Journal of Metallurgy and Materials Science, Vol. 61, No. 3, July-September 2019, pp. 151-160
Printed in India, © NML, ISSN 0972-4257

Typical self-healing materials - their mechanism and emerging applications

SWAPNIL B. DARJI*, DILIPSINH M. ZALA, UPENDRA P. RAJPUT, VANDANA J. RAO and A. K. VAISH
Department of Metallurgical and Materials Engineering,
The Maharaja Sayajirao University of Baroda, Vadodara-390001

Abstract : Any biological system in the world has its own mechanism of response towards cuts and cracks. Whenever there is an injury, it appears as wound and the biology starts the inflammatory (immediate) response followed by cell formation and matrix remodeling. This is kind of a long-term process. It provides perfect healing in the biological system (such as human-bodies, plants, trees etc.). Considering this phenomenon as the source of inspiration, a new kind of materials have been developed, which can response to the damage by their self and repairs known as 'self-healing' materials. Whenever and wherever the damage (crack, cut, rupture etc.) appears in the material, it triggers the healing mechanism and repairs the damage cracks or notches by chemical repair. This is kind of short-range process than biological one. To date, self-healing is demonstrated mainly in polymers and composites by three conceptual approaches namely capsule based healing system, vascular healing system and intrinsic healing system. It can be automatic without human intervention or may require some external energy or pressure. The synthetic self-healing systems work as three-step process. The first response towards the damage is triggering (actuation).The second response is transport of materials to the site of damage. The third response, analogous to matrix remodeling. This is the chemical repair process. Application of the self-healing martials is expected in all fields of science in the future. The very few developed applications to date are mainly in automotive, aerospace and building industries. An attempt has been made to discuss the mechanism of typical self-healing materials and their emerging applications.

Keywords : Self-healing, Mechanism, Biological system, Damage, Matrix remodeling.

INTRODUCTION

In regular practice mostly we observe three stages of material life - Development, Use (Degradation) and failure. During usage of materials when it degrades (for example crack is generated) its remaining life decreases, to increase its remaining life first it is required to check what type of degradation has taken place in material and after that proper repairing procedure is required to carry out. In many cases such type of practice is observed. Inspired from nature self-healing type of materials are developed, in which above mentioned process is not required to carry out, material itself detects crack and heals automatically (known as Autonomic healing) or with some little external input (Ex. Heat)[1]. As in biological systems we observe that materials are able to recover themselves and regain their functionality by using resources inherently available to them. Keeping this idea in mind self-healing materials are developed which are longer-lasting in both regular and fatigue load conditions[2].

Healing process in biological system follows three steps- inflammatory response : blood clotting, cell proliferation and matrix remodeling. Inspired from this self-healing materials also have three stages of healing process - triggering, transport and chemical repair. In synthetic system firstly healing process is actuated by triggering, that involves rupturing of embedded micro capsules immediately. Second stage involves transport of chemicals (known

