

Developments and Prospects of Self-Healing Design for Hierarchical Carbon Fiber Reinforced Polymer Composites

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ABSTRACT: This review is a denote to the detailed analysis of the self-healable features of Carbon Fiber-Reinforced Polymer (CFRP) composites. It discusses the different healing strategies, types of employed healers, time to healing, mechanical recovery, inherent properties such as glass transition temperature, and the advantages and disadvantages of each healing strategy. Composite materials with self-healing capabilities can automatically repair themselves after being degraded. As a result, maintenance tasks are greatly simplified. This paper aims to give a concise overview of the most recent advancements in self-healing composites. The article complements earlier survey papers by offering an updated overview of the many self-healing theories over the preceding two decades and a comparison of healing processes and manufacturing methods for creating micro-capsules and microvascular networks. The review also dispenses a summary of diverse chemistries utilized to fabricate self-healable polymeric composites and their future scope to humankind. To identify significant challenges and prospective research insight, elements that affect healing efficiency are provided based on the research assessment. This provides a basis for the researchers for future applications based on these intelligent self-healing composites.

KEYWORDS: Smart Material; Crack; Delamination; Elaborated Analysis; Recovery; Glass Transition Temperature; Fabrication.

INTRODUCTION

Carbon Fiber Reinforcements (CFR)s with high carbon content (99%) for polymer matrix composites

paved the way in commercial production when *Richard B. Millington et al.* developed a procedure (US Patent

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1021-9986/2023/3/890-915

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No. 3294489) using rayon precursor in the year 1960s [1]. Since then, Carbon Fibers (CF) have typically been the diverse constituting materials utilized in polymeric composites. They possess a higher specific strength-to-weight ratio, rigidity, thermal stability, conductivity, and corrosion resistance. They beneficially enhance the product's efficiency and are reliable for various engineering systems [2]. Carbon Fiber Reinforcement Product (CFRP) composites are generally used in manufacturing aircraft airframe materials [3], automobile parts [4], blades (fans, windmills, and turbines) [5], and sports utilities. Using CFRP composites in commercial aircraft as structural materials mainly reduces the final mass while enhancing the gas mileage. Reducing aircraft weight transforms into increased fuel efficiency and implies the least expense every time the aircraft aviates. CFRP materials accounting for 50%, are utilized to manufacture the fuselage of the Boeing 787 Dreamliner with comparatively 20% enhanced gas mileage than the antecedent, Boeing 767 [6]. As further advancement, the Airbus A350 XWB (eXtra Wide Body) was manufactured with 52% CFRP materials in fuselage and wing spars. It had wide seating layouts with aerodynamics for Mach 0.85 cruise thus, overtaking its predecessor A340, Boeing 787 dream-liner, and a few others in efficiency [7]. All these advantages of CFR over the other fibers compel one to use CF as a property-rich reinforcing material in a polymer matrix composite. A comparison of CF-reinforced polymer composites with other fiber-reinforced polymers and bulk metallic materials is illustrated in Fig. 1.

The composite parts are designed to withstand high mechanical loading in typical structural applications of an engineering system. However, the mechanical performance required of these composites might be transformed by thermo-mechanical impacts, internal micro-cracks, and delamination that tend to appear within the composite material, which goes unnoticed by the naked eye. Hence, Non-Destructive Inspection (NDI) or similar Structural Health Monitoring (SHM) beyond manual eye inspection is required to scrutinize for occurring damages. [9] An NDI system is an expensive and time-consuming survey. In this system, checking is restricted to specific smaller regions and fatigue damages may be undetectable. An extension or improved NDI system is an SHM system that uses different pressure and crack sensors. There are expensive data-transmitting tools and

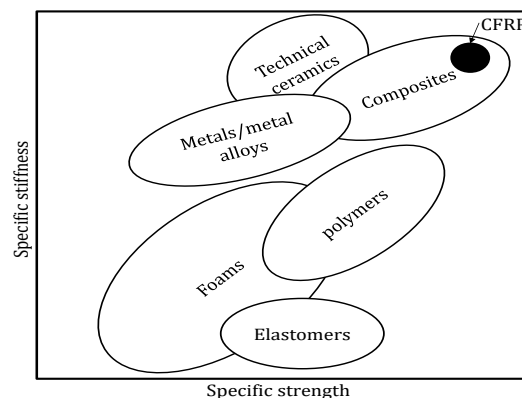


Fig. 1: Simplified log-log Ashby diagram showing the specific stiffness against specific strength for different engineering materials [8].

exterior gadgets for structural health inspection or data storage giving time-to-time notification on the overall integrity of the structure to prevent from leading catastrophic failures. [10–12] The self-healing composite materials can self-heal structural and functional applicability. [13] The need for time-consuming and expensive inspections is diminished for such composites. Self-healing design is a unique substitutive approach for the generally used damage-withstanding methods. It is introduced for the polymer resin matrix and a few cementitious matrix systems. It discards the necessity of damaged polymer matrix composite structures to be temporarily repaired. It has gained encouragement from the natural stimulus to damage animal skin and flesh. The animal's healing process of hemostasis (stopping bleeding). [14] Based on the healing mechanism utilized, the self-healing composites can be mainly differentiated into two classes: Extrinsic and Intrinsic self-healing composites. Some standard direct damage recovery techniques are discussed in this review. However, these techniques have certain drawbacks and are not particularly effective. [15] The principal distinction between these two classes of self-healing techniques depends on their type of chemical interactions.

Extrinsic self-healing

These self-healing techniques depend on exterior healing (healing material) and catalyst (if required) designed as embedded tiny capsules or dispersed vascular networks within the matrix system. [16–19] Typical

layouts utilized for manufacturing design materials comprise:

- (i) Micro-encapsulation and
- (ii) Micro-vascular network

Classically, in the earlier designs, the healing mechanism starts with the fracture in the embedded hollow networks or micro-capsules. Upon crack intrusion, microcapsules or vascular networks attached to the cracked surface break, and the healing agents flow out. A polymerization reaction takes place to heal the cracks, utilizing an external trigger or catalyst (embedded if required). However, microencapsulation techniques have a few drawbacks. Limited healing agents and a liquid form, which provide no structural functionality other than healing and degrade on long-term storage in a capsule, are among the significant drawbacks. Compared to the encapsulation process, the vascular network provides few advantages; if the healing agent in the vascular network finishes or degrades, it can be refilled externally thus, to provide continuous efficient self-healing over time. The capsule shells are generally made up of organic or inorganic complexes such as Polyurea (PU), Poly Urea-Formaldehyde (PUF), [20] Silica shell walls, Polyurethane, Poly Melamine-Formaldehyde (PMF), and Poly Melamine-Urea-Formaldehyde (PMUF).

Intrinsic self-healing

These self-healing system elements require no exterior intervention of healant in embedded form and are established either on supramolecular or active covalent chemistry. The supramolecular method utilizes π - π stacking, hydrogen bonds, and ionomers interaction. The dynamic covalent chemistry method uses cycloaddition (D-A reaction), free-radical reactions, and general chain interchange reactions. The polymer matrix can organize the cleaved reversible bonds in these systems by undergoing a polymerization reaction or crosslinking on exterior influence. [21–24] With multiple damage intrusions, this technique instigates healing cycles as no concept of the externally embedded healing agent is involved. However, some methods need some exterior indulgence to trigger the healing mechanism. Some examples are heat and mechanical stimuli, pH change, UV, and light stimuli. However, self-healing damaged surfaces with significant contact differences becomes challenging, while minor damages are known to be efficiently robust.

Standard straightforward techniques for repairing matrix

The typical repair techniques for damaged matrix materials are bolted or bonded techniques. A bolted repair technique is implemented for damages like de-laminations in high-loading composite structures. Commercial aircraft composites; use titanium and aluminum bolts and adhesive patches to recover the mechanical features. However, the bolted holes in this repairing technique considerably change the stress concentrations and propagating force capacity within the material. Bonded repair techniques are implemented for minor damages like micro-cracks in lightly loaded composite structures. A conventional bonded repair technique injects polymerizing material into the damaged site to cure it. This repairing technique may be implemented either by using a similar matrix or a few discrete matrixes, thus is applicable for different metal and FRP composite systems as a temporary/permanent repair but does not need to be improved long term. Ideally, the injected polymerizing material will fill all voids within the matrix. Once all the holes are lost, high stresses are prevented from concentrating into the damaged sites, thus further preventing crack growth. Patches can be utilized simultaneously after injecting material, thus providing excellent resilience of bending strength, elastic property, and immunity to corrosion. [9] These traditional repairing techniques are principally practiced for healing external/interior fractures; however, the damaged site should be initially detected. [10,25] Additionally, inherent features of the patch and composite part must be appropriate, e.g., when the coefficient of thermal expansion of the patch and material has a significant difference, the temperature may create uneven tensions between the patch and material, causing patch failure. Furthermore, the adhesive properties act are vital because its failure may cause the patch to de-bond and failure loss exposure.

SELF-HEALING: CONCEPT AND MATERIALS

Many research publications concerning self-healing polymers as matrix materials have appeared since the early 1990s. They cover the eagerness of researchers to solve the nature of recurring problems due to damages in composite materials and the exponential increase in the material design of polymers and FRP composites. They can strengthen themselves in response to damages. The typical

polymer matrices (thermoplastic and thermosetting resins) used for the CFRP composites are all inherently brittle; thus, all are susceptible to thermo-mechanical damage initiation (micro-cracks and de-lamination) during service life. For this reason, achieving long-term stability is a challenging obstacle for applying CFRP composites as a prime component in various sectors. Advancements were made in the material designs to minimize the damage to CFRP composites. [12] The matrix material's glass transition temperature (T_g) is also integral as the stiffness significantly drops when the temperature shifts to T_g . To determine which material system suits any application best could first understand all possible healing methods and the techniques to be applied with the respective matrix material to establish the materials in specific applications. Earlier damage-tolerant designs used continuous enhancement of material properties to stop damage propagation within the material. They were not reasonably achievable; thus, a new self-healing design approach was introduced. It can control/eliminate matrix-dominated damages. It was regarded as a technical divergence from regularly practicing composites' repair to autonomous self-healing functional composites. Traditional repair techniques in composite materials are used after noticeable macro-level damage has occurred; the repairing is usually laborious & cost inefficient. However, smaller (micro/nano level) damages are impossible for the naked eye to notice, and they often use costly damage inspection techniques (e.g., NDI and SHM), sensors, and actuators. [10] Once the damage is detected, the next step of Self-healing is an efficient approach to fortify the damaged features of CFRP composites. Ideally, strategies for incorporating this feature within the composite had to come from the polymer resin matrices. All polymer resins, either thermoplastic or thermosetting, tend to self-healing on an external stimulus's influence. [26] Theoretically, any micro-crack/damage initiated in a thermoplastic matrix may be mitigated by liquefying the thermoplastic using thermal stimuli. Nevertheless, that leads to a certain amount of thermoplastic degradation. Furthermore, some researchers have reported the synthesis of polymer blends as self-healing matrices through mixing thermosets with thermoplastic resins or their specific combinations. The structural robustness of self-healing composites could be strengthened after failure, just like living species. However, incorporating self-healing features within

composites might only conduct the healing mechanism once exteriorly stimulated. While designing these self-healable systems, specific attention is paid to the diffusion of healant in extrinsic healing. A few other concerned factors respective to different healing strategies should be adequately controlled. The healing functionality within a CFRP composite enables recovery of a vast range of material properties upon damage intrusion, including fracture strength, hardness, durability, and conductivity (thermal/electrical). It further makes the CFRP composite materials more reliable for application in various sectors. Some efficient desirable properties of self-healing composites can be stated as follows:

Potential for autonomous healing of the composite system.

- Capability to adapt the failure within composite multiple times
- Long service-span durability
- Able to heal large-scale defects of composite
- Able to reduce maintenance expenses
- Manifest higher or equivalent mechanical characteristics compared with conventional composites in use
- Glass transition temperature (T_g) is much higher than the relevant environment temperature
- It is more economical than the presently used material polymers

In this review, the existing literature has been thoroughly analyzed to briefly outline the manufacturing techniques, features, and mechanical characteristics of the self-healing FRP matrix composites. Structural composites utilized over the metal counterparts have shown drastic savings of 20% to 40% on weight with minor maintenance and machining expenses. With the increasing research interest in self-healing composite materials, the results can be safely used to present that they are highly durable, fatigue-resistant, dimensionally stable, easily maintainable, and self-repairable.

Composite materials fail after a prolonged degradation process. That leads to the formation of micro-cracks or internal matrix delaminations unseen to the naked eye. Thus, an All-time manual inspection of these cracks/delaminations is not possible, and this is where self-healing comes as a boon to the damaged composites. However, the standard repairing methods and self-healing techniques introduced to Polymer Matrix Composites (PMC)s have acquired popularity over the past three decades, and

the demand for composites is increasing daily. [6,7] To meet the needs of engineering applications and for large-scale marketing of these composite materials, low-cost manufacturing techniques have been developed worldwide, and the final product is aimed to be recyclable with the help of these flexible techniques.

