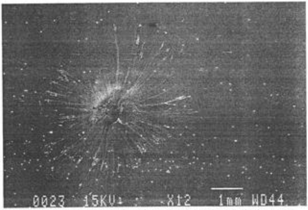
Self-Healing Materials

Self-healing polymers have the potential to enhance and extend the functionality of plastics. The technology also offers an interesting alternative approach for improving material durability.



SEM image showing 7 mm bullet impact on self-healing material. The hole is fully closed within 20 milliseconds of the bullet's passing through.

By Professor Sybrand van der Zwaag

When developing structural materials, engineers must consider two fundamental design concepts: damage prevention and damage management. The latter forms the basis of self-healing materials and is also the foundation for material development in nature. The paradigm is based on the notion that the formation of damage is not problematic so long as a subsequent, autonomous process of "removing" or "healing" the damage counteracts it.

The effect of an autonomous healing process on the development of damage as a function of time is shown in *Fig. 1*. For the material in *Fig. 1a*, there is a single healing action, which almost completely repairs the damage created. Reapplication of the load leads to new damage and finally fracture, as this material was designed for one healing action only.

The material in *Fig. 1b* is capable of multiple healing. Damage is partly removed in each healing cycle, but after several cycles the material runs out of "healing power," and catastrophic failure occurs.

The material in *Fig. 1c* approaches an ideal self-healing scenario: the damage is healed many times and no accumulation of damage leading to catastrophic failure occurs. For the loading (and unloading) conditions imposed, the material has an infinite lifetime.

In order for healing to occur properly, it may be necessary to temporarily relax the loading conditions. The final performance of a self-healing material therefore depends on two

Sybrand van der Zwaag

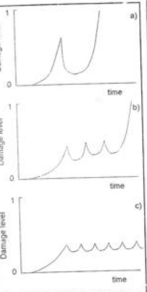


Figure 1: Damage development as a function of time for three levels of self-healing behaviour: a) single healing; b) a restricted number of healing events and partial healing; c) a large number of healing events.

time constants: the rate of damage formation and the rate of healing. If the state of reduced loading does not last long enough for healing to occur properly, the life extension will be lessened, falling short of the maximum improvement. This "rest" or "healing" period is indeed a constraint in making full use of self-healing materials—as anyone who has ever broken a leg will confirm—but it is better that than never healing at all. In *Fig. 2* the effect of a rest period on crack-growth rate in a self-healing polymer system is clearly visible.

Atomic Structure

So what is necessary at an atomic (or molecular) level to make a material potentially self-healing? First, like any structural material, the self-healing material still has to perform a regular mechanical function and must be designed with sufficient numbers of atoms—and the correct atomic configuration—to achieve this. It's fair to assume that most of the atoms in a self-healing material are there to perform this function. As a consequence, almost all self-healing material grades will be designed along the damage-prevention concept, at least at first glance.

To make a material self-healing, it is necessary that defects disappear more or less spontaneously: the defect, void or crack, has to be filled by new matter that also has the capability to locally restore the specific load-bearing properties. Hence, in contrast to standard materials, a fraction of the atoms making up self-healing materials must be mobile over shorter or longer distances in order to fill the local-damage area. The healing agent not only has to move to the

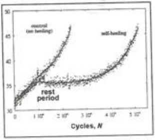


Figure 2: Crack-growth rate is halted after a rest period in a self-healing material.

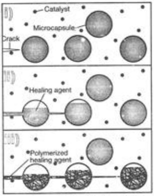


Figure 3: Healing mechanism in the encapsulation system designed by White: (i) initial state with crack approaching microcapsules; (ii) crack ruptures microcapsules and healing agent flows into crack; (iii) healing agent crosslinks as a result of contact with catalyst.

damage site, but once there, also has to permanently bond the two surfaces together, and in doing so it loses its mobility. This transition from a mobile to fixed state can be realised via temperature excursions and chemical reactions; other processes can be envisaged, too.