**Corresponding Authors Email : sbdarji@gmail.com*

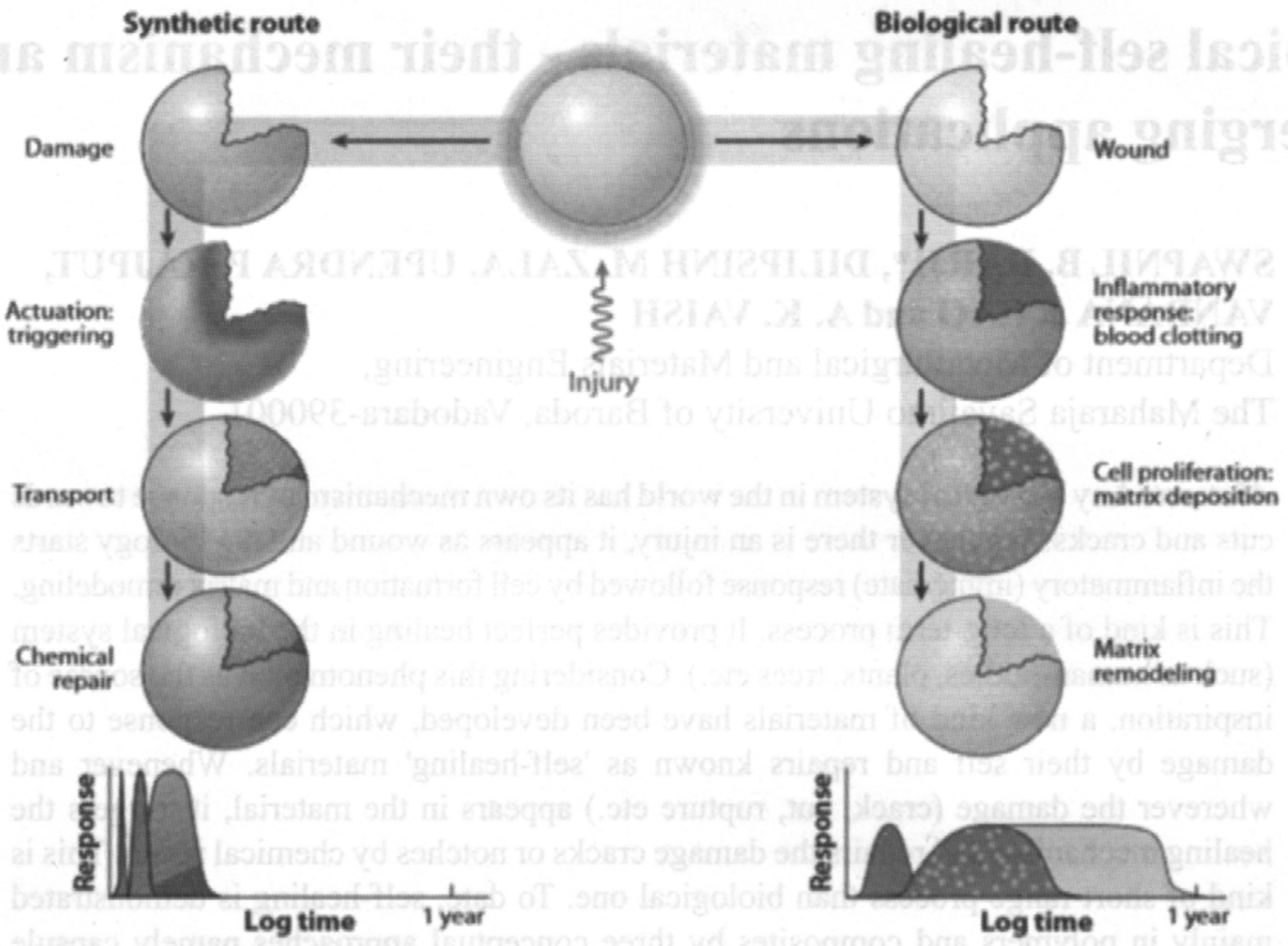


Fig. 1 - Synthetic and biological routes to healing[1]

as healing agent) to the place of crack, this occurs at relatively rapid rate. In third stage actual repairing takes place with the help of chemical reactions, this may take some time. Biological and synthetic healing process is shown in Fig. 1 with time required for each stage.

There are many types of self-healing materials among them mainly cementitious materials, polymers and polymeric composites are discussed. In many of them mechanism of self-healing remains almost same but healing agent may differ accordingly. Sometimes new technique or mechanism can also be adopted according to materials. But encapsulation based self-healing technique is the most common technique.

BASIC REQUIREMENTS OF HEALING AGENTS

Irrespective of the type of material there are some basic requirements which should be fulfilled by healing agents and capsule wall, since these are not necessary requirements some healing agent can have different behavior then mentioned. Healing agent requirements - (a) should release upon requirement. (b) Should be able to encapsulate within carrier. (c) After crack repairing strength should be sufficient to prevent reopening of crack. (d) Should have proper viscosity which decides encapsulation and flow after capsule rupture. Desirable properties for wall of capsule - (a) It shouldn't rupture unnecessarily (b) Should release on requirement (c) Should have proper strength which prevents unnecessary rupture and at the same time ruptures when crack propagates.

SELF-HEALING MATERIALS - THEIR MECHANISM

Self-healing in cementitious materials

In normal cementitious materials many times it is observed that natural process can partially repair concrete cracks[3]. Healing process is believed as combination of complex chemical and physical process. Several possible natural self-healing process are named below. In Fig. 2 graphical explanation is given of possible natural self- healing mechanism.

(a) Calcium carbonate or calcium hydroxide formation
(b) Blocking cracks by impurities in the water
(c) Further hydration of the unreacted cement or cementitious materials
(d) Expansion of the hydrated cementitious matrix in the crack flanks(swelling of C-S-H).

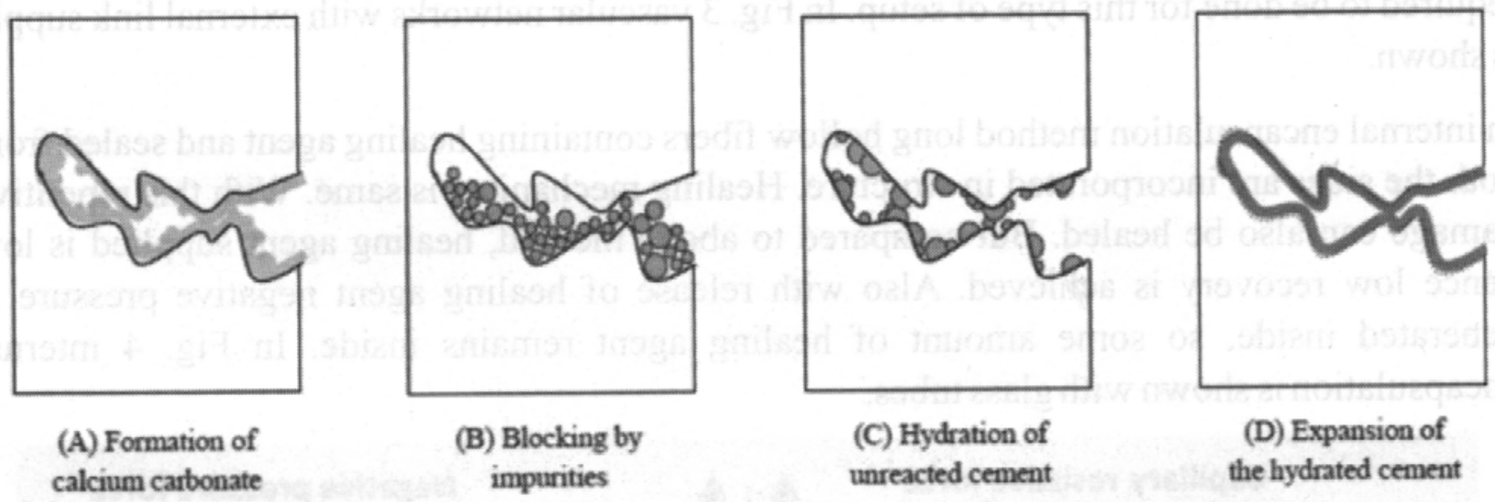


Fig. 2 : Possible mechanisms for natural self-healing in cementations materials[3].