Along with all capabilities, incorporating a self-healing function within composite material would increase its lifetime with reduced inconvenient damages. [25] FRP composite material consists of two chemically/physically separate constituents (Continuous and Discontinuous phases) with robust interfacial bonding. The final composite has unique mechanical and functional properties, which directly depend on the form and amount of both constituents. In contrast, the healing functionality of the composite depends on the healing technique and the type and amount of healable continuous phase (polymer matrix) used. The discontinuous phase (Fiber reinforcement) used for the self-healing composite should not be considered healable as it does not possess any such function. For the desirable features to be incorporated in the finished composite part, one must consider these critical aspects while choosing the reinforcing material:

- Size-aspect ratio and diameter
- Shape-chopped, particulate, continuous, and non-continuous fiber
- Inherent features strength, modulus, conductivity, and density
- Surface morphology and chemistry
- Impurities
- Structural voids

The polymer matrix phase is an essential component of the composite material systems, and one must carefully choose the matrix by considering its chemical stability with the reinforcement and inherent characteristics (gel-time/pot-life, shelf-life, glass transition temperature, toxicity, and curing time); ability to wet the support (viscosity) and processing technique. Further, the critical nature of polymer as the matrix of carbon fibrous reinforcement composite is to:

- Act as a barrier against an unfriendly environment
- Guard the fiber's surface against mechanical abrasion
- Hold the fibers in the proper orientation
- Propagate the load among fibers
- Enhance inter-laminar shear strength
- Improve the performance of composite

EXTRINSICALLY SELF-HEALING COMPOSITES MICROENCAPSULATION DESIGN

The self-healing technique utilizing a microencapsulated design system possesses the capability of core healant to flow in the crack of polymer that requires healing and is stored in the microcapsules. [27] The capsule ruptures/breaks upon a crack intrusion in the matrix, thus discharging healant in the damaged site through the capillarity effect. Additionally, repairing the damaged portion via cross-linking reaction with the catalyst. [28] Emerging extensive interest in this field led many researchers to study and develop various strategic models of microencapsulation, which could incorporate the self-healing feature in the composites. Some of the different microencapsulated healing system models have proven efficiently beneficial and are discussed here.

(i) The Solo Capsule Model – In this model, there is a solo healant encapsulated, which on release reacts with dormant bonds within the matrix to undergo cross-linking reaction under humidity, light, or other external stimulus and produce chain-linking entanglements across cracked surfaces. The core healant may be easily meltable metals, active chemicals, and solvents.

(ii) The Embedded Capsule with dispersed Catalyst Model – It is based on capsules with loaded self-healing monomer and catalyst evenly distributed within the polymer matrix. Upon damage intrusion, the matrix with microcapsules breaks to release the monomer, which then polymerizes and reacts with the neighboring catalyst in the polymer.

(iii) The Dual Capsule Model – These models of microcapsule are used when the polymerizable healing and curing agent is applied for self-healing in Fiber reinforced polymer (FRP) matrix are individually encapsulated. Upon crack propagation, microcapsules break, and the two agents undergo cross-linking polymerization reactions with each other, thus healing the site effect. This encapsulating model has a limitation. Obtaining a uniform distribution of two microcapsules in the matrix phase is a task, and the probability of polymerization on a crack intrusion is small.

(iv) The Phase-separated droplet with embedded Capsule Model. In this model, at least one healing agent undergoes phase separation to form a co-continuous phase, and the other agent is encapsulated in the matrix. On damage occurrence, the capsule breaks, and the two fluids react to polymerize and heal the damaged site.

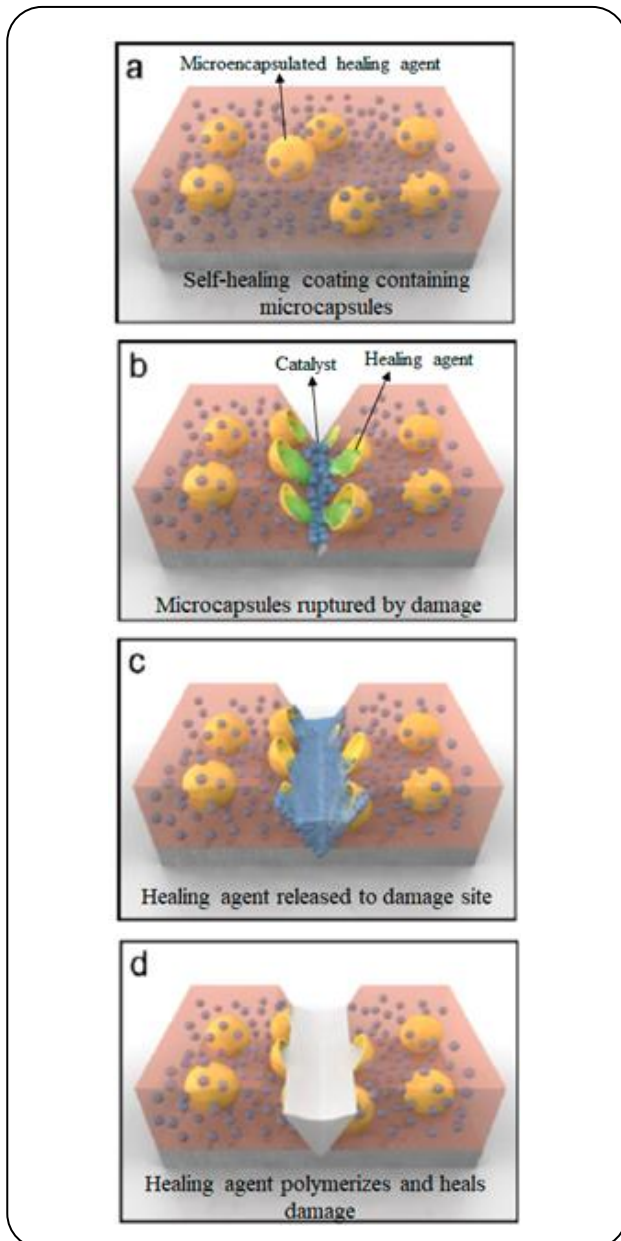


Fig. 2: Healing mechanism of typical microencapsulation design [29].

(v) All-in-One microcapsule Model – The catalyst and healant are contained within various layers of a single microcapsule (totally independent). The catalyst (initiator) and healant needed are to be held either by the shell wall or inside the capsule secluded by partitions (multi-layer capsule) or a single large capsule containing separate small capsules with monomer and catalyst within them (capsule-in-capsule). When capsules break during damage initiation, they release polymerizing healing agents and heal the damage, as depicted in Fig. 2.

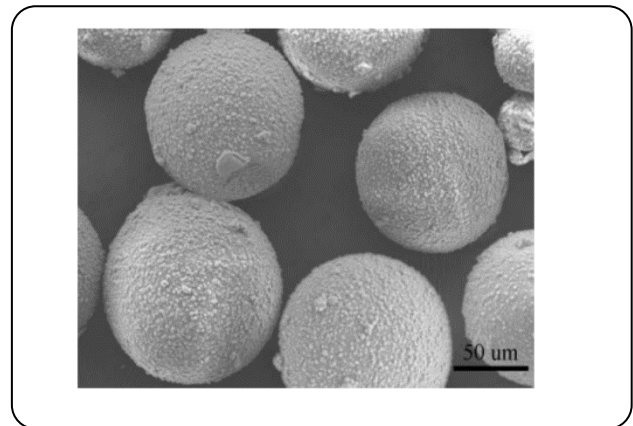


Fig. 3: SEM image of typical microcapsules [20].

Microencapsulation techniques used in self-healing composites

The core healant is encapsulated primarily to guard against environmental matrix influences and avoid pre-reaction, keeping the healing agent dormant for an extended time. The encapsulation method should be processed corresponding to assure the comprehensive necessity of any particular healing composite; thus, careful choice of the encapsulation method for the core healing material and preparation of the shell wall matrix is required [30]. The typical microcapsules made through polyurea-formaldehyde grafted epoxy functional group shell used for microencapsulation techniques to develop self-healing composites are illustrated by an SEM (Scanning Electron Microscopy) image in Fig. 3.

The microencapsulation method, along with the respective shell wall endorsed for this design of healable composites, must consider a few essential features:

- Properties of the shell
- Properties of healing agent to be encapsulated (low viscosity)
- Microcapsule dimension
- Shell wall porosity
- Effectiveness of capsule formation (amount of healing agent encapsulated)
- The interacting interface of the microcapsules with the matrix
- Resistance of capsule to compound with the matrix
- Processing parameters needed for the composite healing system

Emulsification techniques are typically used in preparing microcapsules containing encapsulated healing agents. In this process, polymerization of the monomers

creates a shell structure around the floating droplet-shaped healant. Emerging self-healing methodologies led to the development of various novel encapsulation techniques. Below are some microencapsulation techniques that can embed microencapsulated self-healing agents as core material in the CFRP matrix; however, a range of encapsulation techniques do not necessarily initiate the self-healing mechanism and suit it.

In-situ polymerization technique

The encapsulation technique of in-situ polymerization has been used since the 1980s and found its path in industrial applications in the 1990s. Dynamic agitation (vibration) or sonication of biphasic liquids is utilized in producing oil emulsions of water and water emulsions of oil during in-situ polymerization. The initiators and monomers used to prepare microcapsule walls are diffuse within the scattered or constant phases. Polymerization generally occurs over the external boundary of the healing agent droplet, or it can be said that the resulting polymer accumulates on the droplet surface. Polymers synthesized by monomer attain insolubility in emulsion, thus, producing a microencapsulation of desired core healing agent. [31] Generally, tuning the size of microcapsules is easy by varying the emulsifying agent with the diffusion rate; but ideally, obtaining homogeneous distribution is a task. The prepared microcapsules via in-situ polymerization technique are highly dependent on interior and exterior material and their synthesizing environment, as shown in Fig. 4. The synthesis environment depends on the type of emulsifying agent based on core materials, weight ratio, pH, synthesis temperature, and mixing speed. The introductory self-healing enabling micro-capsule developed by in-situ polymerization contained healant Dicyclopentadiene (DCPD) covered with a wall of Poly-Urea-Formaldehyde (PUF). The obtained microcapsules were spherical with a diameter ranging from 10-1000 μm controllable by variation in agitation speed, and the shell wall thickness varied from 150-220 nm. Following this work, PUF shell microcapsules were synthesized by *Suryanarayana et al.* for encapsulating linseed oil. [32]

PUF is used frequently in the preparation of shells but has some limitations. Limitations include lower sealing attributes, poor weather resistance, and high brittleness, which reduces its use in encapsulating applications.

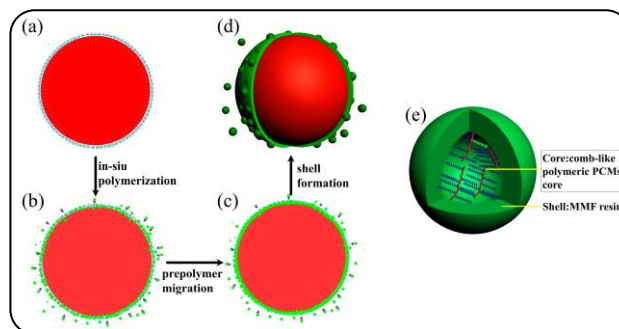


Fig. 4: Illustration of formation of in-situ Polymerized microcapsule: (a) oil core droplets, (b) process of microencapsulation, (c) shell formation by crosslinking, (d) formed microcapsule and (e) fabricated microencapsulated polymeric phase change material [33].

A relatively expensive method was implemented by Yuan and co-workers, who removed the urea unit from the PUF by introducing melamine to produce PMF microcapsules. [34] These composites with microcapsules containing diglycidyltetrahydro-o-phthalate (DTP) (epoxy monomer) and polythiol (hardener for epoxy material) were characterized using fatigue test that showed toughened capability even when exposed for 24hr to a higher temperature approximately 250°C.

As thapproximatelyined interest, *Liu et al.* prepared cost-efficient poly (melamine urea formaldehyde) (PMUF) capsule walls filled with ethylidene norbornene (ENB)– a kind of healing polymer. [35] PMUF microcapsules showed robust, comprehensive properties over the UF\MF capsules for usage in microencapsulated self-healing polymers. In their further study on ethylidene norbornene (ENB) as a healing agent, the same research group inspected a relatively complex and expensive Shirasu Permeable Glass (SPG) membrane emulsifying process via an in-situ method. Unconventional to the earlier prepared microcapsules, the capsules synthesized by this technique showed high thermal stability up to 300°C and narrow space dispersion. Further, the particle size analysis proved more uniformly sized capsules with a mean diameter of 40 μm with a wall depth of range (400-600nm). These UF, PMF, and PMUF compounds were efficiently utilized to heal the known polymer matrices with one essential familiarity. Above 200°C, formaldehyde in these synthesized compounds would be partially removed. Furthermore, the synthesis of PMUF capsules is way easier than the synthesis of PUF and PMF capsules.

Interfacial polymerization technique

The interfacial polymerization technique for encapsulation is analogous to the in-situ polymerization technique as it prepares self-healing, enabling microcapsules using oil or water emulsifying. However, the reactants required to prepare the shell wall are procured from the dual continuous and dispersed phase. Typically in this methodology, the healing agent initially undergoes emulsification or dispersion in a water phase which contains a pre-diffused compound to form a shell wall forming oil in water emulsion. Second is the addition of different compounds emulsifiable within the oil phase. Then after, crosslinking starts near the aqueous phase and organic phase interface, which results in microcapsules with droplet-shaped core healing materials. The third is separating the aqueous phase containing microcapsules from the organic phase, and then transferring microcapsules containing the healing agent as core material to an aqueous solution. Microencapsulation via Interfacial polymerization technique was introduced for preparing polyurea(PU) walled microcapsules by using toluene 2,4-diisocyanate(TDI) pre-polymer with 1,4-butanediol(BD). [36] The synthesized microcapsules were used to encapsulate 2-octyl cyanoacrylate (OCA), an adhesive tissue of cyanoacrylate; for application as self-healing acrylic bone cement in the bio-medical sector, as shown in Fig. 5. The microcapsules had an average diameter ranging from (75-220 μ m) generated with an agitation rate at 350-1100 rpm. [37]

Isophorone diisocyanate (IPDI) is an additional highly active, without any potential accelerator healant for moisture conditions. The P.U. shell microcapsule system encapsulates this self-healing enabling agent. However, the less dense P.U. microcapsules could not protect the moisture-sensitive IPDI from the environment, thus reducing the microcapsules' service life. An alternative approach was proposed to overcome the problem using metal shell walled microcapsules like nickel. [38] The respective microcapsule preparation includes liquid-form synthesizing procedures such as the electroless plating method, Interfacial polymerization technique, and emulsifying process. Capsules developed via this technique had an average width of 50 μ m with a shell thickness of less than 2 μ m. They demonstrated significant advantages over polymer shell wall microcapsules, like enhanced mechanical features and better permeable

resistance from the fluid molecules. These capsules were successfully filled with healing materials and can be approximately preserved for nine months or more. N.R. Sottos *et al.* [39] reported an intermix method utilizing the interfacial technique of P.U. with in-situ U.F. as a modified encapsulation procedure for a liquid healing agent containing capsules featuring separate walls. This synthesis route involved the dissolution of P.U. pre-polymer (Desmodur L75) in the core liquid ethyl phenyleacetate (EPA) at Urea Formaldehyde (U.F.) polymerization. The produced microcapsules showed excellent interfacial bonding with higher temperature stability than the conventional U.F. microcapsules.

