Self-Healing Materials: A Review of Intrinsic and Extrinsic Healing Mechanisms and Their Engineering Applications

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Abstract—Engineering materials accumulate small cracks during service, and these cracks grow until a component must be repaired or replaced. Self-healing materials are designed to repair such damage on their own, or with only a mild external stimulus, in a way inspired by the healing of wounds in living organisms. This review explains the principles behind self-healing and classifies the approaches into extrinsic systems, in which a healing agent is stored in microcapsules, hollow fibres or vascular channels, and intrinsic systems, in which the material itself contains reversible chemical or physical bonds that re-form after fracture. Representative studies on polymers, composites, cement-based materials, coatings and electronic materials are reviewed and compared. A general functional architecture is presented that describes a self-healing system as a sequence of damage, triggering, transport of healing material, repair reaction and property recovery, and the healing efficiency used to measure performance is defined. Applications in civil engineering, aerospace, automotive, coatings, electronics and biomedical devices are discussed. The review also examines current limitations, such as high cost, a limited number of healing cycles and difficulty in repairing large damage, and outlines directions for future research.

Index Terms—Self-healing materials, microcapsules, vascular networks, reversible bonds, self-healing concrete, self-healing polymers, flexible electronics, healing efficiency.

I. INTRODUCTION

Every engineered structure degrades during its service life. Repeated loading, temperature change, moisture and chemical attack create micro-cracks that are often invisible. These cracks grow and join until a component loses strength, leaks or fails. Conventional practice relies on inspection and manual repair, which is expensive and, for components that are hidden or difficult to reach, sometimes impossible.

Living organisms handle damage differently. A cut in the skin triggers bleeding, clotting and tissue regeneration without any outside intervention. Inspired by this behaviour, material scientists have developed *self-healing materials* that can sense damage and restore at least part of their original properties automatically or with a simple stimulus such as heat or light [1], [2]. A widely cited milestone was the demonstration by White *et al.* in 2001 of an epoxy composite containing microencapsulated healing agent and a dispersed catalyst, which recovered a large part of its fracture toughness after cracking [3].Since then, the field has expanded to include polymers with reversible bonds, concrete containing bacteria, conductive materials for electronics and coatings that protect metals from corrosion [4], [5]. This paper reviews these developments. Its contributions are:

- An explanation of the principles of self-healing and a classification into extrinsic and intrinsic mechanisms.
- A review of representative studies across polymers, composites, cementitious materials and electronic materials.
- A general functional architecture of a self-healing system and a definition of healing efficiency.
- A comparison of mechanisms, a survey of applications, and a discussion of challenges and future directions.

Section II gives the background, Section III reviews healing mechanisms, Section IV presents the functional architecture, Section V reviews material classes and applications, Section

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VI compares approaches, Section VII discusses challenges, and Section VIII concludes.

II. BACKGROUND

2.1 The Biological Analogy

Biological healing has three broad stages: an immediate response that stops further damage, an inflammatory stage in which material is transported to the wound, and a remodelling stage in which the tissue regains strength [2]. Synthetic self-healing systems follow a similar pattern. Damage creates a free surface or breaks bonds, a mobile phase flows into the damaged region, and a chemical or physical process rebonds the surfaces.

2.2 Autonomic And Non-Autonomic Healing

Healing is described as *autonomic* when the damage itself triggers repair without any outside action, as in capsule-based systems. It is *non-autonomic* or *stimulus-assisted* when an external input, such as heat, light, pressure or moisture, is required to activate repair, as in many polymers with reversible bonds [6].

2.3 Measuring Healing

The performance of a self-healing material is usually expressed as a healing efficiency η, the ratio of a property after healing to the same property of the undamaged material. For fracture-based tests, White *et al.* and Brown *et al.* used the fracture toughness K_{IC} measured with tapered double-cantilever beam specimens [3], [7]:

$$\eta = K_{IC,\ healed} / K_{IC,\ virgin} \qquad (1)$$

The property can also be tensile strength, stiffness, electrical conductivity or barrier performance, depending on the application. The number of times healing can be repeated at the same location is another key measure.

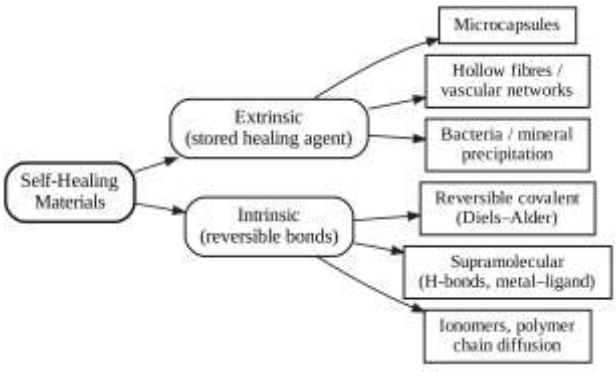


Fig. 1. Classification of self-healing mechanisms into extrinsic and intrinsic approaches.