Apart from natural self-healing process following are several other techniques or mechanism with which cementitious materials can be self-healed

(a) Encapsulation
(b) Expensive agent & Mineral admixtures
(c) Bacteria
(d) Shape memory materials

a) Encapsulation

In this method healing agent is encapsulated within capsule. Upon cracking when crack tip reaches capsule wall, it gets ruptured releasing healing agent. Released healing agent "transports" to crack surface and healing process starts, with completion of healing process majority of strength is recovered. Non-diluted alkali-silica solution and two-component-blended-low-viscosity epoxy resin are some of the examples of healing agents used for cementitious materials self-healing. There can be different strategies of encapsulation as follows :

(a) Vascular networks with external link to supply
(b) Internal encapsulation
(c) Microcapsules

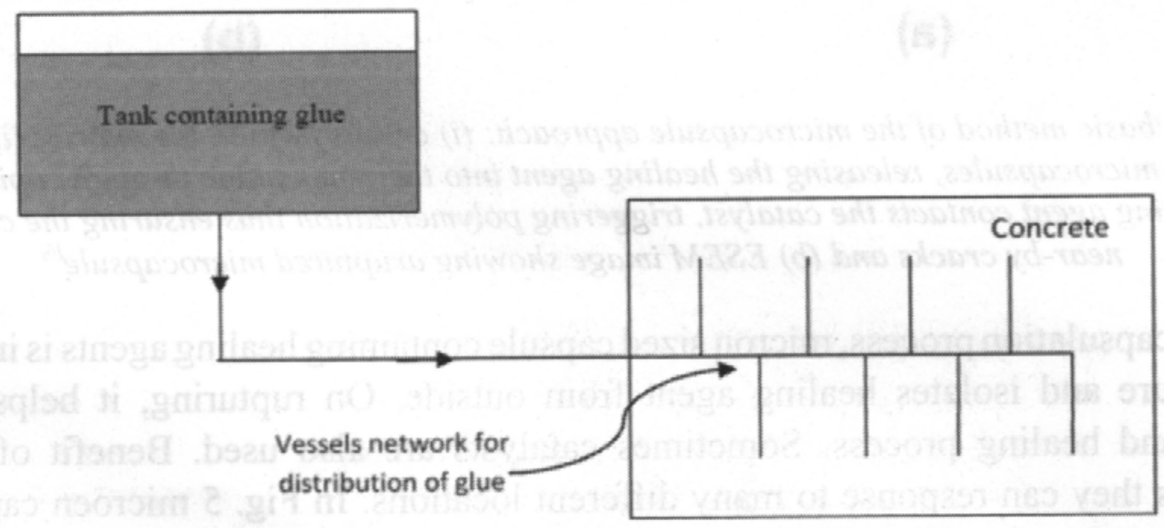


Fig. 3 : Schematic diagram for vascular networks[3]

In vascular networks with external link to supply, healing agent is supplied externally to vascular networks of hollow fibers spared across the cementitious structure. As discussed previously, crack approaches hollow fiber and fiber gets ruptured and healing agent is released. Hollow fiber is sealed from one side and from the other side fiber is connected to supply source. One benefit of this type is high recovery of structure, counter to that external arrangement is required to be done for this type of setup. In Fig. 3 vascular networks with external link supply is shown.

In internal encapsulation method long hollow fibers containing healing agent and sealed from both the sides are incorporated in structure. Healing mechanism is same. With this repetitive damage can also be healed. But compared to above method, healing agent supplied is low hence low recovery is achieved. Also with release of healing agent negative pressure is generated inside, so some amount of healing agent remains inside. In Fig. 4 internal encapsulation is shown with glass tubes.

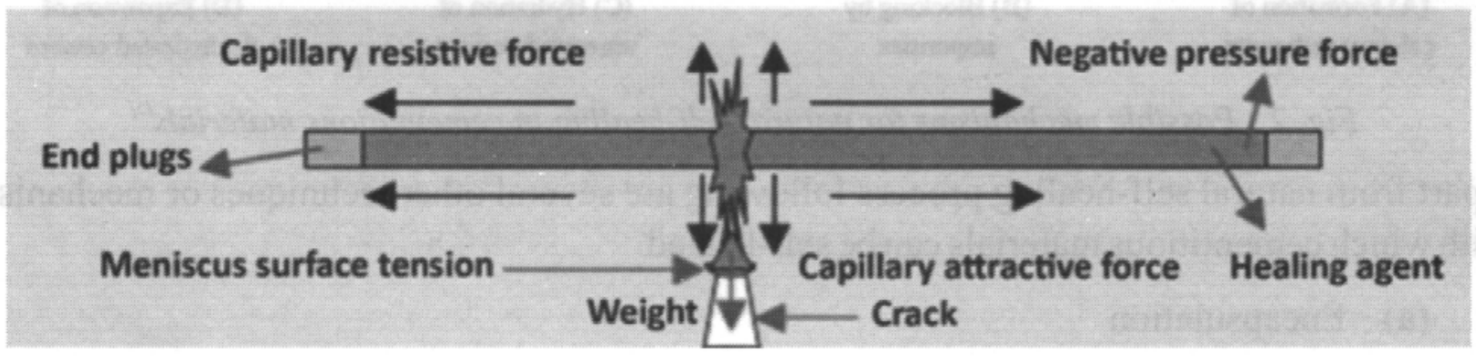


Fig. 4 : Self-healing system of internal encapsulation method with hollow glass tubes Middle section view[9]