Benefits regarding this technique can be stated as follows:

- Encapsulation efficiency is relatively high (high content of healing agent encapsulated)
- Moderate reaction conditions
- Faster encapsulation of core healing material
- Requirements for the number of reactants and their purity are flexible

However, a limitation is that a specific unreacted shell monomer is contained in the generated microcapsules, which can deactivate the core healing material on reacting.

Pickering emulsion templating technique

In the Pickering emulsion templating technique, the emulsion is balanced with particles of solid nature adsorbed onto the interacting region of the dispersed and continuous phase. *Walter Ramsden* (1903) stated its effect [40] and entitled on *S.U. Pickering* (1907) described this phenomenon [41], but using stabilized Pickering emulsion technique in microencapsulation of typical healants was indicated by *Velev* and co-workers in 1996. [42] Healant encapsulation in polymer matrix by this technique utilizes two steps; a stable Pickering emulsion preparation and freezing (no movement) of the colloidal particle adsorbed on droplet-shaped core healing material as illustrated in Fig. 6. Although properties of the solid particles, such as hydrophobicity, shape, and size of a particle affect the stability of an emulsion. Firstly, a mechanical stimulus is required to accumulate colloidal particles in the interface to create a stabilized emulsion. Secondly, with the help of physical or chemical cross-linking reactions, colloidal particles freeze and create a stabilized and dense structural wall. Pickering emulsion templating offers advantages

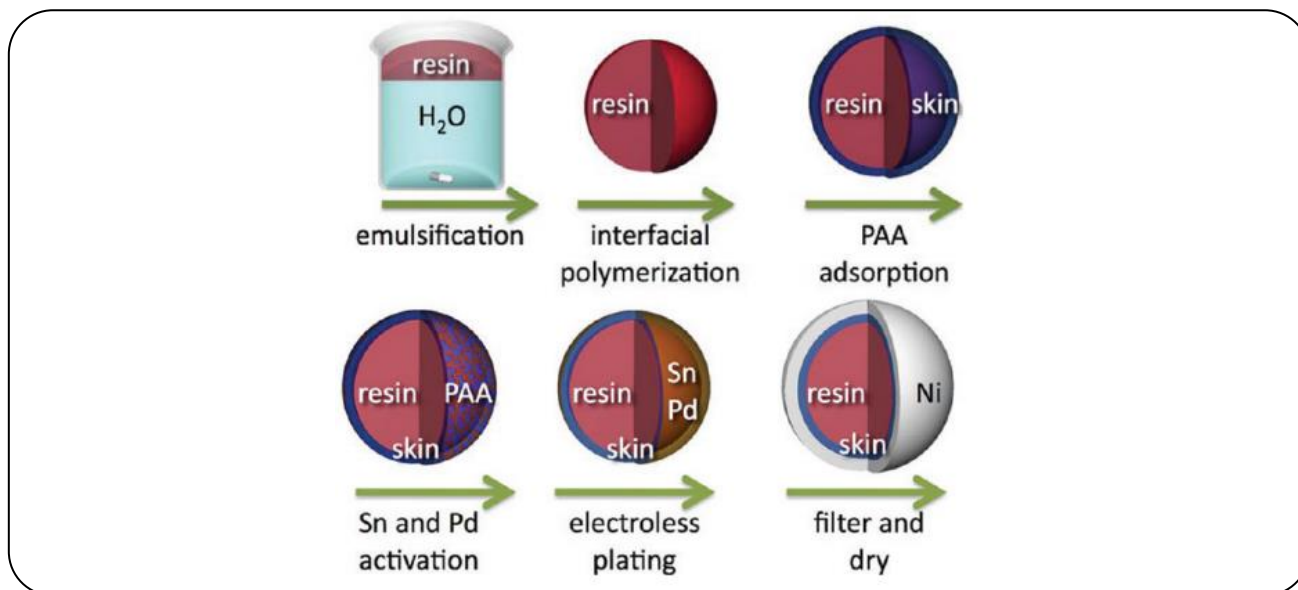


Fig. 5: Synthesis of metal microcapsules containing liquid healant [38].

over traditional molecular agent stabilized emulsions like highly stable emulsion, minimal pollution and low toxicity, recyclability, lower fizziness, and comparatively lower cost. They are efficient in microcapsule formation with distinct features. This method is a better alternative for encapsulating. Challenging to encapsulate chemicals by a typical encapsulation process, and it helps make capsules with specific structures. *Li et al.* [43] developed the microcapsule synthesizing technique to encapsulate core solvents (perfluoroheptane, hexadecane, and xylene) by Pickering emulsion templating interfacial atom transfer radical polymerization (PETI-ATRP) of *N,N*-methylene bisacrylamide. The preparation method utilized better Pickering emulsification, which involved the accumulation of anionic initiators upon surfaces of cationic nanoparticles. *Yang et al.* prepared PU\PMF dual shell wall microcapsules to encapsulate ethylphenylacetate (EPA) as a healing agent *via* a stable oil-in-water emulsifying technique with silica nanoparticles. [44] The pre-dissolved M.F. polymer within the continuous phase interfacially reacted with the oil droplets containing IPDI to form the inner P.U. shell. In contrast, the M.F. prepolymer undergoes in-situ polymerization to form a spherical, rough surface outer PMF shell wall. The formed microcapsules *via* the Pickering emulsion technique represented the all-in-one microcapsule model stated above. The size of the capsule relatively depended on the amount of adsorbed silica nanoparticles on the droplet

surface. With a similar all-in-one microcapsule model in mind, *Yang et al.*, in their proceeding work, prepared PMF-silica hybrid shell microcapsules containing numerous small spherical-shaped di-butyl phthalate (DBP) loaded P.U. capsules *via* Pickering emulsion template technique. [45].

At first, with the help of interfacial polymerization, polyurea microcapsules with an average diameter of 15 μ m containing DBP were synthesized by oil-in-water emulsion. They were balanced with water-absorbing nanoparticles of Silica. Secondly, a water-in-oil emulsion was formed when tiny PU microcapsules dispersed in an aqueous solution and were emulsified in toluene with a hydrophobic silica nanoparticles emulsifier. Finally, loaded PU capsules were compacted inside a PMF-silica hybrid shell of an average diameter of 150 μ m *via* cross-linking between formaldehyde and melamine within the aqueous phase.

Sol-gel reaction technique

Encapsulating technique *via* sol-gel reaction is primarily used to prepare self-healing enabling inorganic capsules (Silica for its impermeability) in micro (μ) to nano (n) range diameter. The reaction takes place at low temperatures in moderate conditions. The sol process is initiated before gelation occurs *via* forming a low viscous solution by dissolving the inorganic precursor for shell material in water (molecular mixing of solution) and further allows for customization of shell material.

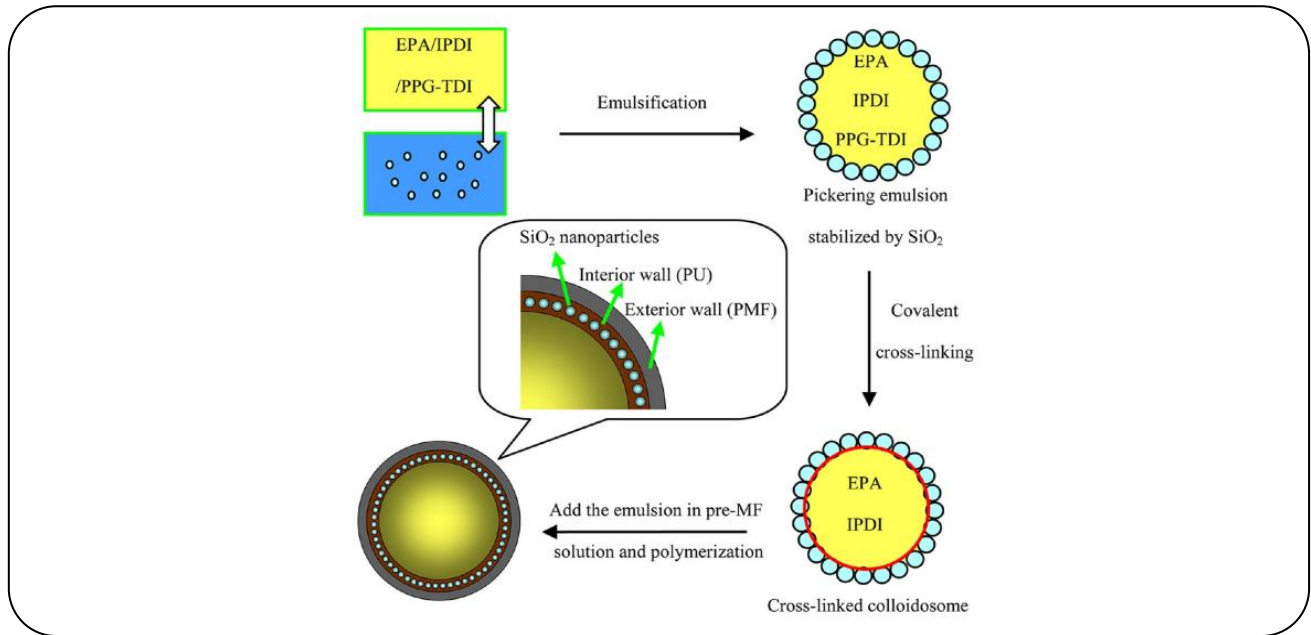


Fig. 6: Schematic synthesis of EPA-filled dual-shell (SiO_2) microcapsules [44].

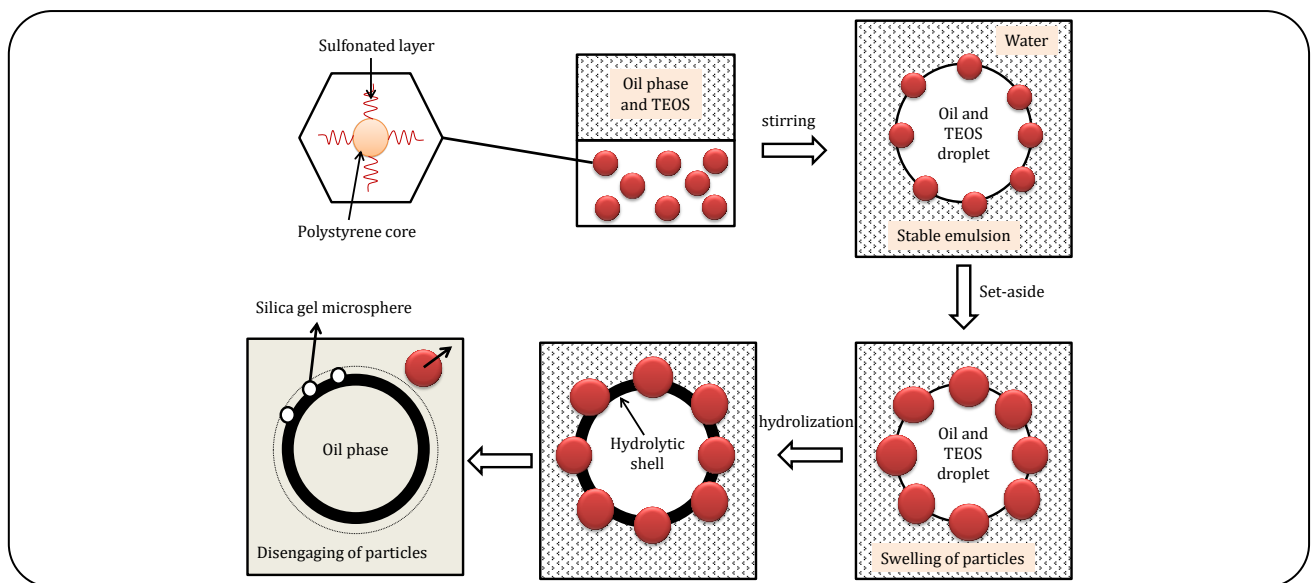


Fig. 7: Schematic for preparation of smart (PS-TEOS) microcapsules.

Synthesis in the Sol-gel technique includes the oxide network created by the polycondensing monomer-monomer reaction within the aqueous phase, which takes quite a long time.

The conventional silica-sol-gel encapsulation technique has gained broad research interest. It has originated from stöber chemistry, which technique involves pre-hydrolysis and condensation of an orthosilicate [such as tetraethyl orthosilicate (TEOS)] via

aqueous glycerol micro-emulsion templating as shown in Fig. 7. [46,47] This self-healing enabling technique is efficient for thermoplastic resin systems like polyvinyl aniline [48]. In another self-healing cementitious research study, the same sol-gel and interfacial techniques were utilized to encapsulate methylmethacrylate (MMA) as a healing agent and triethylborane (TEB) as a catalyst. [46] It showed promising results for implementation in polymer matrix composites. Silica, an inorganic element,

helps encapsulate various aqueous, oil, and solid particles. It maintains the chemical activity of the healing agent on encapsulation. Moreover, the silica microcapsules can be efficiently dispersed in the polymer matrix.

