ISSN No: - 2456 –2165

Study of Self-Healing Materials and Their Applications

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Abstract-Self-healing materials are a class of smart materials which are inspired by biological systems. They have a structurally incorporated ability to repair damage caused by mechanical usage over time. A material that can intrinsically correct damage caused by normal usage could lower costs of different industrial processes through longer part lifetime, reduction of inefficiency as well as prevent costs incurred by material failure. They were first observed during roman times in mortars however their development began only at the close of the 20th century.

It is a well-known fact that the initiators for structural failures include micro cracking and hidden damages. Repairing at remote locations is taxing and not easy or convenient. This is where self-healing materials have a great potential, thereby increasing the longevity of the structural materials.

The property possessed by self-healing materials have a wide range of applications such as self-healing space crafts, satellites, used for geographical studies, GPS and in Automotive industries.Whenever a living organism experiences a superficial injury like a cut or a bruise, the defence system kicks in and forms a protective layer over it called a scab to begin the repair process. Self-healing materials are analogous to these systems. They have the ability to condition the mechanical damage incurred during any operation. There is tremendous growth in investments being made from both government and private industries.

Keywords:-Self Healing; Regenerative, Electrohydro Dynamics.

I. INTRODUCTION

Cut your finger and it will heal anywhere between a couple of days to a week. Crash your car into a wall or scratch its paint work and you might not be so lucky. This is where self healing materials kick in. Self healing materials are a class of smart materials that can repair or fix small cracks and discontinuities independently or autonomously. Self-healing materials are considered to be the greatest advancement in material science technology. These materials have been inspired by nature where we can observe the regeneration of a broken limb by starfishes or the healing of a tree bark after being injured. This property is observed in all living tissues including human beings where the skin or bones repair and heal themselves after being subjected to cuts, burns or injuries. This property is considered vital for the survival of any living organism and now it can be extended to non living materials as *well.*

From incorporating self healing property in space satellites to using them in making roads that last longer these materials have proved to be very useful by cutting costs, imparting longer life to objects, repairing cracks at hard to reach places, ability to be applied to locations that are not easily accessible etc.

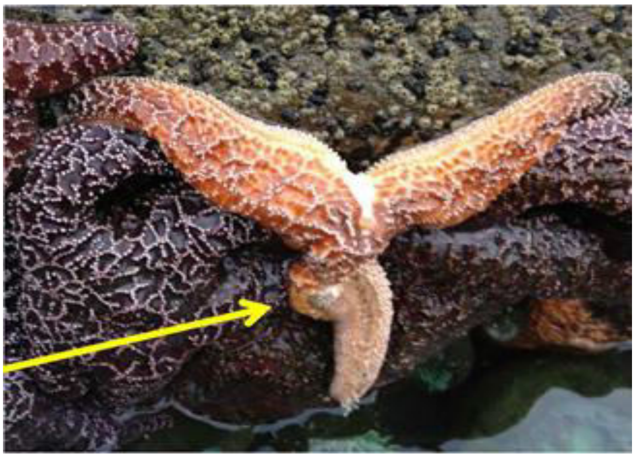

Figure 1- Regeneration of a Limb In Starfish.(Google Images)

Over thousands of years people have tried to make better and stronger materials that wouldn’t fail even after continuous use and variation in loads.The earliest known.

Records of self healing materials date back to the roman ages where this property was used in making certain mortars. Since then there has been a huge advancement in its applications.

In 2011 self healing materials were far beyond the science fiction stage where a type of self healing paints and coatings was introduced that can better survive extreme weather conditions and are also immune to other kinds of surface wear and tear. The best example of this can be observed in Nissan cars that come with a special type of self healing paint called the “scratch shield “.

This clear coat is five times more scratch resistant than a normal clear coat and can also repair small scratches autonomously. A more recent example is stainless steel. It contains highly reactive chromium that forms a protective oxide layer when exposed to scratches thus improving the shelf life of the product.