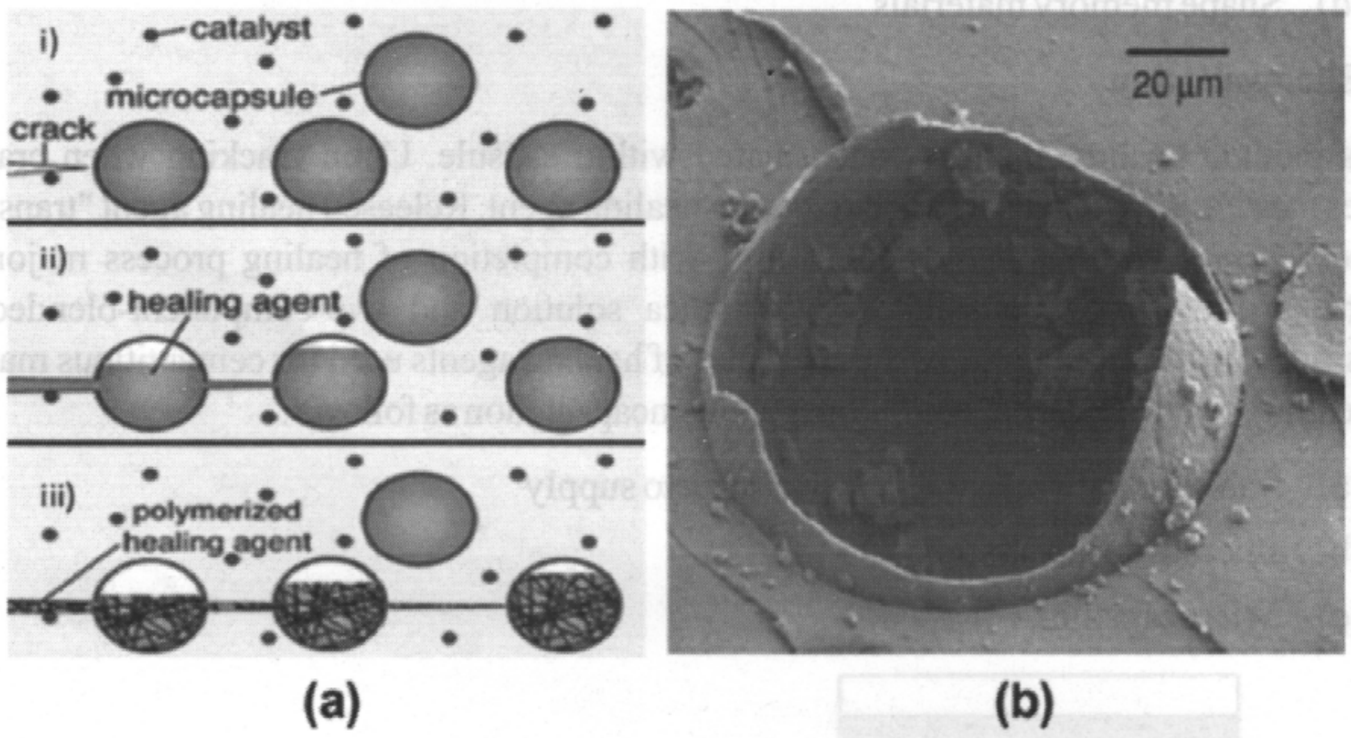


Fig. 5 : (a) basic method of the microcapsule approach: (i) cracks form in the matrix; (ii) the crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; (iii) the healing agent contacts the catalyst, triggering polymerization thus ensuring the closure of the near-by cracks and (b) ESEM image showing aruptured microcapsule[6]

In micro encapsulation process, micron sized capsule containing healing agents is incorporated with structure and isolates healing agent from outside. On rupturing, it helps in further hydration and healing process. Sometimes catalysts are also used. Benefit of using this technique is they can response to many different locations. In Fig. 5 microen capsulation is explained with diagram and ESEM image is also shown.

b) Expensive agent and mineral admixtures

It was observed that with the addition of some expensive agents like $CaSO_4$, CaO (lime) up to some limit and its combination with some mineral like SiO_2, Al_2O_3, geo materials etc. will improve self-healing property. For example it was observed that with the addition of 10% C_4A_3S, $CaSO_4$ and CaO (lime) in regular cement 0.22mm crack was almost cured in 1 month due to rehydration. Also with the addition of carbonates like $NaHCO_3$, N_2CO_3, Li_2CO_3 in regular concrete increases cementitious recrystallization and precipitated particles in concrete. So with the addition of expensive agents self-healing property can be enhanced but sometimes it hydrates with the addition of water in pre-mixture, to prevent it encapsulation of expensive agent can be helpful.

c) Bacteria

This is biological self-healing process. In this type of self-healing mechanism bacteria induced carbonate precipitation is used. Since this is biological process, it is affected by many parameters like environment, PH, concentration of calcium ions etc. higher alkaline environment hinders growth of bacteria. In Table 1 list of different bacteria is given. In Fig. 6 Microbial precipitation of calcium carbonate at crack is shown.

Table 1 : List of microorganisms applicable for developing self-healing concrete[3]

Self-healing mechanisms	Name of References microorganisms
Ureolytic process	SporosarcinaPasteurii (or Bacillus Pasteurii)
	Bacillus megaterium
	Halomonaseuryhaline
	Myxococcusxanthus
	Bacillus sphaericus
	Bacillus lentus
	Slime-producing bacteria
	Acinobactersp
	Escherichia coli
	B. Cohnii

