DIY repairs

Self-healing mechanisms are being developed for protective coatings

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Self-healing coatings which will repair cosmetic damage have been successfully developed for vehicles. However, there is an increasing need for heavy duty coatings which have similar self-healing properties in respect of corrosion damage etc. Several systems have been developed and are reviewed here based upon the release of materials which polymerise when the coating is damaged.

Self-healing concepts in the field of decorative coatings such as, for example, the elimination of visible scratches through reflow in automobile topcoats, have been a subject of research for decades. This effect is achieved via polyurethane networks that exhibit a dense and flexible structure and rather low glass transition temperatures of about 50–60°C [1]. This technology has reached a high level of performance and is the subject of ongoing improvement.

When considering protective coatings for use in heavy corrosion protection, construction or in surface protection of fibre-reinforced plastics (FRP), no practically usable coating systems have so far been developed with self-healing properties. However, the demand for coatings with excellent durability is tremendous and can best be achieved when self-healing properties are inherent in the system.

Self-healing coatings have many application areas

In Germany for example, the largest share of maintenance costs in the wind-energy sector is spent on inspection and repair of rotor blades and amounts to approximately €160 m per year. [2]. Often, initial damage of the coating leads to further damage of the underlying substrate.

During the next few years, several offshore wind energy plants are to be installed and the inspection and repair of their rotor blades and steel structures will be extraordinarily expensive, so that coatings and structural materials with self-healing functions appear highly desirable. In addition to the wind energy sector, other branches such as the aircraft industry, yacht building and heavy duty corrosion protection would probably benefit even more from the availability of self-healing materials.

Thus, it is not surprising that in the "Forschungsagenda Oberfläche" survey recently carried out by DFO (German Research Association for Surface Treatment) covering future research demands in the field of surface technologies in Germany, the subject of self-healing coatings was identified as one of nine major research issues – as a so-called "Lighthouse topic" ("Leuchtturmthema") [3].

Repair materials can be microencapsulated

In this article the main research activities in the field of self-healing materials are reviewed, excluding systems where materials are leached in order to prevent or stop corrosion processes. The most