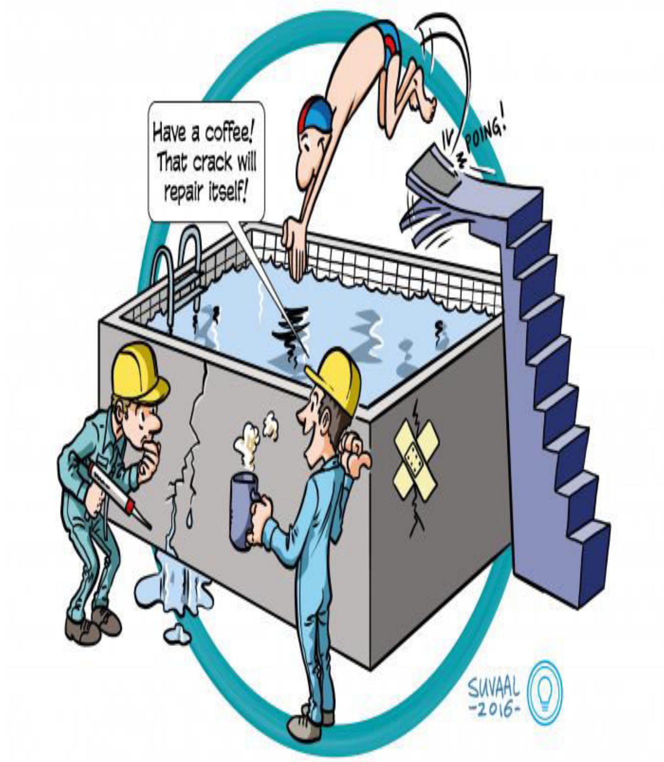

Figure 2 (Google Image)

The self healing property is now being incorporated in various polymers, concrete, ceramics, fiber reinforced composites etc.

These materials are more durable and reliable and function with ease even in extreme load or weather conditions so that they can be used to construct higher buildings or stronger bridges and roads with more load carrying capacity.

Now research is also being conducted to incorporate this property in functional devices used for energy generation (fuel cells, solar cells), energy storage (batteries), light generating devices (LEDs) and in microelectronics.

Figure 3- Self Healing Property Used in Airplane Components.(Google Images)

Testing for cracks in metal parts or objects is tedious, time consuming and very expensive. In non destructive testing the component is immersed in a fluorescent dye for some time and then washed. The dye gets lodged into cracks which will then be detected under UV light. Sometimes the test is prone to human errors also. Undetected cracks in vital airplane components could even cost lives. The best solution to these problems would be self healing materials that could automatically detect internal damage and heal itself up saving time money and in some cases even lives.

II. DESIGN STRATEGIES

The different types of materials such as plastics/polymers, paints/coatings, metals/ alloys and ceramics/concrete have their own self-healing mechanisms. The different strategies of designing these materials include release of healing agents, reversible cross links and miscellaneous technologies like electro hydrodynamics, conductivity, shape memory effect, nanoparticle migration and co-deposition.

Each of these strategies are discussed below:

A. Release of Healing Agents

This process does not need a manual or external intervention, it is autonomic. Liquid active agents such as monomers, dyes, catalysts and hardeners containing microcapsules, hollow fibers, or channels are embedded into polymeric systems during its manufacturing stage. In the case of a crack, these reservoirs are ruptured and the reactive agents are poured into the cracks by capillary force where it solidifies in the presence of pre-dispersed catalysts and heals the crack.

This approach of self-healing material design offers certain advantages, which are as follows:

- Higher volume of healing agent is available to repair damage.
- Different activation methods/types of resin can be used.

- Visual inspection of the damaged site is feasible.
- Hollow fibres can easily be mixed and tailored with the conventional reinforcing fibres.

Besides the above advantages, this approach has the following disadvantages as well:

- Fibres must be broken to release the healing agent.
- Low-viscosity resin must be used to facilitate fibre infiltration.
- Use of hollow glass fibres in carbon fibre-reinforced composites will lead to CTE (coefficient of thermal expansion) mismatch.
- Multi step fabrication is required.