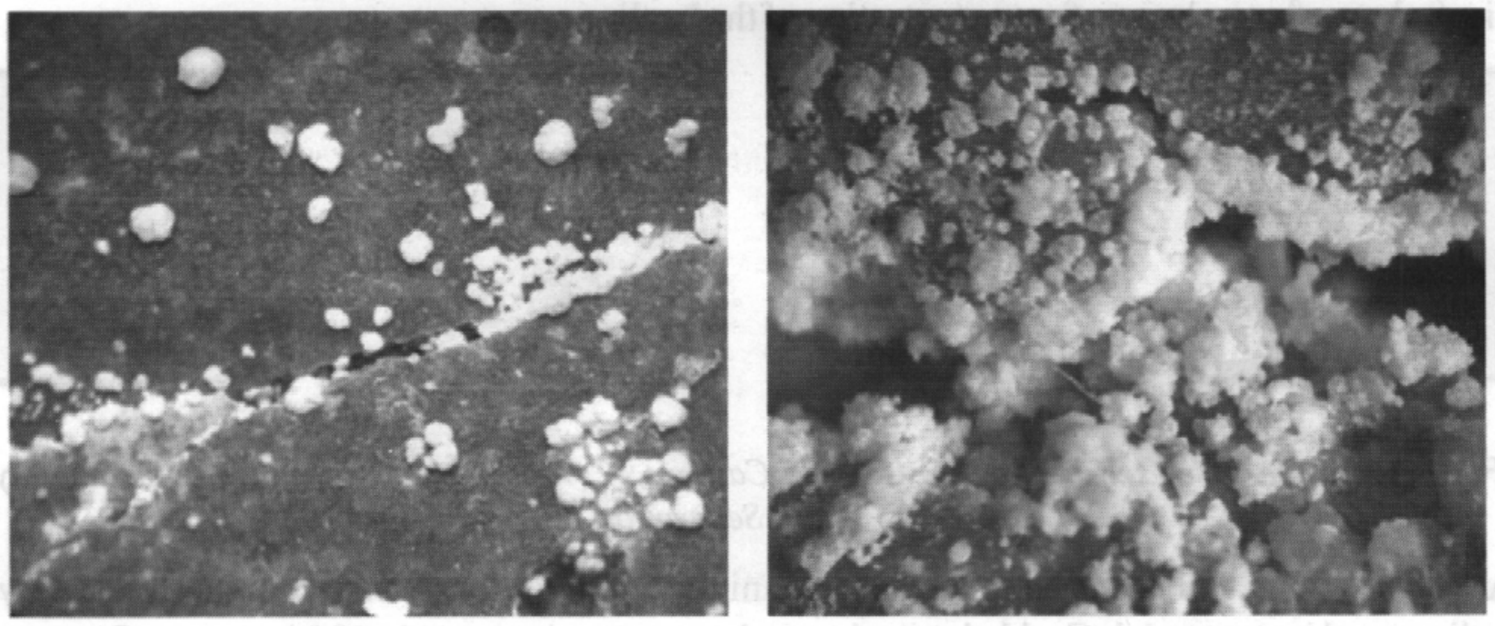


Fig. 6 : Microbial precipitation of calcium carbonate around of a concrete crack[3]

d) Shape memory materials

In this strategy shape memory wires are incorporated in the structure with elongated length than original one. Strain distribution in system can be detected by knowing resistance of wires. When crack is detected, strategy is to shrink shape memory wires along with which concrete will also move and crack will be joined. This can be achieved by heating wire with the help of passing current through it. This can handle macro-sized crack.

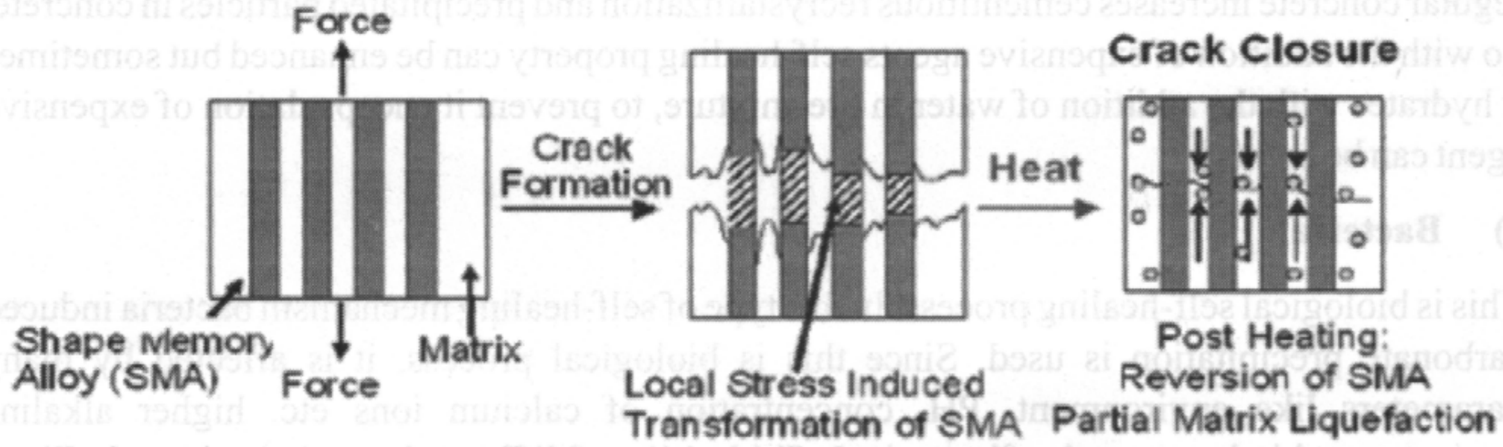


Fig. 7 : Schematic of the proposed mechanism for healing using SMA reinforcement[8]

Self-Healing in polymer and composites

Almost all types of polymers like thermosetting, thermoplastic and elastomers have potential for self-healing[1]. As discussed previously self-healing mechanism is inspired from biological system, it has three stages actuation, transport and repair. There are mainly three conceptual approaches (a) capsule based, (b) Vascular Based and (c) Intrinsic.

Since our main aim of self-healing is to reduce mechanical degradation and extend service life of product. In static load condition it is obtained, but in fatigue load also significant crack arrest and life extension resulted when the in situ healing rate was faster than the crack growth rate[4].

a) Capsule based self-healing

In capsule based self-healing many types of encapsulation techniques are available on the basis of wall formation. Since first encapsulation is done than integration, extreme care is required during integration to prevent rupture of capsules. In capsule mostly monomer healing agent is placed on rupturing, it releases and in presence of catalyst it polymerizes and crack is healed. Mechanical property of system is affected by capsule wall bond strength and volume fraction. Fig. 8 shows four schemes for sequestration of the healing agent.