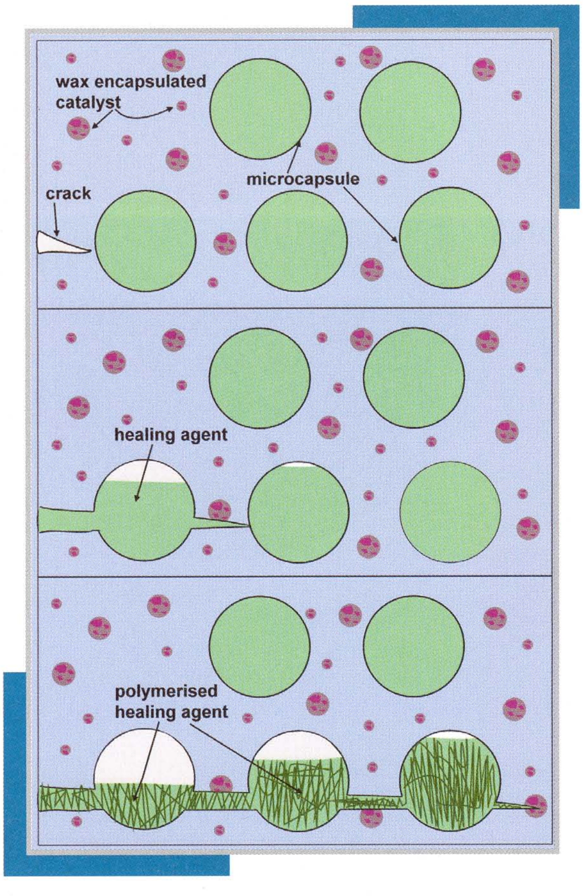

Figure 1: Schematic representation of the self-healing concept

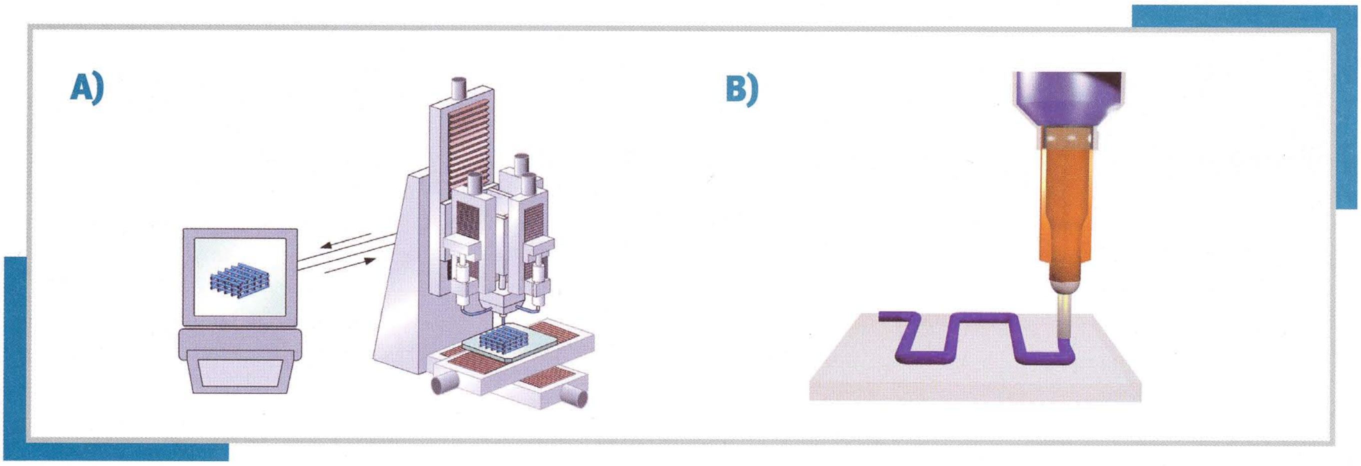

Figure 2: Schematic representations of (a) a robotically controlled deposition machine and (b) robotic deposition of fugitive organic ink (blue) through a cylindrical nozzle onto a moving x-y stage (courtesy of Scott White, University of Illinois)

promising approaches focusing on structural self-healing processes are discussed, together with some results that deal with coating materials based on formulations which are usable in practical situations.

Scott White and *Nancy Sottos* from the University of Illinois at Urbana-Champaign (UIUC) have been working on the development of self-healing materials since the mid-nineties [4]. They designed a composite system where microcapsules filled with liquid monomer are dispersed in an epoxy matrix that also contains a catalyst. As soon as any microcapsule is ruptured by an extending crack, the microencapsulated healing agent is released into the plane of the crack by capillary action, where it is

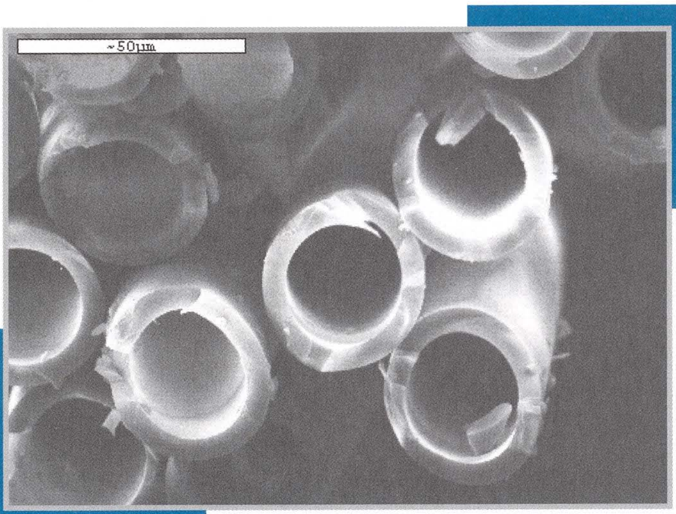

Figure 3: Optical micrograph of hollow borosilicate glass fibres as containers for epoxy hardener and resin (courtesy of Ian Bond, University of Bristol)

exposed to the catalyst and starts to polymerise (see *Figure 1*).

For this approach, dicyclopentadiene (DCPD) was chosen as the monomer as it is liquid at room temperature, has an extended shelf-life and is relatively inexpensive. When the DCPD comes into contact with a wax-encapsulated Grubbs' catalyst dispersed in the matrix, a ring-opening metathesis polymerisation (ROMP) reaction starts and polydicyclopentadiene (pDCPD) is created, which is a tough and highly crosslinked polymer [5].

Recently, a new self-healing system was introduced by White and Sottos, in which the catalyst rather than the monomer is contained in polyurethane microcapsules [6]. The monomers themselves, hydroxyl end-functionalised polydimethylsiloxane (HODMS) and polydiethoxysilane (PDES), are present as microphase-separated droplets in a vinyl ester matrix. The catalyst di-n-dibutyltin dilaurate is released when the capsules are broken by mechanical damage and initiates a polycondensation of the monomers.