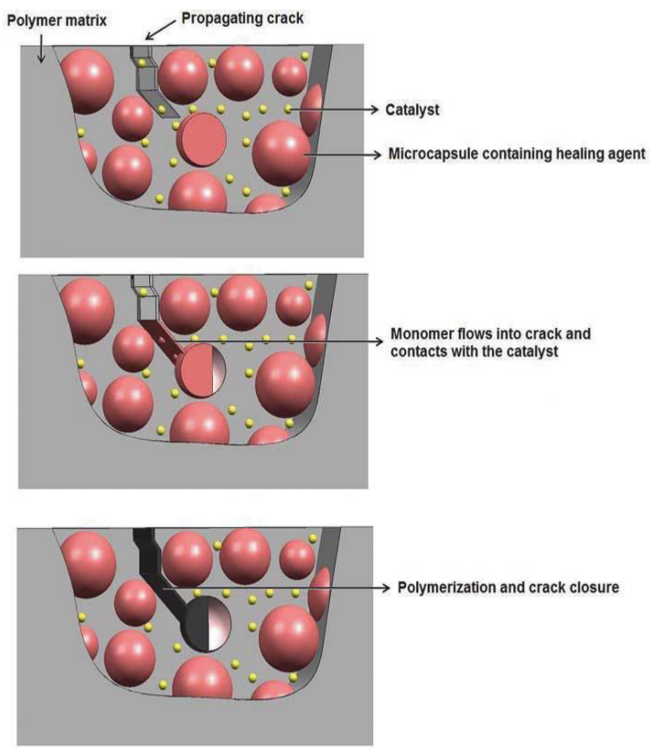

Figure 3- Schematic Representation of Self-Healing Concept Using Embedded Microcapsules.(Google Images)

B. Reversible Cross-links

Cross-linking is an irreversible process performed to achieve superior mechanical properties, such as solvent resistance and high fracture strength. However, highly cross-linked materials are prone to brittleness and have the tendency to crack, it. One remedy to obtain processability of cross-linked polymers is the introduction of reversible cross-links in polymeric systems. In addition to re-fabrication and recyclability, reversible cross-links also exhibit self-healing properties. However, reversible cross-linked system does not show self-repairing ability by its own. An external trigger such as thermal, photo, or chemical activation is needed to achieve reversibility, and thereby the self-healing ability. Thus, these systems show non-autonomic healing phenomenon.

C. Miscellaneous Technologies

i) Electrohydrodynamics

In this approach, the blood clotting process was imitated via colloidal particle aggregation at the defected site using the principle of electrohydrodynamics (EHD) flow to design self-healing materials. By suspending colloidal particles which are enclosed between the walls of a double-walled metallic cylinder. The walls of this cylinder are coated with a conductive layer followed by a ceramic insulating layer. A concentric metal wire is used to apply electric field to this system. When damage occurs in the insulating layer, the current density at the damaged site is increased causing an agglomeration of the colloidal particles at the defected site through EHD flow. The aggregation of particles is insufficient to heal the defects as the voids between colloidal particles prevent formation of a dense surface. Usage of polymeric colloidal particles or a sacrificial anode for simultaneous electro-deposition of metal at the defect site to achieve better healing efficiency.

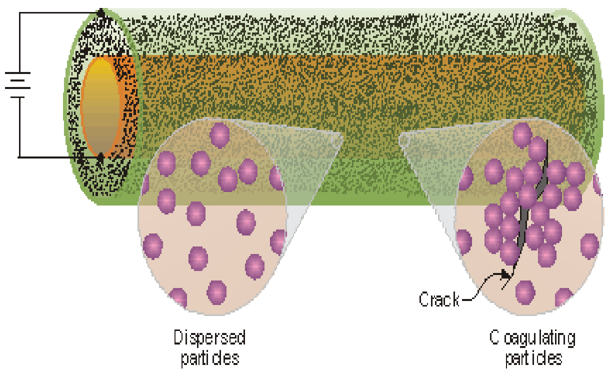

Figure 4- Electrohydrodynamic Aggregation of Particles (Google Images)