Mini-emulsion polymerization technique

A mini-emulsion is a unique emulsion produced by force on the mixture consisting of an unmixable dual aqueous phase (water-oil phase) with single or more co-surfactants. High shearing processes stabilize, and high energy homogenization limits diffusion degradation by helping surfactants/co-surfactants against gravity separation. Ostwald ripening, coalescence, and flocculation occasionally cause instability. Mini-emulsion polymerization of a monomer occurs within pre-existing monomer particles without forming new particles. The dispersed phase droplets have a range diameter (50nm- $1\mu\text{m}$), thus creating small-scale capsules of nano to the micro range with low solid content. The approach of encapsulation via mini-emulsion polymerization was first introduced in 1973. It can be used to prepare functionalized polymer nanocapsules [49], which can encapsulate various materials, initiators, or catalysts with little dose (as per required for healing), either hydrophobic or hydrophilic, irrespective of their state (liquid or solid) [50] by ring-opening metathesis polymerization. It is not limited and has applicability to encapsulate materials in polyaddition or polycondensation polymerization. However, encapsulating the healing agent via mini-emulsion polymerization leads to the formation of microcapsules of smaller size with lower healing content. It provides inefficient healing, as the amount of healing agent filled at the cracked portion is relatively common for efficient self-healing functionality. As an advancement, microcapsules via the mini-emulsion polymerization technique can be used in systems where a low amount of catalyst is needed to be encapsulated for fulfilling the self-healing function. Two methods are applicable to prepare microcapsules via mini-emulsion polymerization: Extreme energy techniques and Inferior energy techniques. The powerful energy technique uses high-shear methods, typically via exposure of the mixture to a high-power ultrasound wave or high-pressure homogenizer. While the inferior energy technique uses a water-in-oil emulsifying process which gradually transforms to an oil-in-water emulsion by altering its temperature and configuration, the

water-in-oil emulsifying process is slowly adulterated and cooled by adding water drop by drop to attain an inversion point and a phase inversion temperature. These factors cause the interfacial tension between two liquids to decrease significantly, forming tiny oil droplets of diameter (50-500nm) in water with lower solid content inside. [51] However, mini-emulsions prepared are generally thermodynamically unstable but are kinetically stable; thus, on leaving the emulsion for some time, the oil and water mini-emulsions separate from each other again. Klumperman and *Van den Dungen et al.* reported the preparation of Poly (styrene-maleic anhydride) (PSMA) shell nanocapsules loaded with pentaerythritol tetrakis(3-mercapto propionate) as a core healing agent via Mini-emulsion polymerization technique. [52] The prepared PSMA nanocapsules were in the range of (150-350nm) in diameter and were stabilized using a suitable length of polystyrene block in a reaction with formaldehyde. Furthermore, they synthesized styrene nanocapsules for their application as healable coating, emphasizing thiol-ene chemistries. Styrene nanocapsules with a diameter ranging from (60-150nm) were prepared to encapsulate DiNorbornene (1, 6-hexanediol di (norborn-2-ene-5-carboxylate)), which serves as a co-surfactant because of its higher hydrophobicity and boiling point. *K. Landfester et al.* showed the first-ever liquid dicyclopentadiene (DCPD) encapsulation as a healing agent in silica capsules of approximately 300nm in diameter via Mini-emulsion free radical polymerization. [50] The preparation procedure is the same with two monomer particles divided by the two mini-emulsion liquid phases, which polymerize to form functional nanocapsule shells containing the core agents (DCPD and Grubb's catalyst) capable of healing by instigating ring-opening metathesis polymerization (ROMP).

EXTRINSICALLY SELF-HEALING COMPOSITES - MICROVASCULAR NETWORK

The self-healing technique using a micro-vascular design system possesses the capability of core healant to flow in a crack of polymer that requires healing and is stored in the vascular tubes. The vascular system ruptures/breaks upon a crack intrusion in a matrix, thus discharging the healant in the damaged site through the capillarity effect and repairing the damaged portion via a cross-linking reaction with the catalyst. Emerging extensive

interest in this field led many researchers to study and develop various strategic techniques to prepare these micro-vascular networks, which were able to incorporate the self-healing feature in composites.

The vascular design of extrinsic healing is an alternative approach to the microencapsulation design but with the same healing chemistry. It mimics the animal circulatory system in which the heart pumps blood through arteries and veins. [54] One of the primary characteristics of this design is that hollow interconnected networks can be connected to an external source and can be refilled once depleted. It eases the maintenance of healing agents within the hollow networks. However, the storage time of the healant whose self-life has lapsed and does not contribute towards healing. [55]

The micro-vascular design approach was initially used for the cementitious matrix to heal and introduced for FRP composites. [56,57] However, they must be expanded to small-scale applications like coatings due to complexities in large-scale models, as illustrated in Fig. 9. [58] Typically, hollow fiber tubes were used to prepare vascular networks. *Dry et al.* [59] demonstrated composite material with an incorporated glass pipette tube channel containing a healing agent (cyanoacrylate). Further, using other fiber materials such as copper and aluminum as hollow tubings enhances the self-healing efficiency of a micro-vascular design approach. [58] A modified sacrificial element was developed to prepare interconnected networks via layer-by-layer and direct write assembly techniques. [19] These tubeless micro-vascular networks were first synthesized by embedding a sacrificial network in composite material and later by eliminating it via thermal stimulus and vacuum. [54] Once the micro-vascular network has been set up within the composite, they are filled with the high-pressurized, low-viscous healing agent. [14] Uniform dispersion of the healing agent inside an interconnected network is required for uninterrupted fluid flow. Nevertheless, the local ambient temperature may affect the healing agent's viscosity. Generally, healing agent dispersion is ensured via capillary forces for large interconnected micro-vascular networks, as shown in Fig. 10. [60] However, the external pump may be required to certify homogeneous dispersion and efficient flow out of healing agents for large-diameter vascular networks. [18] These pumped high-pressure healing agents can cause breakage

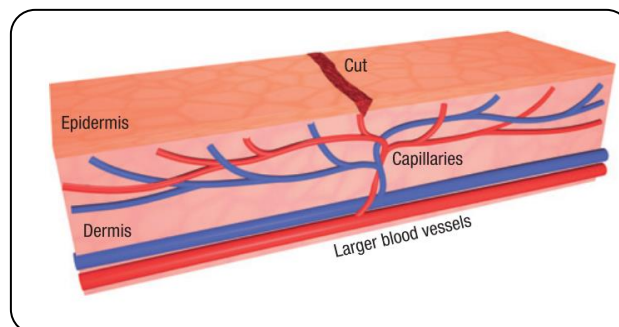


Fig. 8: Human veins inside skin Source [53].

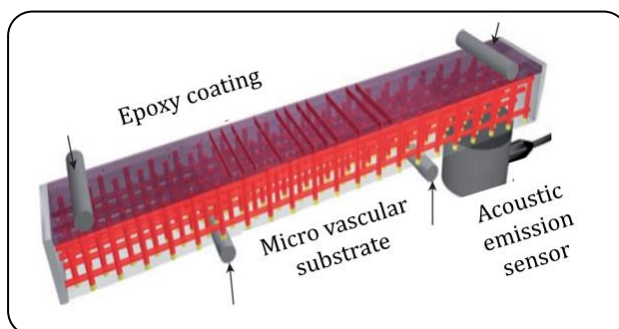


Fig. 9: Micro-vascular design composites [53].

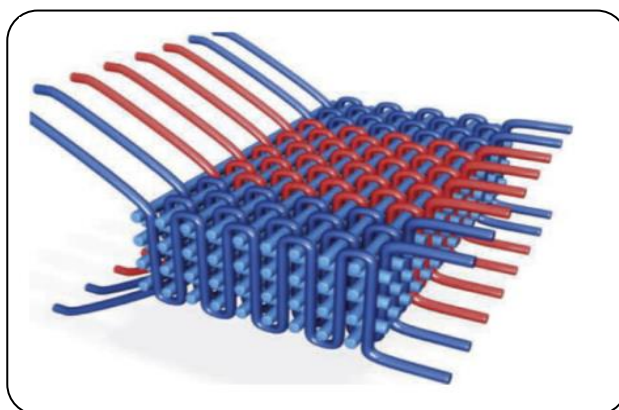


Fig. 10: 3-D Micro-vascular network [63].

of the end of a vascular network, thus leading to the unnecessary release of a healing agent. Additionally, these systems require external intervention for pumping action. As soon as the damage propagates through self-healing composites and breaches through a micro-vascular network, the healant immediately diffuses to the damaged sites and undergoes polymerization to heal sites. Higher fracture toughness healing efficiencies were reported for optimum pressurized vascular networks [61,62].

The architectural design of these hollow networks is crucial for the healing agent circulation dynamics, damage intrusion, and mechanical features, respectively [14].

The additional reinforcing material is utilized to improve the characteristic features of the composite; thus, it helps by altering initial neat matrix mechanical characteristics; the same is the function of the incorporated microcapsules and vascular networks. However, characteristics strictly depend on distribution and inherent properties while affecting damage propagation patterns. [64] Various network designs were proposed for the vascular approach, from simple designs like straight parallel vascular networks [62] too much complicated 3-D herringbone designs. [65] *Esser-khan et al.* utilized polylactide (PLA) fiber as a sacrificial element to develop a herringbone 3-D network within a composite. This system proved to have higher healing efficiency than other network designs. [63]

INTRINSICALLY SELF-HEALING COMPOSITES:

The intrinsically healable materials depend on the type of healable phase used to mimic the healing nature of a flesh injury, such as the growth of underlying tissues and skin. This self-healing composite category is pretty different from extrinsically healing composites due to their inherent chemical integrity and requires no external intervention of any healing agent; however, an external stimulus may be needed to trigger the healing mechanism. [66]

A recombining process of the cleaved chains in polymer achieves this level of healing in the FRP composite system due to the appearing readily synthesizable functional bonds ($-C=C$, $-OH$, $-SH$, $-C=O$, $-NH_2$, $-S-S$, $-COOH$ and $-Si-O$), cyclic bonds and free radicals at the damaged surface. Ideally, the virgin and recombined healed surfaces are identical, as illustrated in Fig. 11. It follows two types of healing chemistry: covalent and supramolecular.

Covalent chemistry

Intrinsic healing chemistry using the durability of the covalent bonds after damage relies on environmental conditions and the applied matrix material. [67] Depending on the used matrix material, these covalent chemistries can be further categorized into chain exchange, free radical, and cycloaddition reactions.

General chain exchange reactions

The general chain exchange reactions include recombining the covalent bonds in a single or extensive network of chains. *Deng et al.* [68] demonstrated the

healing of polyethylene oxide (PEO) with modified ends of acylhydrazines. The chain ends recombining at room temperature (25°C). The silonate end group reaction and disulphide chain exchange reaction are additional examples of healing reactions taking less time. [69,70] *Yoon et al.* [71] developed an ambient self-healing thiol-disulfide-based polymeric film. The end disulphide bonds shuffled their position *via* ionic or free radicals formed due to ionic scission [72,73], heating, and oxidation, respectively, at the damaged surface, as shown in Fig. 12. [74]

Further self-healing at room temperature triggered by light was demonstrated utilizing the thiuram disulfide bond within the polyurethane matrix [75,76]. *Canadell et al.* [77] showed

that many reactive ends lead to higher strength resilience; however, the concentration has to be optimally maintained without affecting the matrix features. As an advanced study, *Bailey et al.* illustrated the electric conductance property of the chain exchange self-healing coatings. [78]

Free radical reactions

Few chain exchange reactions require the formation of free radical ends such as polyurethane bonds and disulphide bonds. [79,80] These free radical ends have low reactivity for the solid phase, while they become more readily reactive for the fluid phase. The healing mechanism instigates when the cleaved free radical ends react with opposite surface ends before responding with other elements such as oxygen. The reaction of free radicals with oxygen consequences in the deprivation of healing functionality and has no further interaction with healing. [81] *Imato et al.* [82] illustrated using diaryl-bi-benzo-furanone (DABBF) as a thermally stable oxygen-tolerant agent. This system healed efficiently at ambient conditions without external intervention. [83]. *Yuan et al.* [84]

demonstrated healable modified polystyrene by alkoxyamine bonds to ensure dynamic cross-linking. The system heals the formation of free radicals on cleavage. Many factors affect the stability of the formed radicals, like environmental temperature [85], pH [86], and the presence of a few compounds. The stabilized free radicals result in better healing performance. The CS_3 functionalized Tri-Thio-Carbonate (TTC's) compounds enable healing within polystyrene, poly methyl methacrylate (PMMA) [87], and n-butyl acrylate (BA) [88,89]. The poly (BA)

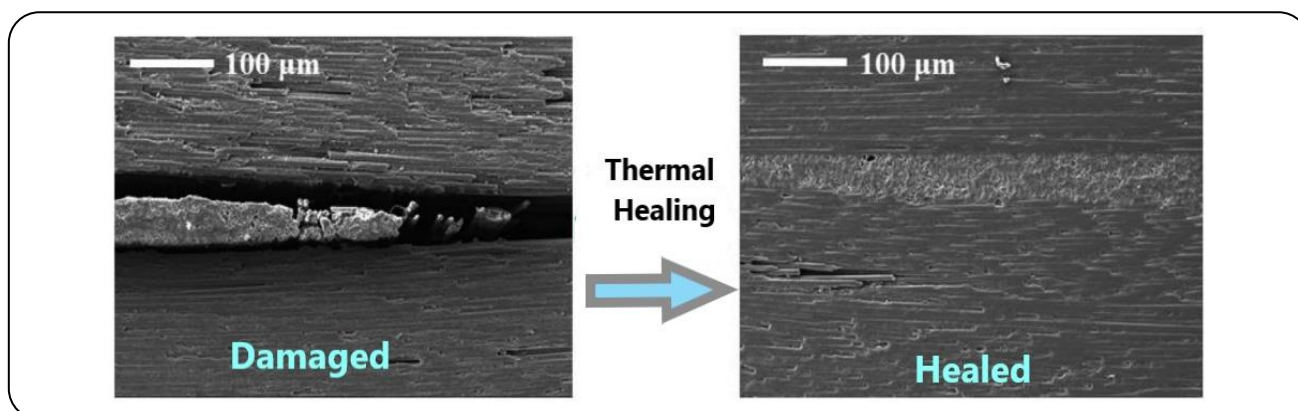


Fig. 11: Intrinsically Healing Mechanism illustrated by SEM images [24].