Continuous networks refuel healing chemical supply

Where the self-repairing components are incorporated in microcapsules, the supply of monomer could eventually become fully exhausted after prolonged use or upon multiple damage events. To overcome this limitation, Scott's autonomic healing research group developed a microvascular self-healing concept [7].

This approach involves the direct assembly of appropriate organic inks which can be robotically deposited onto a moving x-y platform yielding a two-dimensional pattern (see *Figure 2a*). After one layer is generated, the platform is elevated in the z-direction and another layer with a different orientation is generated (*Figure 2b*). When the desired 3-D structure has been created, the interstitial pore space between the printed features is infiltrated with an epoxy resin.

Upon curing, the ink is removed and a 3-D array of cylindrical microchannels is left behind. Self-healing microvascular polymers are created by incorporating a chemical catalyst in the polymer used to infiltrate the ink scaffold, whereas the healing monomer is filled into the channels. It can be circulated within the structure by hydraulic pressure or simply serve as a supply reservoir for healing when damage occurs.

Hollow fibres may prove advantageous

Ian Bond from the University of Bristol, UK, has developed an approach that is designed to counteract damage in glass fibre reinforced plastics [8]. Hollow fibres (see *Figure 3*) are filled in alternate layers with epoxy hardener or uncured epoxy resin. If an impact to the composite leads to a rup-

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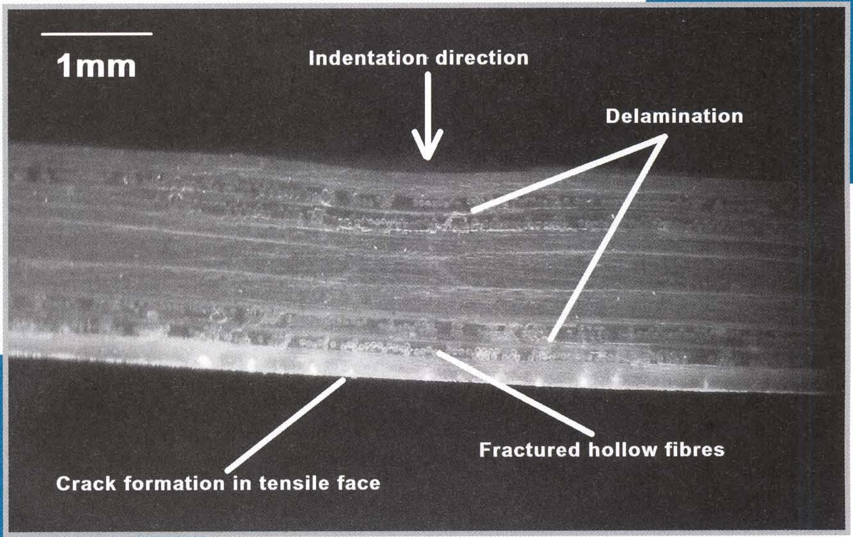

Figure 4: Optical micrograph of cross-section through impact damaged hybrid solid glass/hollow glass/ epoxy laminate (courtesy of Ian Bond, University of Bristol)

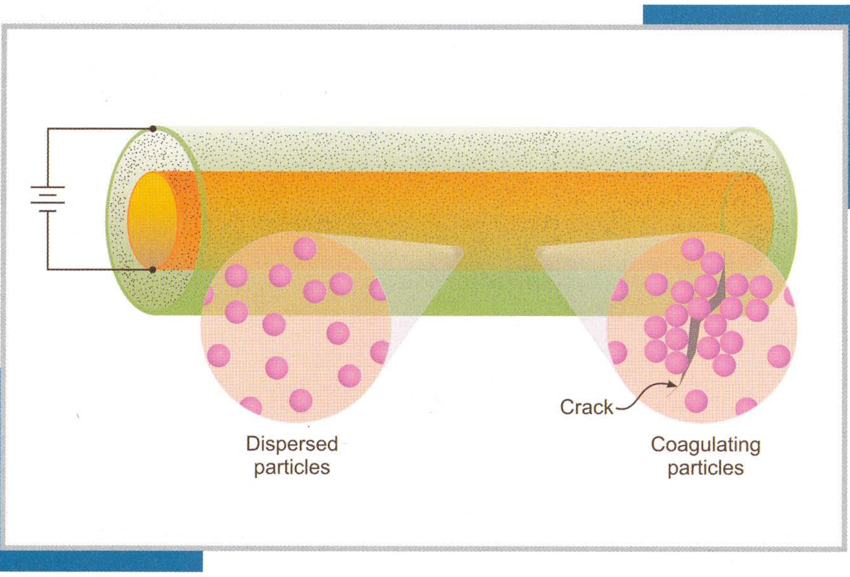

Figure 5: Electrohydrodynamic aggregation of particles (courtesy of Ilhan Aksay, Princeton University)