ii) Conductivity

Polymeric materials are insulators. By imparting conductivity into polymeric systems these materials can be made suitable for electronic applications. Materials having conductivity as well as self-healing capability might be advantageous especially in deep sea or space applications. The conductivity, on the other hand, can also be used for inducing self-healing properties in polymeric systems. Organometallic polymers based on *N*-heterocyclic carbenes and transition metals have been used to design electrically conductive self-healing materials. When a micro crack is formed in a system, it decreases the number of electron percolation pathways and thereby increases the electrical resistance. If an electrical source is connected, this drop in conductivity can be triggered to increase the applied electric field. Thus, if the rise in resistance is due to micro- cracking, then this voltage bias can generate localized heat at the micro crack, which can force the system back to its original state, that is, low resistance/high current situation. The organometallic polymeric systems based on *N*-heterocyclic carbenes and metals can be reversibly formed, which meet the conductivity requirements that make them suitable for self-healing applications.

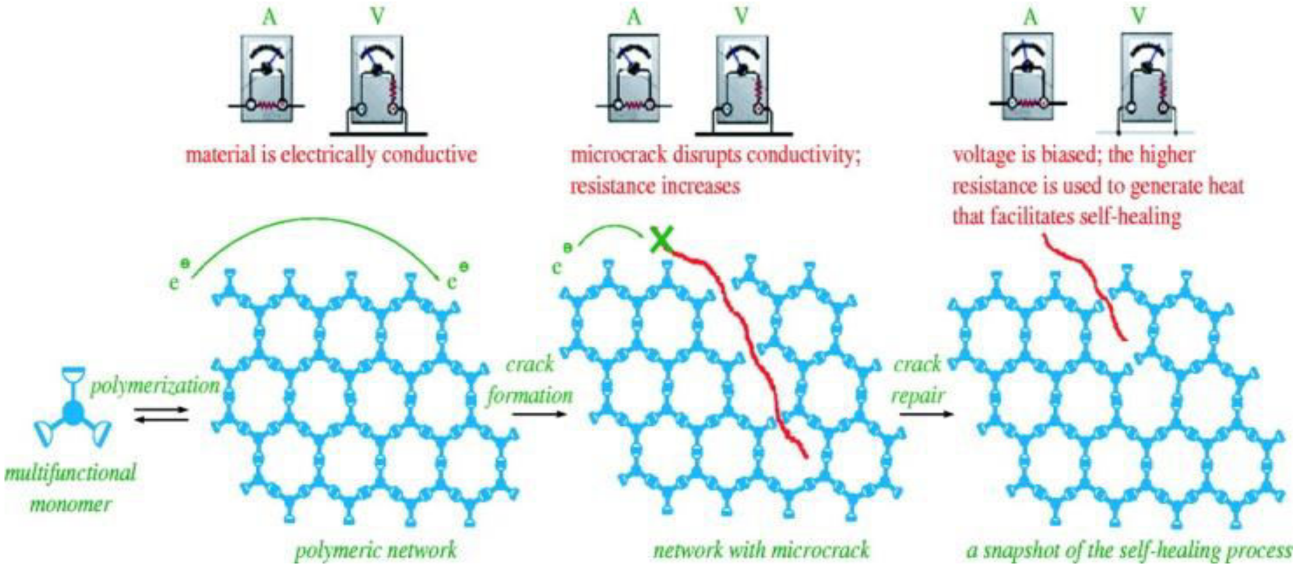

Figure 5- Conductive Self-Healing Materials (Google Images)