Of course, for the healing process to take place, a damage sensor or healing trigger is required, and this feature has to be included in the material's design. The sensor has to detect the occurrence of damage and to initiate healing either by starting the motion of the healing agent or the healing reaction itself.

In order for self-healing to take place, it is crucial that the damaged surfaces stay in or are brought into close contact once a fracture has occurred, and held in a steady, fixed position while the reaction takes place. Self-healing is most successful in partial-cracking situations where the area ahead of the crack tip keeps the fracture surfaces from separating. When damage results in full separation of the fractured material, proper healing generally will not occur unless the fracture surfaces are brought together.

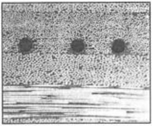


Figure 4: Three hollow glass fibres containing healing agent embedded in carbon-fibre-reinforced composite laminate.

This requirement also means that healing is favoured when the applied load is occasionally reduced or removed, as this leads to a reduction of crack aperture or even closure. Thus, self-healing materials are more promising for applications under cyclic loading and less promising for structures under constant load. It has been shown that the fatigue properties of self-healing epoxy, when tested under the right conditions, are exceptional.

Polymer Systems

The first intentional self-healing polymer was the well-known material system developed by Professor Scott White and his team in Illinois (USA). This system was designed on the basis that any self-healing material should have a mobile component capable of healing damage, and that liquids are intrinsically healing. In the White system, the functional and healing requirements are fully decoupled. The functional requirements are met by the epoxy matrix, while the healing requirement is met by incorporating microcapsules filled with the liquid healing agent di-cyclopentadiene, which crosslinks when in contact with catalyst particles (Grubb's catalyst) also embedded in the epoxy. The crack-healing mechanism is shown in *Fig. 3.*

This system has a 90% healing efficiency; i.e., given sufficient time to heal, the residual strength of a broken sample is 90% of its initial strength.

While little is known about the material's other characteristics, it is safe to assume that they are comparable to, but at a slightly lower level than, those of the epoxy matrix material. Such a drop in material properties is to be expected for all self-healing materials, as some of the atoms/molecules are set aside to provide this healing efficiency. However, in real applications, this can be compensated for by not having to include a "safety factor" covering the effects of damage during a product's lifetime. We can see that self-healing materials require novel design rules.

While the White system probably derives its maximum value as a demonstrator project, the concept of liquid-healing-agent encapsulation has been introduced with a higher chance of commercialisation in fibre-

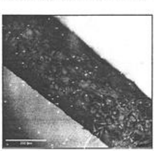


Figure 5: A multicompartmented fibre containing many cavities filled with a liquid healing agent.

composite systems by Professor Ian Bond at Bristol University, U.K. He has developed carbon-fibre composites also containing hollow glass fibres filled with a similar healing agent. A cross section of this composite is shown in *Fig. 4*. While the initial strength of Bond's composites was lower than that of traditional carbon-fibre composite, its (healed) post-impact strength was greater.

A major drawback of the microcapsulation and hollow-fibre approach, which is only partly solved by the multicompartmented fibre *(Fig. 5)* patented by Mookhoek et al. (Technical University Delft), is the fact that once a healing event has taken place, the mobile healing agent is locally consumed and turned into a solid (immobile) material. Hence, the healing is a one-time-only event.

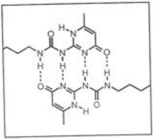


Figure 6: The structure of the quadrupole hydrogen bond unit developed by Meijer et al.

To obtain multiple healings, a more rigorous approach affecting the molecular structure of the polymer is required. The core concept behind multiple self-healing is that once loss of cohesion at the damage site has occurred, the molecular mobility in the damage region is temporarily increased, the cohesion across the crack interface is restored, and the material regains its strength and structure.