Several microcapsule systems have been studied

A self-healing corrosion protection coating system for use on steel enclosures for outdoor equipment was investigated by *Kumar* and co-workers [10]. They used urea formaldehyde microcapsules (with a diameter between 50 µm and 150 µm) containing several types of healants and corrosion inhibitors, mixed into commercially available coatings systems.
Tests showed that when damage occurred by abrasion, the microcapsules released the film-forming and corrosion inhibiting substances. In addition, steel substrates were coated and scribed. It could be shown that undercutting at the scribe was reduced by using microcapsules and that crack growth could be stopped. Nevertheless, the performance of some microcapsules was found to be dependent on the method of application.

ture of at least two layers, the components are released, mix and polymerise to give an epoxy resin, so that some of the damage is immediately repaired.
In order to make use of this concept in industry and be able to identify damage immediately after it occurs, a fluorescent dye is mixed with the resin. When the fibres break to release their ingredients this dye is also discharged.
In this way, visual detection of the damage is possible (*Figure 4*) when inspection is carried out under UV light. Further experiments are needed to reveal the extent to which such a self-healing composite could stop minor damage from escalating to critical levels in aircraft and spacecraft applications.

Biological processes are imitated

At Princeton University, *Ilhan Aksay* and *Dudley Saville* are focusing on a mechanism related to the blood clotting reaction in the human body, using a principle based on electrohydrodynamic (EHD) flow [9]. The test system comprises a suspension of colloidal particles which is enclosed between the walls of a double-walled cylinder (*Figure 5*). These walls are coated with a thin conducting layer, followed by an insulating thin film, and are then attached to an electrical power source.
The double-walled electrode formed in this way is activated if the insulating film fails. If the structure is damaged and cracks are formed in the insulating layer, the colloidal particles aggregate at the defect site by EHD flow and thus trigger the first stage of self-healing. An example using this mechanism is shown in *Figure 6*.
In this system, initial damage of approximately 2 mm² in a film (at t_{field} = 1 h) and an applied field (~1.5 V, 100 mA) healed within 10 minutes. After the film was damaged again (t_{field} = 2 h 10 min), healing occurred at the edges of the damaged region after one hour. After two hours under the applied field the damaged region was "sealed". In a control sample no healing took place during the same period.

Recently a research group in Xian, China, managed to encapsulate epoxy resins in poly-(urea formaldehyde) microcapsules. They used DGEBPA (diglycidyl ether of bisphenol A) and BGE (1-butyl glycidyl ether) as resins and synthesised microcapsules with diameters of around 100 µm, a size that potentially allows their use in self-healing systems [11].
In the paint technology group at Fraunhofer IFAM (Institute for Manufacturing Engineering and Applied Materials Research), various options for self-healing coatings with industrial applications were evaluated. One approach included the transfer of the concept developed by Sot-

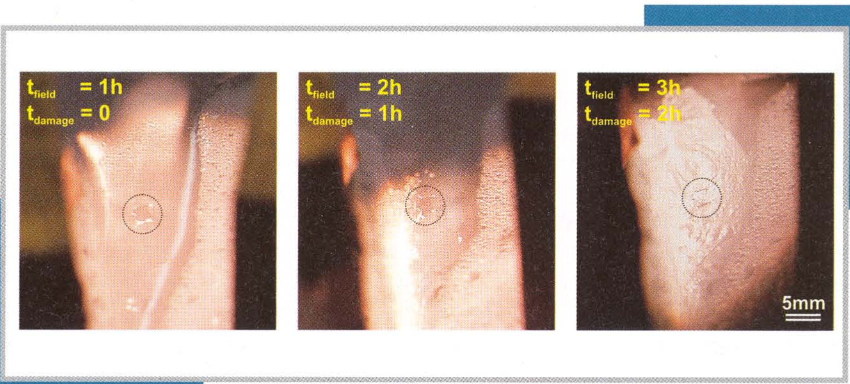

Figure 6:
Healing under an applied electric field (courtesy of Ilhan Aksay, Princeton University)