iii) Shape Memory Effect

Most of us know shape memory materials through relatively trivial everyday applications such as eyeglasses, made from alloys like nitinol (nickel-titanium), that flex exactly back to shape when you bend and then release them. Usually, shape memory works in a more complex way than this; typically you need to heat a material to make it snap back to its original, preferred form. Self-healing shape-memory materials therefore need some sort of mechanism for delivering heat to the place where damage has occurred. In practice, that might be an embedded network of fibre optic cables similar to the vascular networks used in other self-healing materials except that, instead of pumping up a polymer or adhesive, these tubes are used to feed laser light and heat energy to the point of failure. That causes them to flip back into their preferred shape, effectively reversing the damage. When the material cracks, it also cracks the fibre-optic tubes embedded inside it so the laser light they carry leaks out directly at the point of failure. Systems like this are sometimes known as autonomous adaptive structures and have been pioneered by materials engineer Henry Sodano.

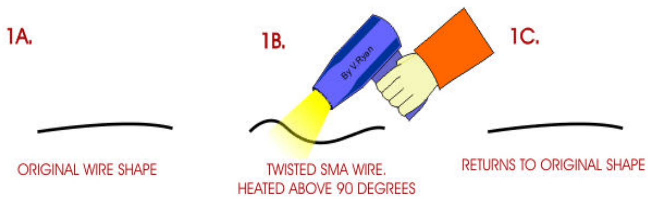

Figure 6- Shape Memory Effect in Wires (Google Images)

iv) Nano-Particle Migrations

Scientists have demonstrated that nanoparticles in a polymer fluid can segregate into cracks due to the polymer-induced depletion attraction between the particles and the surface. Self-healing materials based on the above approach areyet to be demonstrated. Incorporation of nanoparticles into polymeric systems has twofold benefits: it increases the mechanical strength of the system and also segregates to the crack surface. Carbon nanotube is a potential candidate for developing self-healing materials based on this approach due to its superior mechanical properties compared to other particles.

V) Co-Deposition

Electrolytic co-deposition can be employed to design self-healing anticorrosive coatings. Microcapsules containing corrosion inhibitors can be added to composite plating coatings by this method. Either liquid corrosion inhibitors or mesoporous nanoparticles containing absorbed corrosion inhibitors can be used as the core material to synthesize micro or nanocapsules. These capsules can be later deposited with metallic ions such as Zn+2 and Cu+2 to form composite metallic coatings. Upon crack formation in the composite layer, the capsule can release its contents to heal the crack.

III. APPLICATIONS

Self healing materials have done more than only changing our view of materials development – from improving materials towards healing materials.

A branch where self healing materials can play a key role is in construction, for example, to combat decay of reinforced concrete. This means that even a small improvement – for instance, an extension of the period in between two repairs – will give major savings. Also in the field of corrosion, costs can be decreased by using self healing materials, for instance, by applying self healing anti-corrosion coatings onto metal equipment of chemical plants. About 30 per cent of these costs can be prevented or saved by optimizing the corrosion approach.

A few more applications where such materials can be used are discussed here on.

1. At sea-During the transhipment of liquefied natural gas (LNG) in a harbor, variations in temperature between ambient temperature and -162 °C may lead to thermal fatigue of the transport line. Self-healing and also gastight layers in the multilayer pipes are desirable, as currently these lines only last a few times before they have to be replaced due to a too low gas tightness. Since these lines do not transport LNG continuously, the time in between two transports can be used very well to heal.

- High voltage cables at the bottom of the sea need good protection. Even the smallest crack in the sheath can give rise to the highly undesired situation that the surrounding seawater eventually reaches the power cable. Use of self-healing polymers in the sheath may be the solution. For example, polyacrylates, which are released when the sheath gets cracked and immediately react with water to an impervious layer and stop the cracks from further development.

- In offshore industries – for deep sea research or monitoring of oil and gas wells – there is a need for application of self-healing materials at so-called ‘umbilicals’. These are complex cables that are used for bringing power supply, data signals, hydraulic pressure or lubrication liquids to and from submersed systems. They have to withstand a high external pressure and endure many movements and loads, to prevent seawater from penetrating the umbilicals. Self-healing materials may prevent such a penetration by being able to repair fatigue cracks, or by making use of coatings that can repair damage by expansion or filling up.