An example of such an approach is the ionomers (polymers containing up to 20% of metallic ions attached to the polymer backbone) used for ballistic applications. Because of the unavoidable, but in this case highly desirable, frictional heating that a projectile causes when it passes through a material, the material is locally heated and becomes mobile while still retaining its resilience because of the special molecular structure. Within 20 milliseconds of a bullet's passing through the material, the hole closes and the material quickly regains its strength as the physical crosslinks (attributable to the metallic ions) are re-established. Dr. Russell Varley (CSIRO Australia) has shown that holes up to 12 mm in diameter can be fully closed, provided that the bullet did not remove too much material on impact.

Finally, an even more radical approach for designing self-healing polymers is to alter the nature of the chemical bonds along and in between the polymer molecules. Currently, all polymers used as base ingredients for structural plastics have backbones based on covalent bonds. These bonds lack the ability to reform once broken; hence, to make polymers self-healing, it is necessary to include reversible chemical bonds. In contrast to regular covalent bonds, these can reform upon application of a temperature rise (below the melt temperature). There are also some reversible types that will function without temperature increases.

Several reversible bond systems have been identified, two of which currently receive much attention: the supra-molecular polymers based on quadrupole hydrogen bonds *(Fig. 6)* developed by Professor Bert Meijer (Netherlands), and the reversible Diels Alder reactions based on furan-maleimide networks. Quadrupole hydrogen bonds work in the same way as hook-and-loop fasteners: many weak bonds working together to produce effective overall strength.

In both cases, TPE materials were obtained that display thermal healing abilities and also can regain up to

90% of their initial strength by a modest thermal excursion. In contrast to polymers based on the liquid encapsulation routes, in these polymers the healing can be applied many times. The first commercial self-healing material based on this concept has been brought to market by the young Dutch company Suprapolix.

First Applications

While the development of self-healing materials is in a relatively early stage, it's interesting to consider where their first applications will be. As discussed, to make materials self-healing, a drop in common mechanical properties will almost unavoidably result. However, this is fully acceptable if the application of the material leads to either a substantial increase in long-term reliability or performance, or if it is used in applications where repairs are very costly or otherwise undesirable.

Some typical examples include self-healing coatings that retain their pristine appearance even when scratched; satellite components (including seals currently used in the International Space Station); self-healing snow goggles that heal shallow surface scratches overnight; underground polymer pipes; self-healing car interiors that look "as good as new" for many years; covers for IC chips; coatings on train windows; and self-restoring score cards on firing ranges.

Clearly, to advance the technology, application engineers are challenged to come up with new and potentially successful areas where self-healing materials will make the difference. In Japan, civil engineers have already used self-healing concrete containing PVA fibres to build the decks of suspension bridges and the pillars of high-rise buildings in earthquake areas.

Sybrand van der Zwaag is professor at the faculty of Aerospace Engineering at the Technical University Delft in The Netherlands, where he leads a group working on the development of novel materials. Since 2005, self-healing materials have been his primary research interest. He chairs the Dutch research programme in this field and is editor of the book Self-Healing Materials: An Alternative Approach to 20 Centuries of Materials Science.

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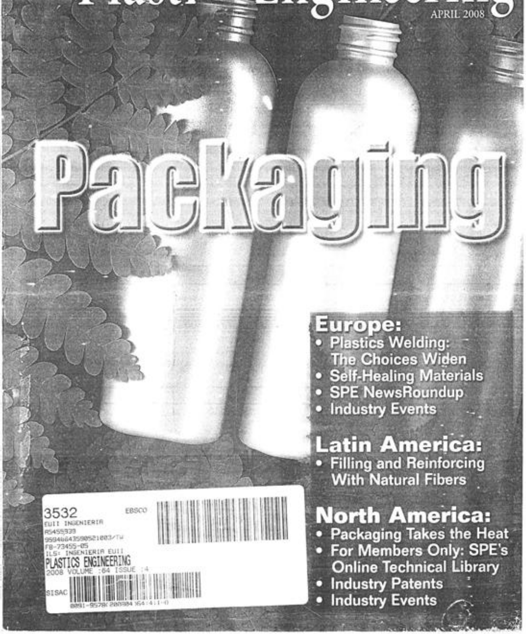

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