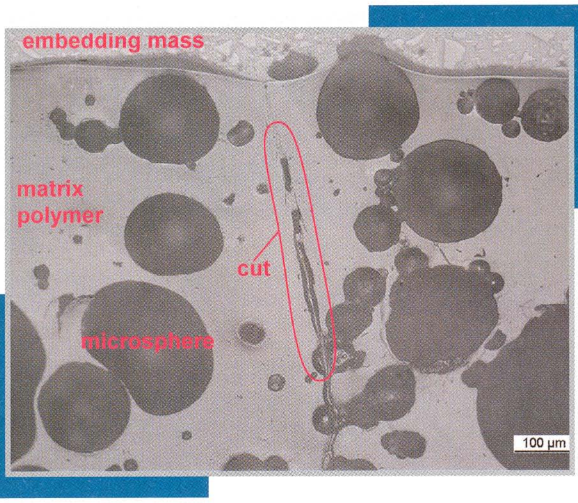

Figure 8: Optical micrograph of transverse cross-section of a polyurethane model paint containing HDI microcapsules (Fraunhofer IFAM, paint technology)

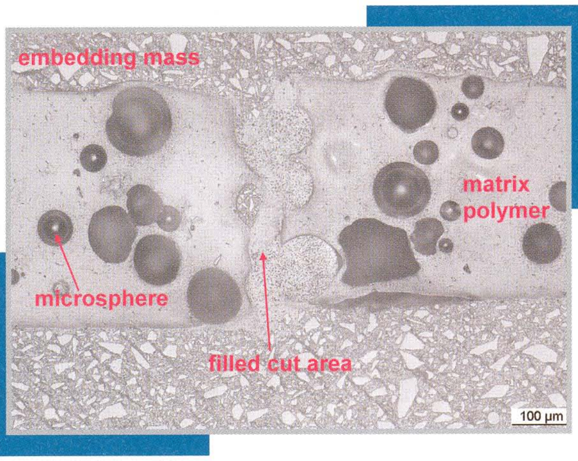

Figure 7: Optical micrograph of transverse cross section of polyurethane paint film (matrix-polymer) with DCPD-microcapsules (Fraunhofer IFAM, paint technology)

tos and White into an industrially relevant polyurethane coating formulation.
Accordingly, dicyclopentadiene was encapsulated in urea formaldehyde and a Grubbs catalyst was encapsulated in paraffin wax. The sizes of the microcapsules and their wall thicknesses were optimised for use in coating systems. These two components were embedded in a polyurethane coating with a layer thickness of about 450 µm.
To prove the self-healing properties of the system, a crack was introduced perpendicular to the substrate surface. Then the free paint film was embedded in an epoxy matrix and a transverse cross-section of the sample was analysed optically and by energy dispersive X-ray analysis (EDXA). A microscopic image is shown in *Figure 7*.
It can be seen that the substance in the cut, which is probably composed of pDCPD, differs significantly from that of the paint matrix. EDXA confirmed the different chemical compositions of the two areas. In principle, a system of this kind might be used in wind energy applications and for coatings in environments subject to heavy corrosion.

A second approach involves the use of encapsulated isocyanates in polyurethane matrices containing dispersed di-n-dibutyltin dilaurate as catalyst. It was found possible to use paraffin wax to encapsulate isocyanates such as TMXDI (tetramethyl-m-xylylene diisocyanate) and HDI (hexamethyl-1,6-diisocyanate) and thus the isocyanates could be protected from reaction during formation of the paint film. When damaged, the capsules release the isocyanates which then react with excess hydroxyl groups in the paint matrix or humidity in the air.
In initial experiments, isocyanate-containing microcapsules were dispersed in a polyurethane model paint and a crack was introduced into the matrix. A transverse cross section of encapsulated HDI in such a polyurethane model paint is shown in *Figure 8*. The appearance of the area in and around the crack suggests that capsule material was released into the crack. Further experiments are necessary to elucidate the system's healing mechanism.

In spite of all the ideas described above, there is still a great need for further research in order to successfully implement industrial applications of self-healing coating systems.

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Results at a glance

- Self-healing coatings which will repair cosmetic damage have been successfully developed for vehicles, but there is also a need for self-healing coatings in heavy-duty and anti-corrosive applications.
- Several such self-repair systems based on the use of encapsulated materials which will polymerise when the capsules are ruptured have been demonstrated.
- Hollow fibres containing repair materials have been similarly used in composites.
- To avoid the risk of the healing compounds becoming depleted over time, a system has been developed in which it is stored in a connected series of channels.
- Further research is needed in order to make these systems effective in practical applications.