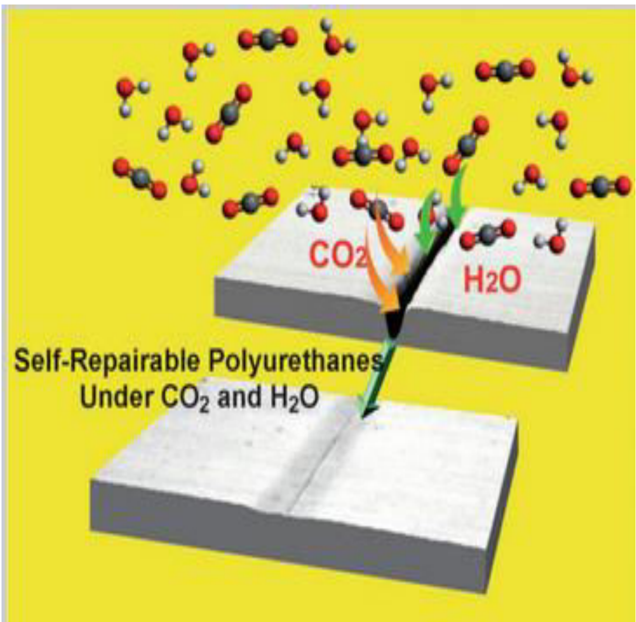

Figure 7- Self Repair in The Presence of Water (Google Images)

2. In residential areas-To extend the lifetime of asphalt roof covering, oil-containing capsules are embedded in the bituminous binder. Due to the application conditions, the bitumen becomes somewhat rigid. When a micro crack in the bitumen further develops and enters a capsule, oil flows into the crack. Diffusion of bitumen and oil rejuvenates the asphalt, decreasing the stiffness of the bituminous binder.

- White plastic garden chairs or window frames turn yellow as time goes by due to exposure to UV radiation in sunlight. To maintain their colorfastness during their entire lifetime, polymers with ‘self-healing colors’ can be used, where the self-healing capacity is present in fillers or in the polymers themselves. Wooden garden chairs or window frames can be protected in a sustainable way using self-healing paint coating systems.

- Self-healing joints in fittings in waterworks or sewer systems that become active at the moment a leakage is imminent, or leaking cracks in the sewer that close themselves using self-healing polymers. Hydrolysis sensitivity is relevant for these tubes, and the deterioration of the (polymer) material by the internally or externally present water can be prevented or repaired using suitable polymers.

- To limit the consequences of (ground) water penetration in brick walls of buildings - especially underground - expensive maintenance is necessary. These activities can be reduced to a large extent by applying once-only a coating onto the walls which forms a water-impermeable barrier after getting in contact with water. As an alternative, the particles from that coating can be incorporated once-only in the brickwork.