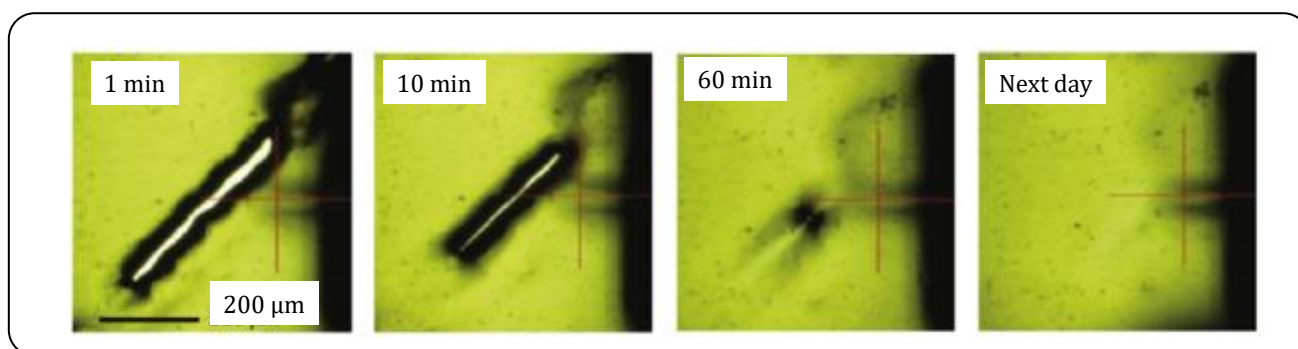


Fig. 12: Optical micrographs under an atmosphere of the thiol-functionalized polymer [71].

cross-linked with TTC through reversible addition-fragmentation chain transfer (RAFT) healed under UV light (330 nm) stimulus for 24 hrs. Ghosh *et al.* [79] demonstrated two types of self-healing composite networks (PU + oxetane (OXE) + chitosan (CHI)) [79,90] and (PU + oxolane (OXO) + chitosan (CHI)). [91,92] Both composites healed at different times under UV light. Fig. 13 delineates the damaged BA polymer and healed source during the healing of BA polymer.

Cycloaddition reactions

Cycloaddition reactions are another kind of self-healing synthesis where molecules undergo ring formation. Typically Diels-Alder (DA) synthesis is a cycloaddition reaction method. However, materials like polyacrylates, polyamides, and epoxies self-heal using reversible cross-linking via (4+2) electron exchange cycloaddition. [93] These systems' diene and dienophile cleave under thermal or mechanical stresses [94] and heal when the temperature is lowered. [95] Analysis of diene (furan) and dienophile (maleimide) illustrate the effect of cross-linking concentration on healing features. [96]

Another type of cycloaddition reaction for the self-healing mechanism is (2+2) cycloaddition. Chung *et al.* [97] formed cyclobutane rings with 1,1,1 Tris-Cinnamoyloxy Methyl) Ethane (TCE) via (2+2) cycloaddition synthesis under UV stimulus greater than 280nm, as depicted in Fig. 14. Zhang *et al.* utilized this reaction for coumarin [98], and Klukovich *et al.* developed a stress-induced healing mechanism via [2+2] cycloaddition of perfluorocyclobutane. [99] Similar to this reaction [4+4], cycloaddition was utilized by K. Landfester and co-workers to polymerize the anthracene derivatives [100]. The triggering stimulus of heat and light for healing shows much assurance for future applications. However, a constant source has to be maintained, which can harm the composite material [70].

Supramolecular chemistry

Intrinsic self-healing via supramolecular chemistry has attracted many researchers for decades due to its faster cross-linking mechanism than covalent chemistry. [101,102] This chemistry depends on the whole network structure rather than the specific bonds, which are relatively compassionate and are not used to heal structural composites.

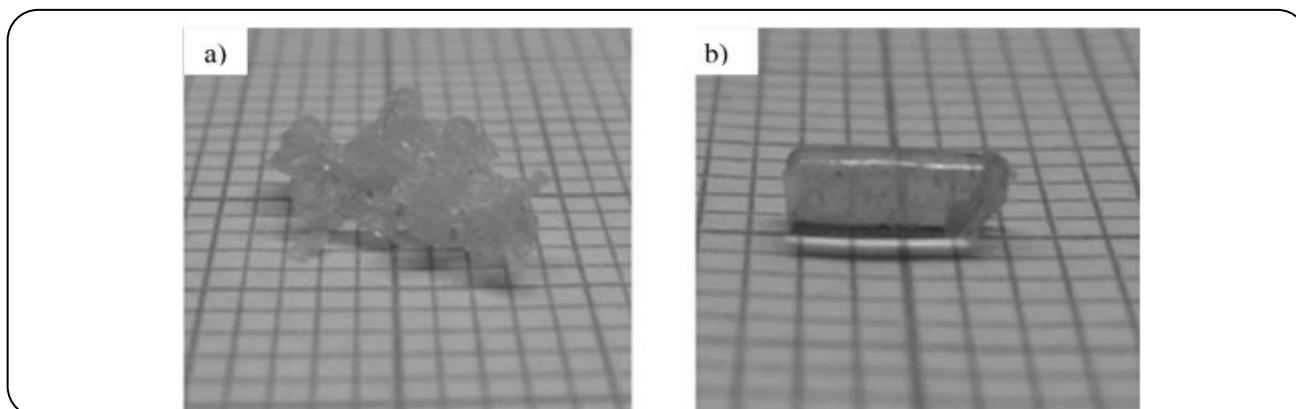


Fig. 13: Images of BA polymer (a) Damaged (b) Healed Source [89].

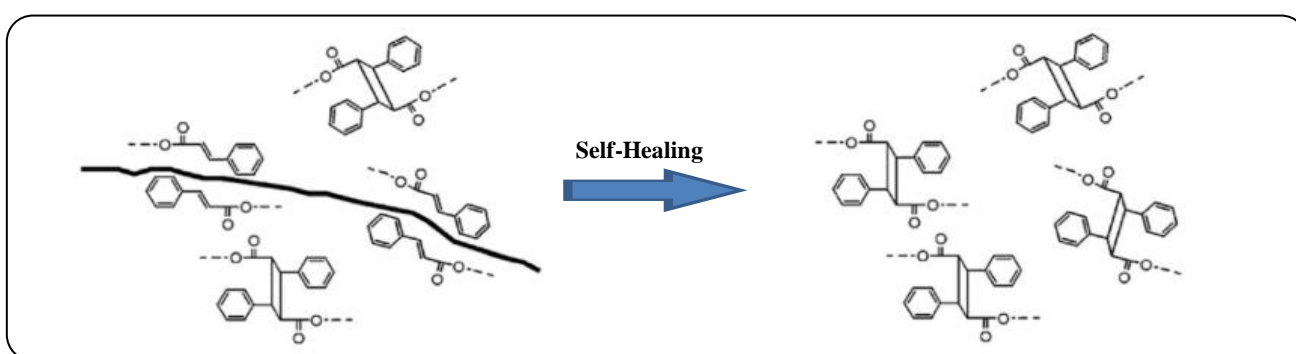


Fig. 14: Intrinsic healing via (2+2) cycloaddition in cinnamoyl group (optical) [97].

Nevertheless, both intrinsic healing chemistries are based on the direction of networks. The supramolecular chemistry can further be grouped into three classes such as hydrogen bonds, interaction via Ionomer healing, and π - π stacking.

Hydrogen bonding

Collectively aligned solo, double, and quadruple hydrogen bonds in a chain dominate a few material properties such as viscosity, chain length, and mechanical strength. Although these hydrogen bonds have inadequate strength compared to covalent bonds, they can be utilized to provide quality strength. [103] Increasing hydrogen bonds increases strength and stability linearly. [104,105] Various studies on ureidopyrimidinone (UPy) having quadruple hydrogen bonds revealed that they are highly temperature dependent [106], stable [107], and easy to synthesize. *Foster et al.* demonstrated healable cellulosic material via UV stimulus by incorporating UPy with poly(ethylene-co-butylene) as a matrix. [108] Few researchers suggest using Poly-Iso-Butylene (PIB) to show

hydrogen bonding features. [109,110] *Banerjee et al.* developed a self-healable coating for photovoltaic cells under sunlight using PIB functionalized with coumarin. [111] Carboxylic acids connected to a functional group of thermoreversible rubbers act as a promising self-healing candidate under ambient conditions. [112] However, high temperatures and moisture restrict the healing nature of these materials. [113] Synthesis of these systems is easy [114], and the damage event itself instigates the healing, thus autonomous. *Tuncaboylu et al.* utilized the hydrophobic interaction of stearyl methacrylate (C18) with acrylamide as self-healable hydrogels. [115] A polyvinyl alcohol (PVA) hydrogel made by the freezing/thawing process can self-heal at room temperature without a stimulus or healing agent. With a high fracture stress and mechanical strength, PVA hydrogel can mend quickly. Hydrogen bonding between PVA chains at the interface of the cut surfaces is what causes the phenomena, according to research on the impact of hydrogel preparation conditions. Fig. 15 illustrates the hydrogen bonding phenomenon of self-healing properties of PVA hydrogel and their stretching

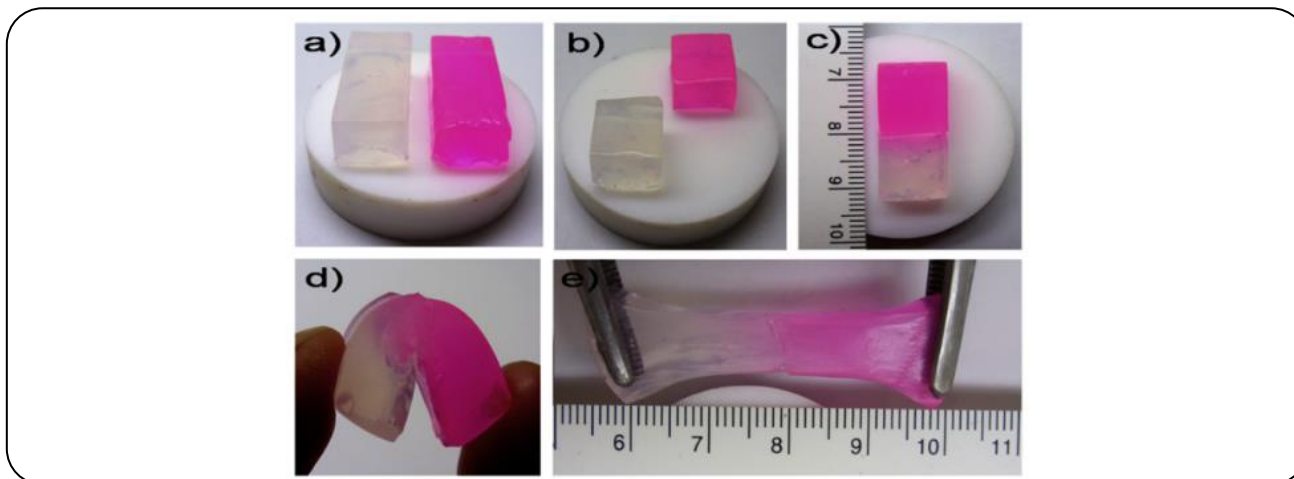


Fig. 15: Optical images of PVA gel (a) Separate gels (b) Half-cut gels (c) Undergoing healing in ambient (d) Healed and bent (e) Healed & stretched [88].

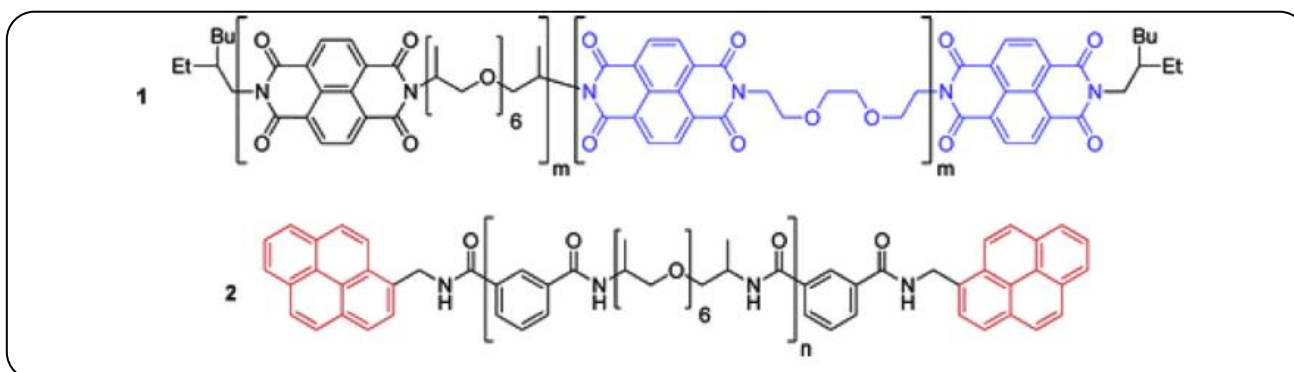


Fig. 16: Molecular structure of $(\pi-\pi)$ bond in blended healing polymer [118].

capability after developing a hydrogen bonding upon bringing two separate halves in contact for 12 hours at room temperature without any external stimulus.