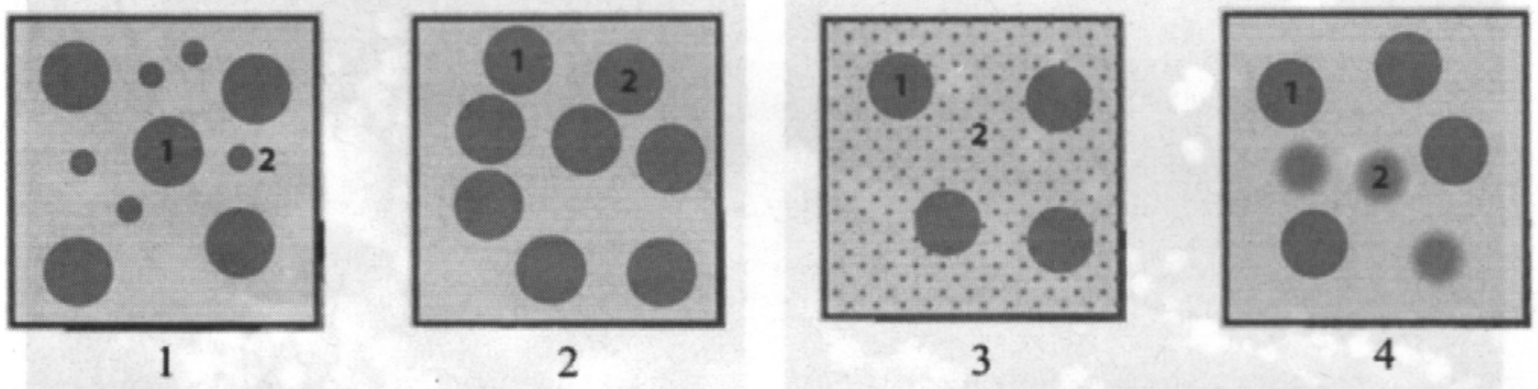


Fig. 8 : Capsule-based self-healing (1) Capsule-Catalyst, (2) Multicapsule, (3) Latent Functionality, (4) Phase Separation[1]

As shown in Fig. 8(1) in capsule-catalyst technique healing agent is encapsulated and catalyst is dispersed in a material. Grubbs' capsule-catalyst system is example of this system. In second technique as shown in Fig. 8(2) both healing agent and catalyst (polymarizer) are encapsulated.

Benefit of this technique is, more number of distinct capsules can be incorporated. In the third technique (latent functionality) as shown in Fig. 8(3), the healing agent is encapsulated or dispersed as particles, and the polymerizer is residual reactive functionality in the matrix or an environmental stimulus. In fourth technique of phase separation as name suggests any one of the two components (either healing agent or polymarizer) is phase separated inside a material and other is encapsulated as shown in Fig. 8(4).

b) Vascular self-healing materials

In vascular self-healing hollow fibers filled with healing agent and polymarizer are incorporated in the structure. Mechanism of healing is same as in capsule based system but it differs in fabrication and integration process of fibers within main matrix. Hollow fibers are mainly glass fibers. Glass fibers can be combined with carbon fibers pile in composite structures. Since hollow fibers are interconnected, healing agent can transport from one part of the structure to the other, also refiling becomes easy and more amount can be refilled.

As in capsule based system healing agent is not filled inside with the beginning, healing agent is introduced after fabrication of fibers so in addition to all other properties wettability of healing agent also becomes important which also affects transportation and realizing phenomenon. Mechanical property of the whole structure is decided by (a) volume fraction of fibers, (b) wall stiffness, (c) matrix network bonding and (d) channel distribution pattern.

On the basis of channel distribution pattern there are three types

(A) One-dimensional (1D) networks.

(B) Two -dimensional (2D) networks.

(C) Three-dimensional (3D) networks.