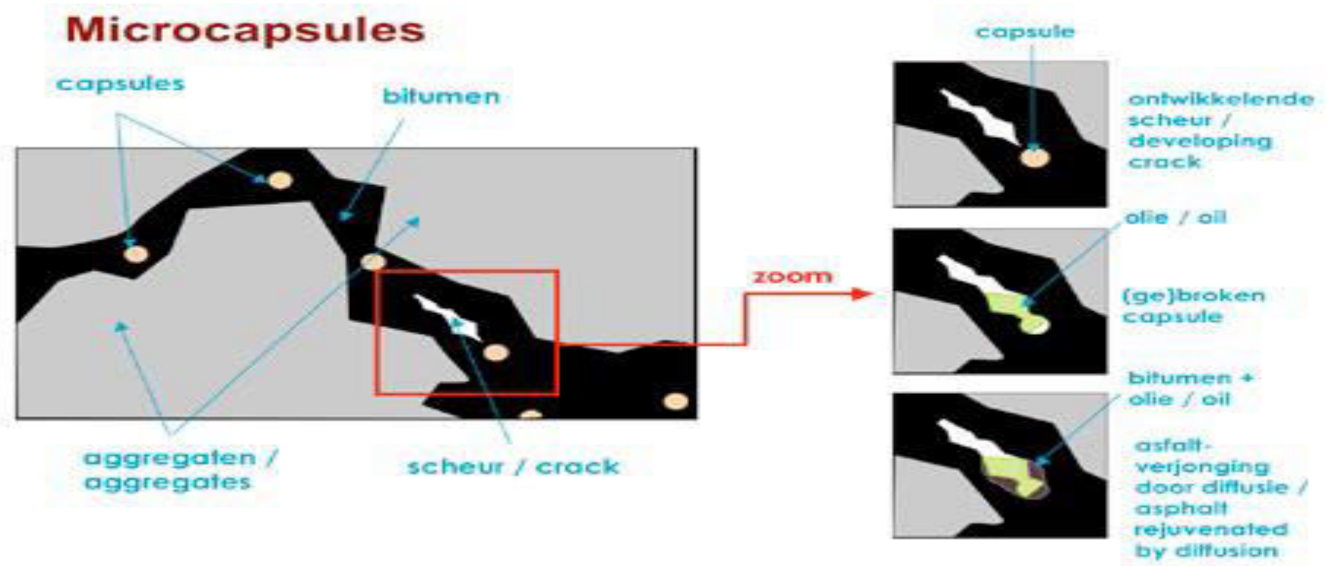

Figure 8- Self Repair in Asphalt (Google Images)

3. Traffic and general Transportation-Scratches on self-healing train or car windows will disappear by heating for a short time. It will also be possible to apply a transparent self-healing coating on the window glass which flows out very slowly when a scratch triggers the material.

- The transparent topcoat on a car can retain its gloss by incorporating 'dormant' reactive groups in this layer which render the layer a self-healing character under the influence of UV radiation from sunlight (As shown in the figure). One step further: the barrier properties of such a layer can be improved by using the action of (rain) water as a trigger.

- Not only asphalt, but also signs on the road surface have to endure much due to alternating loads: traffic, the weather, expansion or shrinkage of the road surface substrate to name a few. Self-healing road paint can make an end to the deterioration or peeling-off of these signs

- Partly inspired by weight reduction - and consequently a decrease in fuel consumption -polymers and composites more and more replace metal bodywork parts of cars like front-ends. By applying self-healing polymers, the lifetime will increase even more. Also interior parts and motor engine parts of the car benefit from self-healing polymers. Both the lifetime - long-term repair - as the tension retaining capacity - short-term repair - of V-belts in car engines can be improved by using self-healing materials.

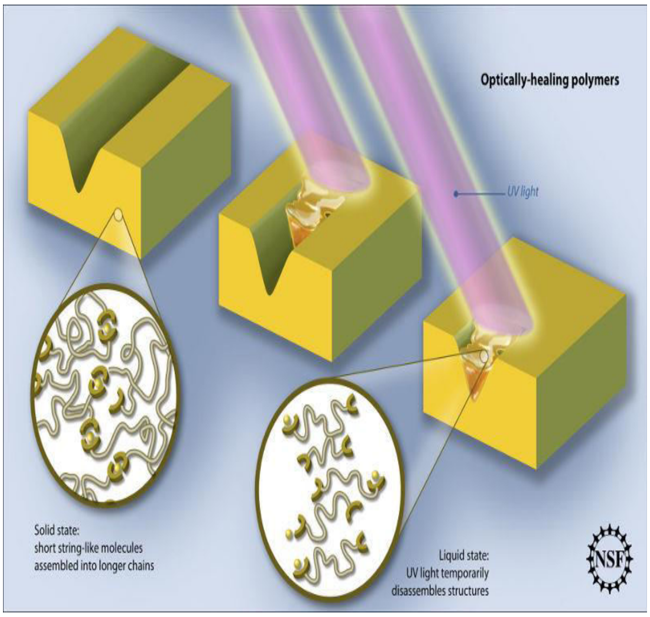

Figure 9- Self Repair with UV rays (Google Images)

4. Sports-Small scratches in (plastic) spectacle lenses lead to light scattering, disturb the view and reduce safety. So there is a need for lenses that retain their clearness, where small scratches disappear, by placing the spectacle – and also ski goggles – at night on the radiator of the central heating system.