III. HEALING MECHANISMS

3.1 Extrinsic: Microcapsule-Based Healing

In capsule-based systems, a liquid healing agent is sealed inside small polymer shells that are dispersed throughout the matrix together with a catalyst. When a crack propagates, it ruptures the capsules in its path; the released liquid flows into the crack by capillary action, contacts the catalyst and polymerises, bonding the crack faces. White *et al.* used dicyclopentadiene as the healing agent and a Grubbs catalyst, achieving recovery of up to about 75% of virgin fracture toughness [3]. The approach is fully autonomic, but each location can heal only once because the capsules are consumed.

3.2 Extrinsic: Hollow Fibre And Vascular Networks

To allow repeated healing, researchers embedded continuous channels that can deliver healing agent many times. Toohey *et al.* produced a coating on a substrate containing a three-dimensional microvascular network, inspired by human skin, and demonstrated repeated healing of cracks at the same location [8]. Hollow glass fibres filled with resin have also been used in fibre-reinforced composites for aerospace structures. Vascular systems require more complex manufacturing and must be designed so that the channels do not weaken the structure [4].

3.3 Extrinsic: Bacteria-Based Healing In Concrete

Concrete cracks easily under tension, and cracks allow water and chlorides to reach the steel reinforcement. Jonkers *et al.* added spores of alkali-resistant bacteria together with a calcium-based nutrient to the concrete mix. When water enters a crack, the spores become active and convert the nutrient into calcium carbonate, which precipitates and seals the crack [9]. A review by Van Tittelboom and De Belie compared autogenous healing, which is the natural ability of concrete to close fine cracks through continued hydration and carbonation, with autonomous approaches using bacteria, capsules or vascular systems [5].

3.4 Intrinsic: Reversible Covalent Bonds

Intrinsic materials heal because their own chemical structure can break and re-form. Chen *et al.* prepared a cross-linked polymer based on the thermally reversible Diels–Alder reaction; on heating, the bonds open, and on cooling they re-form, so a crack can be mended repeatedly by a heat treatment [10]. Such materials can heal many times but generally need an external trigger and close contact between crack faces.

3.5 Intrinsic: Supramolecular And Physical Interactions

Supramolecular polymers are held together by non-covalent interactions such as hydrogen bonds, metal–ligand

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coordination or ionic clusters. Cordier *et al.* designed a rubber-like material from small molecules that associate through multiple hydrogen bonds; when cut pieces were pressed together at room temperature, they rejoined and recovered much of their stretchability [11]. These materials can heal at ambient conditions but are often soft and have limited strength [6].

3.6 Self-Healing In Electronic Materials

Flexible and wearable electronics suffer from cracks in thin conductive tracks. Blaiszik *et al.* placed microcapsules containing a liquid metal or conductive material over circuits; when the line cracked, the released material restored electrical conductivity within a short time [12]. Tee *et al.* developed a composite of a supramolecular polymer and nickel microparticles that healed both mechanically and electrically at room temperature and could serve as an electronic skin [13]. In energy storage, Wang *et al.* used a self-healing polymer binder to keep silicon anode particles connected as they expanded and contracted, improving the cycle life of lithium-ion batteries [14].

Table I Summary Of Representative Studies On Self-Healing Materials

Ref.	Material System	Mechanism	Key Result	Limitation
[3]	Epoxy with capsules and Grubbs catalyst	Extrinsic, microcapsule	Up to about 75% toughness recovery	Single healing event per site
[8]	Coating with 3-D microvascular network	Extrinsic, vascular	Repeated healing at same location	Complex fabrication
[9]	Concrete with bacterial spores	Extrinsic, biological	CaCO3 precipitation seals cracks	Limited to fine cracks; slow
[10]	Diels–Alder cross-linked polymer	Intrinsic, reversible covalent	Multiple thermal mending cycles	Needs heating and contact
[11]	Hydrogen-bonded supramolecular rubber	Intrinsic, supramolecular	Room-temperature rejoining	Low mechanical strength
[12]	Circuit with conductive capsules	Extrinsic, microcapsule	Rapid conductivity restoration	One-time repair
[13]	Supramolecular polymer with Ni particles	Intrinsic, composite	Mechanical and electrical healing	Limited conductivity range

IV. GENERAL FUNCTIONAL ARCHITECTURE

Although the chemistry varies, all self-healing systems can be described by the same functional sequence. Fig. 2 presents this sequence as a layered architecture.