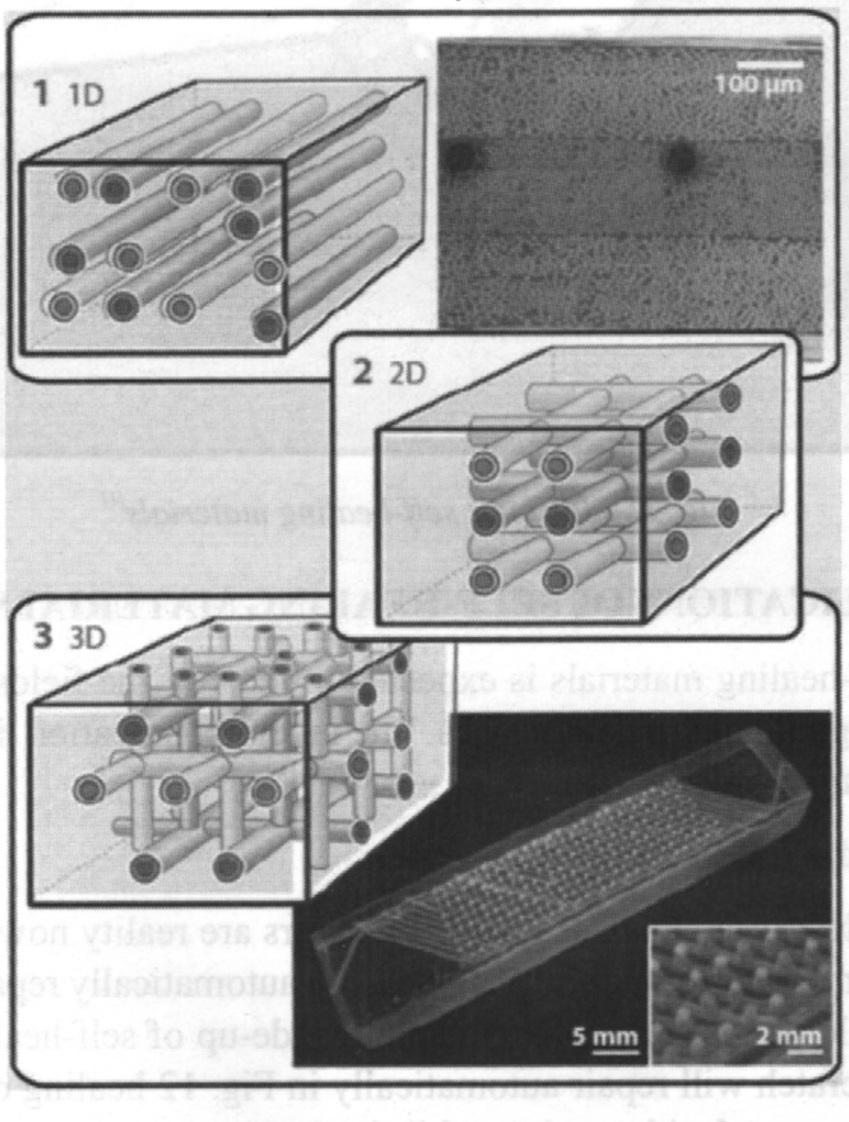


Fig. 10 : vascular self-healing according to the connectivity of the vascular network[1]

In one-dimensional (1D) networks as shown in Fig. 10(1) - individual fibers are installed in on particular direction with the view of fabrication and integration of fibers in the structure, this is simplest type. In two-and- three dimensional (2D& 3D) networks, interconnected fibers are comparatively difficult to incorporate in the structure.

c) Intrinsic self-healing materials

Intrinsic self-healing materials achieve self-healing through reversible bonding in polymer matrix. There are different types of reactions, thermally reversible reaction is popular.

(a) Diels-Alder (DA) and retro-Diels-Alder (rDA) reactions are most widely used reversible reactions, in which with external energy monomeric state can reversibly transform to cross linked polymeric state.

(b) Thermoplastic polymers are dispersed when crack is generated. Heat is given thermoplastic will melt and with mechanical interlocking crack will be filled.

Likewise there are many mechanisms with which intrinsic self-healing is carried out. Above mentioned methods are two of them.