- Despite the incorporated UV stabilizer, a safety helmet made of polycarbonate has a lifetime of about 5 years due to the action of heat and UV radiation. It is desirable to extend the maximum lifetime with several years, where the self-healing capacity of suitable polymers prevent – or at least delay – the increasing brittleness of the helmet.

- Finally, to end with a typical Dutch application: a self-healing bicycle tire would be a relief for many cyclists. In such a tyre, self-healing ionomers can be part of the rubber network. As an alternative, allow the tyre to repair itself with for example, pressure, light, air or heat as aid: use pressurized nitrogen inside the tyre to react with modified rubber to close the puncture.

- A small stone in the snow can easily result in a scratch on the gliding surface of a ski or snowboard. A self-healing material just below this surface that reacts through the scratch with 'reactive' oxygen from the air can restore the functionality of the original gliding surface.

IV. CONCLUSION

Self healing materials can be of great value for society and economy, most certainly for top sectors such as chemistry, high-tech and energy. They not only reduce maintenance costs but also promote sustainable manufacturing and construction, because the life span of a road, tunnel or airplane increases strongly when cracks 'vanish' spontaneously! Even under unpredictably heavy conditions.

We can predict that in the future, self healing materials will be found mainly in places where reliability and durability are essential. These aspects are especially relevant in constructions that can be difficultly accessed and repaired (at high altitude, under water, underground) or that have to maintain an intact surface with a protective or aesthetic function. And also in installations that have to comply with high safety requirements (as in aviation) and applications where large repairs result in social hindrance (like roads).

Figure 10- Self Healing Artificial Skin-Considered To Be Science Fiction in 1984 Being Depicted In the Movie Terminator (Google Images)

Currently the Netherlands are the front runners in developing new materials that can easily self heal. Several innovation oriented research programs with the aim to make the research world more accessible to industry and to improve and intensify contacts between research world and business community have been set up by the Dutch government. At present research is being conducted at several top universities, non-profit research centers and various companies that will fulfill the long term needs of the manufacturing industry. Now other countries like America, Germany, England and a few other EU countries have also started setting up research facilities devoted to improving and extending the self healing property to various materials. A lot of international research and interactions are underway that will undoubtedly lead to interesting new developments.

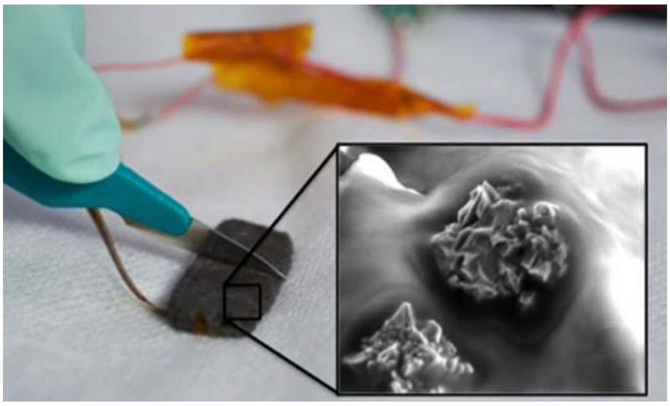

Figure 11- Artificial Self Healing Skin Being Developed By Scientists At Stanford University in 2016 (Google Images)

One day we are sure to see self healing materials being mass produced the first of which could be a class of self healing coatings and paints. It is not difficult to imagine that more advanced self healing materials will be likely to follow on. We could also have replacement parts for the human body that can heal themselves faster than their natural equivalents. At that point, the science of self-healing will truly have come round full circle.

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