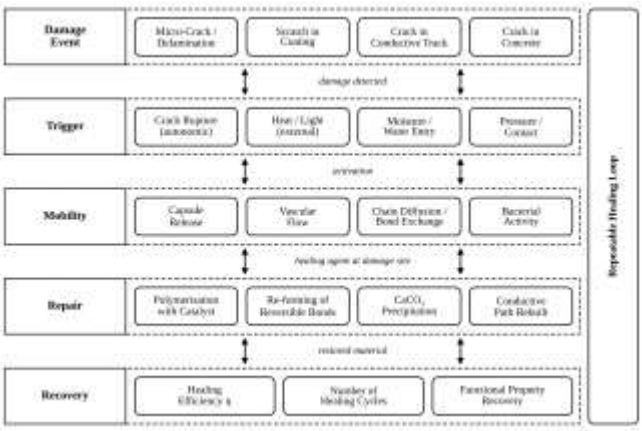


Fig. 2. General functional architecture of a self-healing material system, from damage to property recovery.

The **damage layer** represents the event that starts the process, such as a micro-crack, scratch, puncture or broken conductive track. The **trigger layer** identifies what activates healing: the crack itself in autonomic systems, or an external stimulus such as heat, light, moisture or pressure in non-autonomic systems [6]. The **mobility layer** describes how healing material reaches the damage, by release from ruptured capsules, flow through vascular channels, diffusion of polymer chains or growth of bacteria [3], [8], [9]. The **repair layer** contains the reaction that rebonds the surfaces, such as polymerisation, reformation of reversible bonds or mineral precipitation [10], [11]. Finally, the **recovery layer** measures the outcome in terms of healing efficiency, number of healing cycles and recovery of functional properties such as conductivity or water-tightness. Designing a self-healing material involves choosing a suitable option in each layer for the intended service conditions.

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V. MATERIAL CLASSES AND APPLICATIONS

5.1 Civil Engineering

Self-healing concrete can seal fine cracks, reducing water and chloride ingress and therefore corrosion of reinforcement. Bacteria-based and capsule-based concretes have been tested in laboratory and field trials, and their main benefit is a longer service life with less maintenance of bridges, tunnels and water-retaining structures [5], [9].

5.2 Aerospace And Automotive

Fibre-reinforced composites can suffer internal delamination after impact, which is hard to detect. Capsule and vascular healing systems can restore part of the lost strength and delay failure [4]. In vehicles, self-healing clear coats can recover from light scratches through reversible polymer networks.

5.3 Protective Coatings

Coatings containing capsules of corrosion inhibitor or film-forming agent release them when scratched, re-protecting exposed metal. This can extend the life of pipelines, ships and steel structures [15].

5.4 Electronics And Energy Storage

Self-healing conductors and dielectrics improve the reliability of flexible circuits, wearable sensors and electronic skin [12], [13]. Self-healing binders improve the durability of high-capacity battery electrodes [14].

5.5 Biomedical Devices

Soft self-healing hydrogels and polymers are being studied for tissue scaffolds, drug delivery and implants, where repeated motion causes small damage that the body cannot easily repair [6].

VI. COMPARATIVE ANALYSIS

Table II compares the main families of healing mechanisms.

Criterion	Microcapsule	Vascular Network	Bacteria-Based	Reversible Covalent	Supramolecular
Trigger	Crack (autonomic)	Crack (autonomic)	Water entry	Heat or light	Contact, ambient
Healing cycles	One per site	Many	Several	Many	Many
Damage size	Micro-cracks	Larger cracks	Fine cracks	Small, faces in contact	Small, faces in contact
Healing speed	Minutes to hours	Minutes to hours	Days to weeks	Minutes with heating	Minutes to hours
Typical matrix	Epoxy, coatings	Composites, coatings	Concrete	Thermosets	Elastomers, gels
Example	[3]	[8]	[9]	[10]	[11]

VII. CHALLENGES AND FUTURE DIRECTIONS

Several issues limit wide use. Cost is the first: capsules, catalysts, vascular networks and specialised polymers raise material price, so self-healing is currently justified mainly where repair is expensive or failure is dangerous. Second, extrinsic capsule systems heal only once at each location, while intrinsic systems that heal many times often need heat or close contact and may have lower strength [4], [6]. Third, large cracks or missing material remain difficult to repair because the volume of available healing agent is limited. Fourth, the healing agent and its shells must survive processing and long service without degrading, and must not reduce the original properties of the host material. Fifth, standard test methods and long-term field data are still limited, which makes certification for structural use difficult [5]. Future research is directed towards materials that combine high strength with multiple autonomic healing cycles, integration of damage sensing with healing, low-cost bio-based healing agents, and design tools that predict healing performance over the life of a structure.

VIII. CONCLUSION

Self-healing materials offer a new way to extend the life of engineered products by repairing damage from within. Extrinsic systems based on microcapsules, vascular networks and bacteria store a healing agent that is released when damage occurs, while intrinsic systems rely on reversible chemical and physical bonds in the material itself. The reviewed studies show successful healing in polymers, composites, concrete, coatings and electronic materials. A common functional architecture links damage, trigger, mobility, repair and recovery, and provides a framework for

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comparing designs. Although cost, limited healing cycles and repair of large damage remain challenges, continued research is likely to make self-healing materials a practical choice for more durable, reliable and sustainable structures and devices.

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