$\pi-\pi$ Stacking

A typical type of supramolecular chemistry is $\pi-\pi$ stacking. It has been generally found in several polymers in pyrenyl derivatives and diimide. The molecular structure of the $\pi-\pi$ bond in blended healing polymer is illustrated in Fig. 16. *Burattini et al.* have reported using polyimide in conjunction with other compounds. Using polysiloxane with polyimide as a self-healing polymer heals at 100 °C. [116] In contrast, the polyamide with polyimide heals the tensile strength completely at 50°C. [117] They healed the polyimide with the help of pyrenyl component. [118,119] Hydrogen bonding in combination with $\pi-\pi$ stacking used polyimide with polybutadiene modified by pyrenemethylurea. [120] Polyimide functionalized with

bis-pyrenyl showed healing ability at 140 °C. [121] *Xu et al.* developed a higher-strength gel by utilizing nitrobenzoxadiazole modified with cholesterol derivatives; however, no healing efficiency was reported [122].

IONOMER INTERACTION

This type of supramolecular chemistry is also known as ionic interaction [70] and usually requires two steps to instigate self-healing. First, the damaging impact generates heat and cleaves the ionic bonds in the matrix. This heat further softens the damaged site via partial melting, as illustrated in Fig. 17. Secondly, the damaged molten site is buoyant, like the mobile polymer chains, and optimal concentrations of these ions are required for efficient healing. [123,124] This healing functionality is remarkably differentiable compared to other known counterparts and is typically emphasizing poly(ethylene-co-methacrylic acid) [125,126].

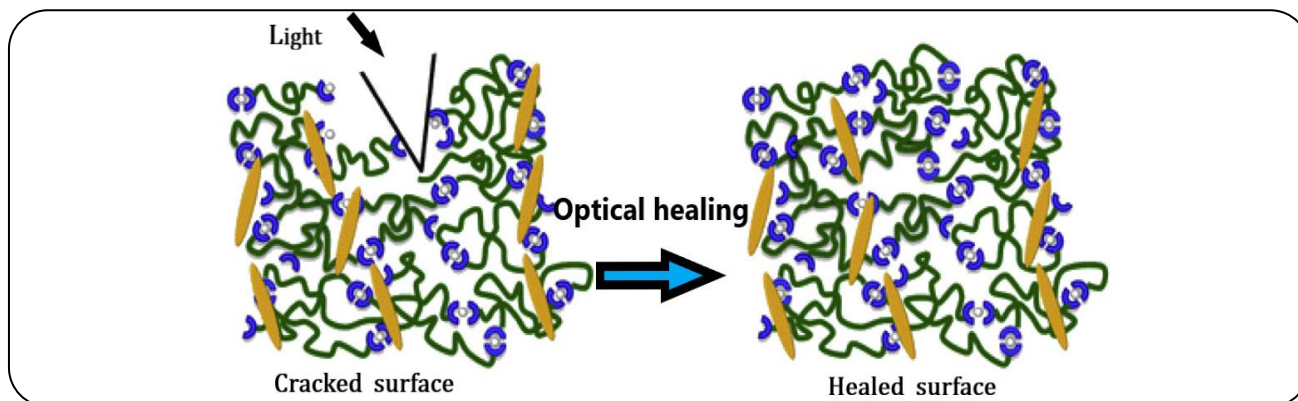


Fig. 17: Intrinsic optical healing via Ionic interaction [125].

Summary and future perspective

This review paper manifests the application of CFRP composite with self-healing enabling matrix material for advanced structural applications. These functional composites are prone to damage during their service. Although many traditional approaches to repair exist, they need to ensure complete reliability for use, and costly maintenance must be done regularly. Self-healing composites have a promising future in the development of novel products. Many researchers are working to restore functional characteristics upon healing material defects using these innovative hybrid materials, as considered in Table 1. However, self-healing composites have some limitations regarding the healing function's durability and the healing mechanism's comprehension. The self-healing composite's most significant hurdles are identifying defects and advancing the healing process. Researchers in this field continuously develop new healable composite designs that can heal themselves while functioning. Emerging literature and highly developed healing-filled extrinsic microcapsule design and micro-vascular design healing strategy prove efficient for extensive scale damages. However, the microcapsules/microvascular being hollow do not provide any structural strength to the fabricated composites.

Further, the design of these extrinsic techniques helps at the time of crack initiation/ propagation to spread the damage and may lead to an unhealable catastrophe. Thus, an optimal amount of microcapsules/microvascular are to be embedded within the matrix material so that the technique provides efficient healing without any adverse effect. The self-healing function in microcapsule design strictly depends on the helant content stored in the

capsules and enables single-time healing. In contrast, in micro-vascular design, the tubular network can be fixed with an external source, enabling repeated healing. The stored helant inside these microstructures also depends on their shelf-life, thus cannot provide efficient healing once the healant crosses its shelf-life (generally between 7-10 months).

In contrast to extrinsic techniques, intrinsic healing techniques do not use any embedded micro-structures and thus retain their strength. They have minimal crack growth and can supply repeatedly. Intrinsic technique strictly depends on the chemistry of the healable matrix and the stimulus employed to instigate the healing; further, the damage in the internal sections (interlaminar regions) of the composite depends on the depth of effect of stimuli such as heat, light, moisture, electricity, electromagnetic waves, and pH. Out of these stimuli, heat, electricity, moisture, and pH have a significant depth, thus healing internal damages. In contrast, the others have limited effect on the surface of the composite and can leave internal fatigue damages unhealed. However, intrinsic technique healing is known to strengthen minor-scale damages, while large-scale damages may not heal efficiently. A remedy to this disadvantage can be using Shape Memory Alloy (SMA) in conjunction with an intrinsic technique [not discussed in this work], which can minimize damage scale and provide efficient healing.

To this end, self-healing CFRP composites can be structurally solid and have functional properties comparatively. They reduce the need for costly temporary repairs, proving better than damage-tolerant designs used earlier. This review work systematically analyzes current development in the growing field of self-healing

Table 1: Summary of healing performance and healing mechanism of self-healing composites.

S. No.	Materials	Healing Mechanism	Healing environment	Mechanical properties	Healing efficiency(%)	Ref.
1	P(AM-co-DAC)/graphene oxide(GO) Hydrogels	Hydrogen bonds, electrostatic interaction	Drop water	Tensile strength,	>92	[127]
2	Polyurethane (PU) nanocomposite	Disulfide (S-S) exchange reactions	Heating and laser irradiation	Tensile strength	90.1	[128]
3	PAA-GO-Fe ³⁺ Hydrogel	Ionic bonding	Contact and immersed in FeCl ₃ /HCl	Tensile strength	~100	[129]
4	Cinnamoyl mechanophore/epoxy	Photochemical cycloaddition	UV irradiation	Recovery	24	[130]
5	Silicon rubber/ graphene nanoplatelets composites	Reversible bonds	Thermal annealing	Tensile strength	87	[131]
6	Graphene/PU	Diels-Alder reactions	Infrared (IR) radiation	Tensile strength	96	[132]
7	Chitosan/GO Hydrogel	π - π stacking, hydrogen bonding	Contact (room temperature)	Recovery	91	[133]
8	Dihydroxyl coumarin-based PU	Photochemical cycloaddition	UV irradiation	Tensile strength	64.4	[98]
9	Reduced functionalized GO/ PU composites	Diels-Alder chemistry	Microwaves	Young's modulus	93	[134]
10	Thermoset rubber (dipropyl disulfide, dibutyl disulfide, 1-pentanethiol)	Disulfide-thiol exchange reactions	Room temperature (RT)	Tensile strength	~99	[135]
11	PU elastomer	Alkoxyamine	80°C, Argon	-	70	[136]
12	Polythiourethane networks	Aromatic exchange reaction	160°C, 20 min	-	Complete removal of cracks	[137]
13	Hydrogels (acrylamide and hydrophobic acrylic)	Metal-ligand coordination	RT	Tensile strength	100	[138]
14	Cyclodextrin and adamantane	Host-guest interactions	60°C, 10min	Tensile strength	70-72	[139]
15	Lignin-modified graphene and waterborne PU	Diffusion of polymer chains	IR radiation	Elastic modulus	171	[140]
16	Thermosetting vitrimer/ thermoplastic PU	Polymer blends	RT	-	Fracture surface joined	[141]
17	GO/thermoset PU	Shape memory assisted	Near-infrared (NIR) radiation	Tensile strength	85	[142]
18	PU nanocomposite/carbon nanotubes	Remote self-healing	NIR radiation	-	80	[143]
19	Glass fibers epoxy composites	Microcapsules and hollow fiber	Diluted epoxy by heat	Tensile strength	97.6	[144]
20	Cementitious structure	Microvascular network	Sodium silicate at RT	Crack closing	81	[145]
21	Glass fiber reinforced vitrimerbased shape memory polymer	Shape memory alloy (SMA) wires (Flexinol)	Heat @150°C	Tensile strength	100	[146]
22	Graphene-glass fiber-reinforced polymer nanocomposites	SMA wires	-	Bending strength	64	[147]

composites with the outlook of designing and fabrication as a critical factors. It would help in promoting emerging advancements in self-healable system materials.

Received : Dec. 7, 2022 ; Accepted : Mar. 6, 2023

REFERENCES

- [1] Millington R.B., Nordberg R.C., [Process for Preparing Carbon Fibers](#), US Patent 3294489A (1961).
- [2] Campbell F.C., ["Manufacturing Processes for Advanced Composites"](#), Elsevier Inc, New York, (2003).
<https://doi.org/10.1016/B978-1-85617-415-2.X5000-X>
- [3] Williams G., Trask R., Bond I., [A Self-Healing Carbon Fibre Reinforced Polymer for Aerospace Applications](#), *Compos Part A Appl Sci Manuf* , **38(6)**:1525–1532 (2007).
<https://doi.org/10.1016/j.compositesa.2007.01.013>.

- [4] Cole G.S., Sherman A.M., [Light Weight Materials for Automotive Applications](#), *Mater. Charact*, **35**: 3–9 (1995).
[https://doi.org/10.1016/1044-5803\(95\)00063-1](https://doi.org/10.1016/1044-5803(95)00063-1)
- [5] Liu Y., Guo Y., Zhao J., Chen X., Zhang H., Hu G., Yu, X., Zhang, Z., [Carbon Fiber Reinforced Shape Memory Epoxy Composites with Superior Mechanical Performances](#), *Compos. Sci. Technol.*, **177**:49-56 (2019).
<https://doi.org/10.1016/j.compscitech.2019.04.014>.
- [6] George M., [Reclaiming Value from Post-Use Carbon Composite](#), *Reinf Plast*, **52(7)**: 36–39 (2008).
[https://doi.org/10.1016/S0034-3617\(08\)70242-X](https://doi.org/10.1016/S0034-3617(08)70242-X)
- [7] Vision A.C., Aerodynamics I.F.E., [Metering Pumps for Chemical Feed Applications](#), *World Pumps*, Elsevier Ltd, (2004).
[https://doi.org/10.1016/S0262-1762\(04\)00159-2](https://doi.org/10.1016/S0262-1762(04)00159-2).
- [8] Speranza G., [The Role of Functionalization in the Applications of Carbon Materials: An Overview](#). *C Journal of Carbon Research*, **5(4)**:84 (2019).
<https://doi.org/10.3390/c5040084>.
- [9] Mahdi S., (2007, May 7-11), *Airbus - Composites Repair Analysis*. CACRC Meeting Amsterdam
- [10] Okoli O.I., Abdul-Latif A., [Failure in Composite Laminates: Overview of an Attempt at Prediction](#). *Compos - Part A Appl. Sci. Manuf.*, **33**: 315–321 (2002).
[https://doi.org/10.1016/S1359-835X\(01\)00127-0](https://doi.org/10.1016/S1359-835X(01)00127-0).
- [11] Liu X., Wang G., [Progressive Failure Analysis of Bonded Composite Repairs](#), *Compos Struct*, **81**: 331–340 (2007).
<https://doi.org/10.1016/j.compstruct.2006.08.024>.
- [12] Sohn H., Farrar C.R., Hemez F., Czarnecki J., [A Review of Structural Health Monitoring Literature](#), (1996-2001), Article, January 1, (2002), United States.
<https://digital.library.unt.edu/ark:/67531/metadc927238/>: Accessed March 18, 2023), University of North Texas Libraries, UNT Digital Library, <https://digital.library.unt.edu>; crediting UNT Libraries Government
- [13] Wang S., Urban M.W., [Self-Healing Polymers](#), *Nat Rev. Mater.*, **5**: 562–583 (2020).
<https://doi.org/10.1038/s41578-020-0202-4>.
- [14] Norris C.J., Meadway G.J., O’Sullivan M.J., Bond I.P., Trask R.S., [Self-healing Fibre Reinforced Composites Via a Bioinspired Vasculature](#), *Adv. Funct. Mater.*, **21**:3624–3633 (2011).
<https://doi.org/10.1002/adfm.201101100>.
- [15] Kahar N.N.F.N.M.N., Osman A.F., Alosime E., Arsat N., Azman N.A.M., Syamsir A., Itam Z., Abdul Hamid Z.A., [The Versatility of Polymeric Materials as Self-Healing Agents for Various Types of Applications: A Review](#), *Polymers*, **13(8)**: 1194 (2021).
<https://doi.org/10.3390/polym13081194>.
- [16] Billiet S., Hillewaere X.K.D., Teixeira R.F.A., Du Prez F.E., [Chemistry of Crosslinking Processes for Self-Healing Polymers](#), *Macromol Rapid Commun*, **34**:290–309 (2013).
<https://doi.org/10.1002/marc.201200689>.
- [17] White S.R., Sottos N.R., Geubelle P.H., Moore J.S., Kessler M.R., Sriram S.R., Rown N.E., [Autonomic Healing of Polymer Composites](#), *Nature*, **409**:794–797 (2001).
<https://doi.org/10.1038/35057232>.
- [18] Hamilton A.R., Sottos N.R., White S.R., [Pressurized Vascular Systems for Self-Healing Materials](#), *J. R. Soc. Interface.*, **9**: 1020–1028 (2012).
<https://doi.org/10.1098/rsif.2011.0508>.
- [19] Olugebefola S.C., Hamilton A.R., Fairfield D.J., Sottos N.R., White S.R., [Structural Reinforcement of Microvascular Networks Using Electrostatic Layer-by-Layer Assembly with Halloysite Nanotubes](#), *Soft Matter*, **10**: 544–548 (2014).
<https://doi.org/10.1039/c3sm52288a>.
- [20] Wang R., Li H., Hu H., He X., Liu W., [Preparation and Characterization of Self-Healing Microcapsules with Poly \(urea-formaldehyde \) Grafted Epoxy Functional](#), *Group Shell*, **113(3)**: 1501–1506 (2009).
<https://doi.org/10.1002/app30001>
- [21] Heo Y., Sodano H.A., [Thermally Responsive Self-Healing Composites with Continuous Carbon Fiber Reinforcement](#), *Compos Sci Techno*, **118**: 244–250 (2015).
<https://doi.org/10.1016/j.compscitech.2015.08.015>.
- [22] Xu Y., Chen D., [A Novel Self-Healing Polyurethane Based on Disulfide Bonds](#), *Macromol. Chem. Phys.*, **217**: 1191–1196 (2016).
<https://doi.org/10.1002/macp.201600011>.

