantum mechanics. But there have been persistent loopholes in these experiments, allowing alternative interpretations of the data. On page 791 of this issue, however, Rowe *et al.*[1] describe how they measured the quantum correlations between two beryllium ions with nearly perfect detection efficiency — thereby closing the last experimental loophole, and providing compelling evidence that some basic ideas inherited from classical physics must be abandoned.

Non-separability, or entanglement, has emerged as the most emblematic feature of quantum mechanics. Briefly stated, it says that one can define 'entangled' quantum states of two particles in such a way that their global state is perfectly defined, whereas the states of the separate particles remain totally undefined. In other words, the information contained in such an entangled state is all about the correlation between the two particles, and nothing is said — even more, nothing can be known — about the states of the individual particles.

Some thinking is necessary to realize how weird this is. In 1935 it led Einstein, Podolsky and Rosen to suggest that quantum mechanics is incomplete, on the basis that any theory of nature must be both 'local' and 'realistic'. Local realism is the idea that, because the properties of one particle cannot be affected by a particle that is sufficiently far away, all properties of each particle must exist before they are measured. But non-separability contradicts this sort of local realism.

For a long time, this debate about the nature of quantum mechanics was largely theoretical, but in 1964 Bell introduced a set of mathematical equations — Bell's inequalities — that could be tested experimentally. The inequalities must be obeyed by any local realistic (classical) theory, whereas they are violated by quantum mechanics. It became clear at the beginning of the 1980s that the overwhelming majority of experiments supported the predictions of quantum mechanics. But two important experimental loopholes meant the evidence was inconclusive — at least to supporters of local realism.

The first of these loopholes, the so-called locality loophole, arises whenever measurements are performed on two spatially separated particles, because any possibility of communication between the two parts of the apparatus must be excluded. This can be achieved if the two measurements occur in different 'light cones', which means they cannot be connected by a signal travelling

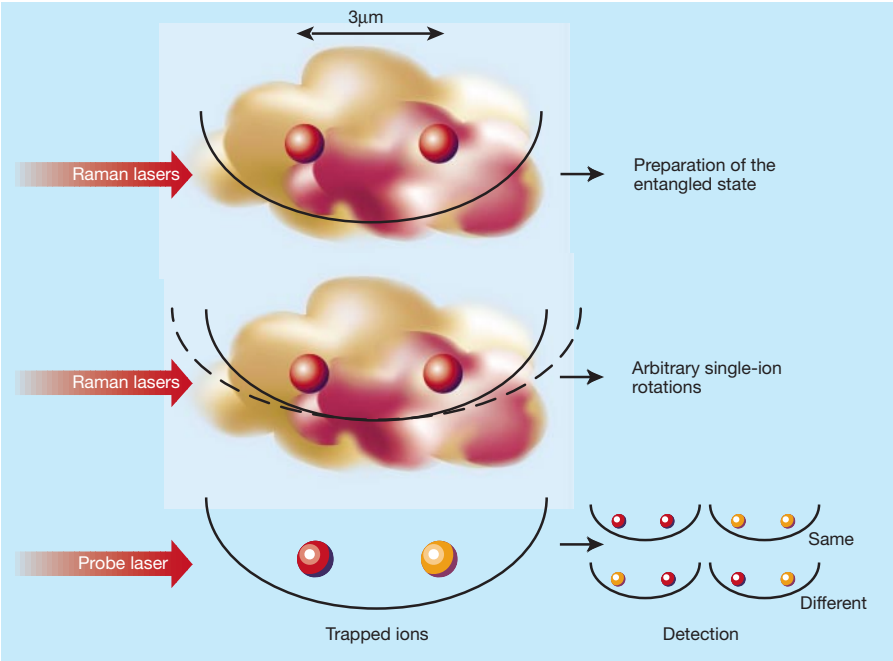

Figure 1 **Testing our quantum picture of the world. Rowe *et al.*[1] prepared two ions in an entangled state by using Raman laser beams. Next, they applied an arbitrary rotation to each ion by simultaneously controlling the phase of the Raman beams and the strength of the ion trap. Finally, they determined the quantum state of each ion by shining light (the probe laser) on the ion pair to identify whether each ion fluoresces. There are four possible outcomes: two in which the states are the same (both ions are bright or both are dark), and two in which they are different (only one ion or the other fluoresces). The measurements give the ratio of $(N_{same}-N_{different})/(N_{same}+N_{different})$, where N is the number of detected ion pairs. The experimental result violates Bell's inequalities — thereby confirming the predictions of quantum mechanics — in a way that escapes the 'detection-efficiency' loophole.**