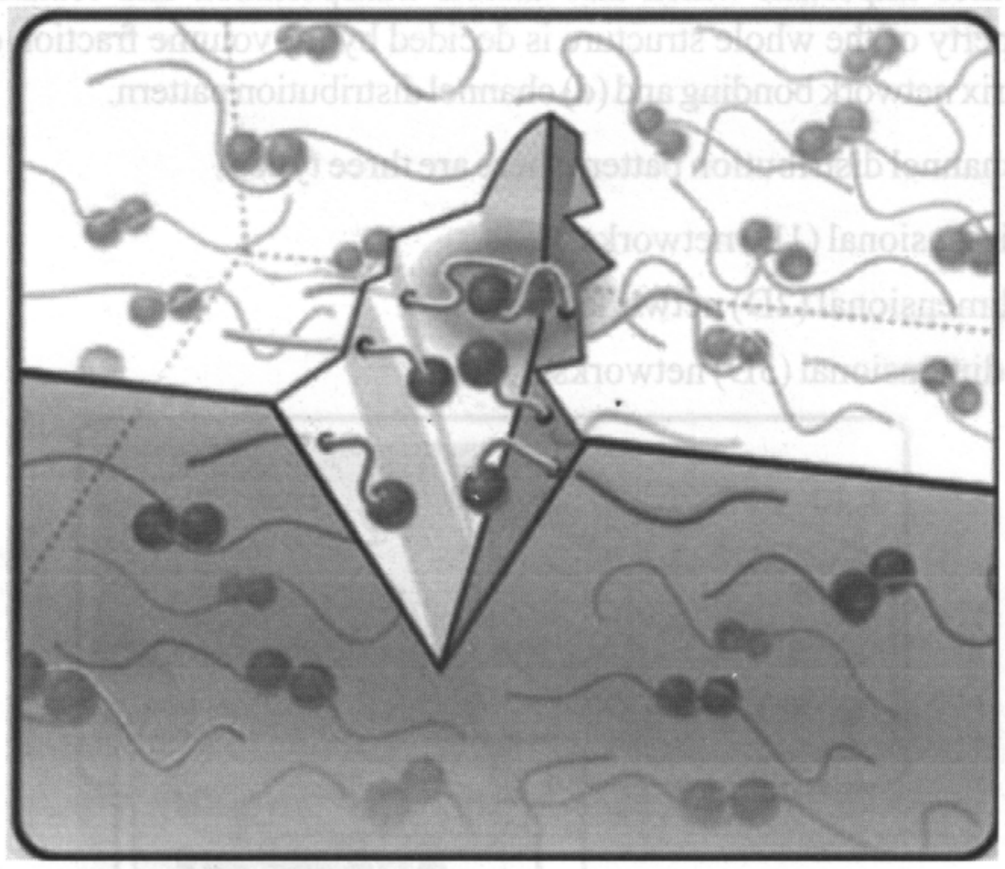


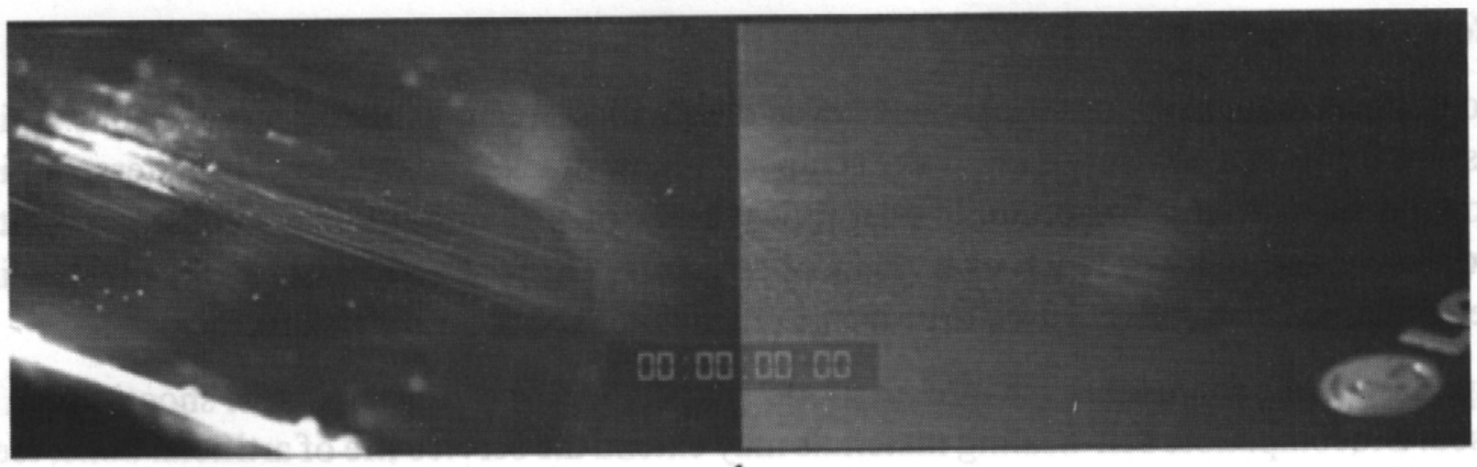
Fig. 11 : Intrinsic self-healing materials[1]

EMERGING APPLICATIONS OF SELF-HEALING MATERIALS

Applications of self-healing materials is expected in most of the fields of science in future, since it reduces degradation and increases life in communication industry, automotive, aerospace and building industries.

Communication industry

In mobile phone industry scratch free guards or covers are reality now which is example of self-healing polymer, scratch in mobile phone case is automatically repaired and appears like new one. Also mobile phone screen cover can be made-up of self-healing polymer or glass which on crack or scratch will repair automatically in Fig. 12 healing of scratch is shown in mobile back cover compared with regular mobile back cover.



1 2

Fig. 12 : Self-Healing in mobile (1) scratch is produced at time 0 on back cover of two mobile first is regular second is with self-healing property (2) after 2 min. scratch is healed in second one while in first one scratch remains as it is.

Based on optical responsive property

In day to day life scratch on transparent polymeric materials like spectacle glass, helmet shield etc. is main problem, to deal with it self-healing materials can be used which can remove scratches on it.

Automotive industry

Scratch shield paint is used in Nissan car, as shown scratch is healed within period of 7 days.

Fig. 13 : Scratch shield paint of Nissan

Aerospace industry

In aerospace industry by using healing technology on composite materials, it is possible to have advanced maintenance capabilities, combining self-healing structure with alternative materials[5]. In fiber reinforced composite, crack is not easily detectable but it is important to repair it in aircraft parts. Self-healing composite is best solution to reduce maintenance cost and increase reliability.

Construction

Sometimes though, the ramifications of even the smallest fractures are far more serious. A tiny fissure forms in a concrete dam. A sky scraper window cracks and eventually shatters, raining down debris. So it is important to heal tiniest crack of structure. In heavy construction it is expensive and risky to reach every part of structure, check it and repair it. So self-healing cementetious materials are used to prevent high maintenance cost and risk factor.

Apart from this some other uses are -in sports, puncture self-healing targets for shooting can be used. Biocompatible self-healing materials may extend the service life of artificial bone, teeth etc.

CONCLUSIONS

- In modern technologically developing world long life less maintenance materials are promising solution over conventional materials for good performance. Inspired from nature self-healing materials are developed to fulfil such requirement, which are smart enough to sense crack generated in it and are able to heal it with or without external stimuli. Different strategies are available for self-mechanism depending upon type of material.
- In cementetious material for small crack natural self-healing is possible, apart from that different strategies like encapsulation, expensive agent & mineral admixture, bacterial or shape memory materials can help to achieve self-healing.
- In polymeric and composite materials capsule based, vascular or intrinsic self-healing may be one of the strategies.
- Application of self-healing materials is almost in all the areas including construction, aerospace, sports, electronics etc., so self-healing materials are good alternate solution over conventional materials.

REFERENCES

[1] Blaiszik S.K.S.O. B.J., (2010), Self-Healing Polymers and composites, *Annual Review of Materials Research*, pp. 179-211.
[2] Brown N.S.a.S.W. E.N., (2001), Fracture Testing of a Self-Healing Polymer Composite, *Experimental Mechanics : An International Journal*, pp. 20.
[3] Amirreza Talaiekhozan A.K.A.S., (2014), A Review of Self-healing Concrete Research Development, *Journal of Environmental Treatment Techniques*, pp. 1-11.
[4] Brown S.W.N.S. E.N., (2005), Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite-Part II: In situ self-healing, *Composites Science and Technology*.
[5] Suman M., (2017), Self Healing Materials for Aircraft Applications, https://contest.techbriefs.com/2017/entries/aerospace-and-defense/7555.
[6] Min Wu B.J., (2012), A review: Self-healing in cementitious materials and engineered, *Construction and Building Materials*, pp. 13.
[7] Yashpal Kumar E.K.K. Er., (2017), A REVIEW: SMART CEMENTIOUS MATERIALWITH SELF-HEALING PROPERTIES., *International Journal of Latest Research in Science and Technology*, pp. 46-48.
[8] Self-healing, Shape Memory Alloy Reinforced Self-healing Metal Matrix Composites, University of Wisconsin Milwaukee Theses, pp. 1-109, 2013.
[9] Gupta H.K. Souradeep, (2016), Encapsulation Technology and Techniques in Self-Healing Concrete, *Journal of Materials in Civil Engineering*, pp. 1-16.