- [23] Huang L., Ningbo Y., Yingpeng W., Zhang Y., Zhang Q., Huang Y., Yanfeng M., Yangsheng C., Multichannel and Repeatable Self-Healing of Mechanical Enhanced Graphene-Thermoplastic Polyurethane Composites, *Adv. Mater.*, **25**:2224–2228 (2013).
<https://doi.org/10.1002/adma.201204768>.
- [24] Zhang L., Tian X., Malakooti M.H., Sodano H.A., Novel Self-Healing CFRP Composites with High Glass Transition Temperatures, *Compos. Sci. Technol.*, **168**: 96–103 (2018).
<https://doi.org/10.1016/j.compscitech.2018.09.008>.
- [25] Liu D., Lee C.Y., Repairability of Impact-Induced Damage in SMC Composites, *J. Compos. Mater.*, **27**:1257–1271 (1993).
<https://doi.org/10.1177/002199839302701302>.
- [26] Zhong N., Post W., Self-Repair of Structural and Functional Composites with Intrinsically Self-Healing Polymer Matrices: A Review, *Compos. PART A Appl. Sci.*, **69**: 226–239 (2015).
<https://doi.org/10.1016/j.compositesa.2014.11.028>.
- [27] Kadam S., Chavan S., Kanu N.J., An Insignificantly Advanced Self-Healing Composites, *Mater. Res. Express*, **8**(5): 052001, (2021).
<https://doi.org/10.1088/2053-1591/abfba5>.
- [28] Ilyaei S., Sourki R., Akbari Y.H.A., Capsule-Based Healing Systems in Composite Materials: A Review, *Crit. Rev. Solid State. Mater. Sci.*, **46**(6): 491–531, (2021).
<https://doi.org/10.1080/10408436.2020.1852912>.
- [29] Mashkoo F., Lee S.J., Yi H., Noh S.M., Jeong C., Self-Healing Materials for Electronics Applications. *Int. J. Mol. Sci.*, **23**(2): 622 (2022).
<https://doi.org/10.3390/ijms23020622>.
- [30] Dong W., Li W., Shen L., Zhang S., Vessalas K., Integrated self-Sensing and Self-Healing Cementitious Composite with Microencapsulation of Nano-Carbon Black and Slaked Lime, *Mater. Lett. Materials*, **282**: 128834 (2021).
<https://doi.org/10.1016/j.matlet.2020.128834>.
- [31] Zhu D.Y., Rong M.Z., Zhang M.Q., Self-Healing Polymeric Materials Based on Microencapsulated Healing Agents: from Design to Preparation, *Prog. Polym. Sci.*, **49–50**: 175–220 (2015).
<https://doi.org/10.1016/j.progpolymsci.2015.07.002>.
- [32] Suryanarayana C., Rao K.C., Kumar D., Preparation and Characterization of Microcapsules Containing Linseed Oil and its Use in Self-Healing Coatings. *Prog. Org. Coatings*, **63**:72–78 (2008).
<https://doi.org/10.1016/j.porgcoat.2008.04.008>.
- [33] Li W., Geng X., Huang R., Wang J., Wang N., Zhang X., Microencapsulated Comb-Like Polymeric Solid-Solid Phase Change Materials Via in-Situ Polymerization. *Polymers*, **10**(2): 172 (2018).
<https://doi.org/10.3390/polym10020172>.
- [34] Yuan Y.C., Rong M.Z., Zhang M.Q., Preparation and Characterization of Microencapsulated Polythiol, *Polymer*, **49**(10): 2531–2541 (2008).
<https://doi.org/10.1016/j.polymer.2008.03.044>.
- [35] Liu X., Sheng X., Lee J.K., Kessler M.R., Synthesis and Characterization of Melamine- Urea-Formaldehyde Microcapsules Containing ENB-Based Self-Healing Agents, *Macromol. Mater. Eng.*, **294**:389–395 (2009).
<https://doi.org/10.1002/mame.200900015>.
- [36] Jinglei Y., Keller M.W., Moore J.S., White S.R., Sottos N.R., Microencapsulation of Isocyanates for Self-Healing Polymers, *Macromolecules*, **41**:9650–9655 (2008).
<https://doi.org/10.1021/ma801718v>.
- [37] Brochu Alice B.W., Chyan W.J., Reichert W.M., Microencapsulation of 2-Octylcyanoacrylate Tissue Adhesive for Self-Healing Acrylic Bone Cement, *J. Biomed. Mater. Res. - Part B Appl. Biomater.*, **100 B**(7): 1764–1772 (2012).
<https://doi.org/10.1002/jbm.b.32743>.
- [38] Patchan M.W., Baird L.M., Rhim Y.R., LaBarre E.D., Maisano A.J., Deacon R.M., Xie Z., Benkoski J.J., Liquid-Filled Metal Microcapsules. *ACS Appl. Mater. Interfaces*, **4**: 2406–2412 (2012).
<https://doi.org/10.1021/am201861j>.
- [39] Caruso M.M., Blaiszik B.J., Jin H., Schelkopf S.R., Stradley D.S., Sottos N.R., Wight S.R., Moore J.S., Robust, Double-Walled Microcapsules for Self-Healing Polymeric Materials, *ACS Appl. Mater. Interfaces*, **2**:1195–1199(2010).
<https://doi.org/10.1021/am100084k>.
- [40] Ramsden W., Separation of Solids in the Surface-Layers of Solutions and ‘Suspensions’(Observations on Surface-Membranes, Bubbles, Emulsions, and Mechanical Coagulation), *Preliminary Account. Proc R Soc London*, **72**:156–164 (1904).
<https://doi.org/10.1098/rspl.1903.0034>

- [41] Pickering S.U., *CXCVI.—Emulsions*, *J. Chem. Soc. Trans.*, **91**: 2001–2021 (1907).
<https://doi.org/10.1039/CT9079102001>.
- [42] Velev O.D., Furusawa K., Nagayama K., *Assembly of Latex Particles by Using Emulsion Droplets as Templates. 2. Ball-Like and Composite Aggregates*, *Langmuir*, **12**: 2385–2391 (1996).
<https://doi.org/10.1021/la950679y>.
- [43] Li J., Hitchcock A.P., Stöver H.D.H., *Pickering Emulsion Templated Interfacial Atom Transfer Radical Polymerization for Microencapsulation*, *Langmuir*, **26**: 17926–17935 (2010).
<https://doi.org/10.1021/la102867v>.
- [44] Yang Y., Wei Z., Wang C., Tong Z., *Versatile Fabrication of Nanocomposite Microcapsules with Controlled Shell Thickness and Low Permeability*, *ACS Appl. Mater. Interfaces*, **5**: 2495–2502 (2013).
<https://doi.org/10.1021/am302963d>.
- [45] Yang Y., Ning Y., Wang C., Tong Z., *Capsule Clusters Fabricated by Polymerization Based on Capsule-in-Water-in-Oil Pickering Emulsions*, *Polym. Chem.*, **4**: 5407–1545 (2013).
<https://doi.org/10.1039/c3py00620d>.
- [46] Yang Z., Hollar J., He X., Shi X., *A Self-Healing Cementitious Composite Using Oil Core/Silica Gel Shell Microcapsules*, *Cem. Concr. Compos*, **33**:506–512 (2011).
<https://doi.org/10.1016/j.cemconcomp.2011.01.010>.
- [47] Galgali G., Schlangen E., Van Der Zwaag S., *Synthesis and Characterization of Silica Microcapsules Using a Sustainable Solvent System Template*, *Mater. Res. Bull*, **46**:2445–2449 (2011).
<https://doi.org/10.1016/j.materresbull.2011.08.028>.
- [48] Brandrup J., Immergut E.H., Grulke E.A., Abe A., Bloch D.R., “*Polymer Handbook*”, vol. 89. John Wiley & Sons Inc., New York, (1999).
- [49] Ugelstad J., El-Aasser M.S., Vanderhoff J.W., *Emulsion Polymerization: Initiation of Polymerization in Monomer Droplets*, *J. Polym. Sci. Polym. Lett. Ed.*, **11(8)**: 503–513 (1973).
<https://doi.org/10.1002/pol.1973.130110803>.
- [50] Fickert J., Makowski M., Kappl M., Landfester K., Crespy D., *Efficient Encapsulation of Self-Healing Agents in Polymer Nanocontainers Functionalized by Orthogonal Reactions*, *Macromolecules*, **45**:6324–6332 (2012).
<https://doi.org/10.1021/ma301013p>.
- [51] Crespy D., Landfester K., *Miniemulsion Polymerization as a Versatile Tool for the Synthesis of Functionalized Polymers*, *Beilstein. J. Org. Chem.*, **6**: 1132–1148 (2010).
<https://doi.org/10.3762/bjoc.6.130>.
- [52] Vougioukalakis G.C., Stamatopoulos I., Petzetakis N., Raptopoulou C.P., Psycharis V., Terzis A., Kyrtisis P., Pitiskalis M., Hadjichristidis N., *Controlled Vinyl-Type Polymerization of Norbornene with a Nickel (II) Diphosphinoamine / Methylaluminumoxane Catalytic System*, *Polymer*, **48**:1–10, (2009).
<https://doi.org/10.1002/pola>.
- [53] Kumar Banshiwal J., Nath Tripathi D., *Self-Healing Polymer Composites for Structural Application*, *Funct. Mater.*, **10**: 1–13 (2019).
<https://doi.org/10.5772/intechopen.82420>.
- [54] Toohy K.S., Sottos N.R., Lewis J.A., Moore J.S., White S.R., *Self-Healing Materials with Microvascular Networks*, *Nat. Mater.*, **6**: 581–585 (2007).
<https://doi.org/10.1038/nmat1934>.
- [55] Pang J.W.C., Bond I.P., *A Hollow Fibre Reinforced Polymer Composite Encompassing Self-Healing and Enhanced Damage Visibility*, *Compos. Sci. Technol.*, **65**:1791–1799 (2005).
<https://doi.org/10.1016/j.compscitech.2005.03.008>.
- [56] Dry C.M., *Three Designs for the Internal Release of Sealants, Adhesives, and Waterproofing Chemicals into Concrete to Reduce Permeability*, *Cem. Concr. Res.*, **30**: 1969–1977 (2000).
[https://doi.org/10.1016/S0008-8846\(00\)00415-4](https://doi.org/10.1016/S0008-8846(00)00415-4)
- [57] US6527849B2 - Self-Repairing, Reinforced Matrix Materials - *Google Patents* n.d.
<https://patents.google.com/patent/US6527849B2/en> (Accessed January 30, 2023).
- [58] Kanu N.J., Gupta E., Vates U.K., Singh G.K., *Self-Healing Composites: A State-of-the-Art Review*, *Compos Part A Appl. Sci. Manuf.*, **121**: 474–486 (2019).
<https://doi.org/10.1016/j.compositesa.2019.04.012>.
- [59] Dry C., *Procedures Developed For Self-Repair Of Polymer Matrix Composite Materials*. *Compos Struct*, **35**: 263–269 (1996).
[https://doi.org/10.1016/0263-8223\(96\)00033-5](https://doi.org/10.1016/0263-8223(96)00033-5).
- [60] Hamilton A.R., Sottos N.R., White S.R., *Self-Healing of Internal Damage in Synthetic Vascular Materials*, *Adv. Mater*, **22**: 5159–5163 (2010).
<https://doi.org/10.1002/adma.201002561>.

- [61] Williams H.R., Trask R.S., Bond I.P., **Self-Healing Sandwich Panels: Restoration of Compressive Strength After Impact**, *Compos Sci. Technol.*, **68**: 3171–3177 (2008).
<https://doi.org/10.1016/j.compscitech.2008.07.016>.
- [62] Williams H.R., Trask R.S., Bond I.P., **Self-Healing Composite Sandwich Structures**, *Smart. Mater. Struct.*, **16**: 1198–1207 (2007).
<https://doi.org/10.1088/0964-1726/16/4/031>.
- [63] Esser-Kahn A.P., Thakre P.R., Dong H., Patrick J.F., Vlasko-Vlasov V.K., Sottos N.R., Moore J.S., White S.R., **Three-Dimensional Microvascular Fiber-Reinforced Composites**, *Adv. Mater.*, **23**: 3654–3658 (2011).
<https://doi.org/10.1002/adma.201100933>.
- [64] Kim H.S., Khamis M.A., **Fracture and Impact Behaviours of Hollow Micro-Sphere/Epoxy Resin Composites**, *Compos - Part A Appl. Sci. Manuf.*, **32**: 1311–1317 (2001).
[https://doi.org/10.1016/S1359-835X\(01\)00098-7](https://doi.org/10.1016/S1359-835X(01)00098-7).
- [65] Patrick J.F., Hart K.R., Krull B.P., Diesendruck C.E., Moore J.S., White S.R., Sottos N.R., **Continuous Self-Healing Life Cycle in Vascularized Structural Composites**, *Adv. Mater.*, **26**: 4302–4308 (2014).
<https://doi.org/10.1002/adma.201400248>.
- [66] Smojver I., Ivančević D., Brezetić D., **Modelling of Micro-Damage and Intrinsic Self-Healing in Unidirectional CFRP Composite Structures**, *Compos Struct*, **286**:115266 (2022).
<https://doi.org/10.1016/j.compstruct.2022.115266>.
- [67] Imato K., Otsuka H., **Self-Healing Polymers through Dynamic Covalent Chemistry**, *Dyn. Covalent. Chem.*, John Wiley & Sons Ltd, (2018).
<https://doi.org/10.1002/9781119075738.ch9>.
- [68] Deng G., Tang C., Li.F., Jiang H., Chen Y., **Covalent Cross-Linked Polymer Gels with Reversible Sol-Gel Transition and Self-Healing Properties**, *Macromolecules*, **43**: 1191–1194, (2010).
<https://doi.org/10.1021/ma9022197>.
- [69] Garcia S.J., **Effect of Polymer Architecture on the Intrinsic Self-Healing Character of Polymers**, *Eur. Polym. J.*, **53**: 118–125 (2014).
<https://doi.org/10.1016/j.eurpolymj.2014.01.026>.
- [70] Yang Y., Urban M.W., **Self-healing Polymeric Materials**, *Chem. Soc. Rev.*, **42**: 7446–7467 (2013).
<https://doi.org/10.1039/c3cs60109a>.
- [71] Yoon J.A., Kamada J., Koynov K., Mohin J., Nicolaj R., Zhang Y., Balazs A.C., Kowalewski T., Matyjaszewski K., **Self-Healing Polymer Films Based on Thiol–Disulfide Exchange Reactions and Self-Healing Kinetics Measured Using Atomic Force Microscopy**, *Macromolecules*, **45**: 142–149 (2012).
<https://doi.org/10.1021/ma2015134>.
- [72] McAllan D.T., Cullum T.V., Dean R.A., Fidler F.A., **The Preparation and Properties of Sulfur Compounds Related to Petroleum. I. The Dialkyl Sulfides and Disulfides**, *J. Am. Chem. Soc.*, **73**: 3627–3632 (1951).
<https://doi.org/10.1021/ja01152a021>.
- [73] Eldjarn L., Pihl A., **The Equilibrium Constants and Oxidation-Reduction Potentials of Some Thiol-Disulfide Systems**, *J. Am. Chem. Soc.*, **79**: 4589–4593 (1957).
<https://doi.org/10.1021/ja01574a005>.
- [74] Nelander G., Sunner S., **Effect in Dialkyl Disulfides**, *J. Am. Chem. Soc.*, **94(10)**: 3576–3577 (1972).
<https://doi.org/10.1021/ja00765a053>.
- [75] Amamoto Y., Otsuka H., Takahara A., Matyjaszewski K., **Self-healing of Covalently Cross-Linked Polymers by Reshuffling Thiuram Disulfide Moieties in Air Under Visible Light**, *Adv. Mater.*, **24**: 3975–3980 (2012).
<https://doi.org/10.1002/adma.201201928>.
- [76] Milligan B., Rivett D.E., Savige W.E., **The Photolysis of Dialkyl Sulphides, Disulphides, and Trisulphides**, *Aust. J. Chem.*, **16**: 1020–1029, (1963).
<https://doi.org/10.1071/CH9631020>
- [77] Canadell J., Goossens H., Klumperman B., **Self-Healing Materials Based on Disulfide Links**, *Macromolecules*, **44**:2536–2541 (2011).
<https://doi.org/10.1021/ma2001492>.
- [78] Bailey B.M., Leterrier Y., Garcia S.J., Van Der Zwaag S., Michaud V., **Electrically Conductive Self-Healing Polymer Composite Coatings**, *Prog. Org. Coatings*, **85**: 189–198 (2015).
<https://doi.org/10.1016/j.porgcoat.2015.04.013>.
- [79] Ghosh B., Urban M.W., **Self-Repairing Oxetane-Substituted Chitosan Polyurethane Networks**, *Science*, **323(5920)**: 1458-1460 (2009).
<https://doi.org/10.1126/science.1167391>.

- [80] Weiner S., Patricia M., Dove., [An Overview of Biomineralization Processes and the Problem of the Vital Effect](#), *Reviews in Mineralogy and Geochemistry*, **54**(1): 1-29 (2003).
<https://doi.org/10.2113/0540001>
- [81] Urban M.W., [Dynamic Materials: The Chemistry of Self-Healing](#), *Nat. Chem.*, **4**: 80–82 (2012).
<https://doi.org/10.1038/nchem.1249>.
- [82] Korth H.G., [Carbon radicals of Low Reactivity Against Oxygen: Radically Different Antioxidants](#), *Angew Chemie*, **46**:5274–6, (2007).
<https://doi.org/10.1002/anie.200701569>.
- [83] Imato K., Nishihara M., Kanehara T., Amamoto Y., Takahara A., Otsuka H., [Self-Healing of Chemical Gels Cross-Linked by Diarylbibenzofuranone-Based Trigger-Free Dynamic Covalent Bonds at Room Temperature](#), *Angew. Chemie.*, **51**(5): 1138–1142 (2012).
<https://doi.org/10.1002/anie.201104069>.
- [84] Yan C.Y., Min Z.R., Ming Q.Z., Chen J., Gui C.Y., Xue M.L., [Self-Healing Polymeric Materials Using Epoxy/Mercaptan as the Healtant](#), *Macromolecules*, **41**: 5197–202 (2008).
<https://doi.org/10.1021/ma800028d>.
- [85] Higaki Y., Otsuka H., Takahara A., [A Thermodynamic Polymer Cross-Linking System Based on Radically Exchangeable Covalent Bonds](#), *Macromolecules*, **39**: 2121–2125 (2006).
<https://doi.org/10.1021/ma052093g>.
- [86] Krogsgaard M., Behrens M.A., Pedersen J.S., Birkedal H., [Self-Healing Mussel-Inspired Multi-pH-Responsive Hydrogels](#), *Biomacromolecules*, **14**: 297–301 (2013).
<https://doi.org/10.1021/bm301844u>.
- [87] Nicolaj R., Kamada J., van Wassen A., Matyjaszewski K., [Responsive Gels Based on a Dynamic Covalent Trithiocarbonate Cross-Linker](#), *Macromolecules*, **43**: 4355–4361 (2010).
<https://doi.org/10.1021/ma100378r>.
- [88] Zhang H., Xia H., Zhao Y., [Poly\(vinyl alcohol\) Hydrogel Can Autonomously Self-Heal](#), *ACS Macro. Lett.*, **1**: 1233–1236 (2012).
<https://doi.org/10.1021/mz300451r>.
- [89] Amamoto Y., Kamada J., Otsuka H., Takahara A., Matyjaszewski K., [Repeatable Photoinduced Self-Healing of Covalently Cross-Linked Polymers Through Reshuffling of Trithiocarbonate Units](#), *Angew. Chemie.*, **123**:1698–1701 (2011).
<https://doi.org/10.1002/ange.201003888>.
- [90] Ghosh B., Chellappan K.V., Urban M.W., [Self-Healing Inside a Scratch of Oxetane-Substituted Chitosan-Polyurethane \(OXE-CHI-PUR\) Networks](#), *J. Mater. Chem.*, **21**: 14473–14486 (2011).
<https://doi.org/10.1039/C1JM12321A>.
- [91] Ghosh B., Chellappan K.V., Urban M.W., [UV-Initiated Self-Healing of Oxolane-Chitosan-Polyurethane \(OXO-CHI-PUR\) Networks](#), *J. Mater. Chem.*, **22**: 16104–16113 (2012).
<https://doi.org/10.1039/c2jm31126g>.
- [92] Kubisa P., Penczek S., [Cationic Activated Monomer Polymerization of Heterocyclic Monomers](#), *Prog. Polym. Sci.*, **24**: 1409–1407 (1999).
[https://doi.org/10.1016/S0079-6700\(99\)00028-3](https://doi.org/10.1016/S0079-6700(99)00028-3)
- [93] Liu Y.L., Chuo T.W., [Self-Healing Polymers Based on Thermally Reversible Diels-Alder Chemistry](#), *Polym. Chem.*, **4**: 2194–2205 (2013).
<https://doi.org/10.1039/c2py20957h>.
- [94] Stevens M.P., Jenkins A.D., [Crosslinking of Polystyrene Via Pendant Maleimide Groups](#), *J. Polym. Sci. Polym. Chem. Ed.*, **17**: 3675–3685 (1979).
<https://doi.org/10.1002/pol.1979.170171123>
- [95] Laita H., Boufi S., Gandini A., [The application of the Diels-Alder Reaction to Polymers Bearing Furan Moieties. 1. Reactions with Maleimides](#), *Eur. Polym. J.*, **33**: 1203–12011 (1997).
[https://doi.org/10.1016/S0014-3057\(97\)00009-8](https://doi.org/10.1016/S0014-3057(97)00009-8).
- [96] Toncelli C., De Reus D.C., Picchioni F., Broekhuis A.A., [Properties of Reversible Diels-Alder Furan/Maleimide Polymer Networks as Function of Crosslink Density](#), *Macromol. Chem. Phys.*, **213**: 157–165 (2012).
<https://doi.org/10.1002/macp.201100405>.
- [97] Chung C.M., Roh Y.S., Cho S.Y., Kim J.G., [Crack Healing in Polymeric Materials via Photochemical \[2+2\] Cycloaddition](#), *Chem. Mater.*, **16**: 3982–3984, (2004).
<https://doi.org/10.1021/cm049394+>.
- [98] Ling J., Rong M.Z., Zhang M.Q., [Photo-Stimulated Self-Healing Polyurethane Containing Dihydroxyl Coumarin Derivatives](#), *Polymer.*, **53**: 2691–2698 (2012).
<https://doi.org/10.1016/j.polymer.2012.04.016>.
- [99] Klukovich H.M., Kean Z.S., Iacono S.T., Craig S.L., [Mechanically Induced Scission And Subsequent Thermal Remending of Perfluorocyclobutane Polymers](#), *J. Am. Chem. Soc.*, **133**: 17882–17888 (2011).
<https://doi.org/10.1021/ja2074517>.

- [100] Froimowicz P., Frey H., Landfester K., [Towards the Generation of Self-Healing Materials by Means of a Reversible Photo-Induced Approach](#), *Macromol. Rapid. Commun.*, **32**: 468–473 (2011).
<https://doi.org/10.1002/marc.201000643>.
- [101] De Espinosa L.M., Fiore G.L., Weder C., Johan Foster E., Simon Y.C., [Healable Supramolecular Polymer Solids](#), *Prog. Polym. Sci.*, **49–50**: 60–78 (2015).
<https://doi.org/10.1016/j.progpolymsci.2015.04.003>.
- [102] Menke W., [Structure and Chemistry of Plastids](#), *Annu. Rev. Plant. Physiol.*, **13**: 27–44 (1962).
<https://doi.org/10.1146/annurev.pp.13.060162.000331>.
- [103] Murray T.J., Zimmerman S.C., [New Triply Hydrogen Bonded Complexes with Highly Variable Stabilities](#), *J. Am. Chem. Soc.*, **114**: 4010–4011 (1992).
<https://doi.org/10.1021/ja00036a079>.
- [104] Faghihnejad A., Feldman K.E., Yu J., Tirrell M.V., Israelachvili J.N., Hawker C.J., Kramer E.J., Zeng H., [Adhesion and Surface Interactions of a Self-Healing Polymer with Multiple Hydrogen-Bonding Groups](#), *Adv. Funct. Mater.*, **24**:2322–2333 (2014).
<https://doi.org/10.1002/adfm.201303013>
- [105] Aida T., Meijer E.W., Stupp S.I., [Functional Supramolecular Polymers](#), *Science*, **335(6070)**: 813–817 (2012) .
<https://doi.org/10.1126/science.1205962>.
- [106] Sijbesma R.P., Meijer E.W., Bosman A.W., [Supramolecular Polymers at Work](#), *Mater. Today*, **7(4)**: 34–39 (2004).
[https://doi.org/10.1016/S1369-7021\(04\)00187-7](https://doi.org/10.1016/S1369-7021(04)00187-7)
- [107] Van Gemert G.M.L., Peeters J.W., Söntjens S.H.M., Janssen H.M., Bosman A.W., [Self-Healing Supramolecular Polymers In Action](#), *Macromol. Chem. Phys.*, **213**: 234–242 (2012).
<https://doi.org/10.1002/macp.201100559>.
- [108] Biyani M.V., Foster E.J., Weder C., [Light-Healable Supramolecular Nanocomposites Based on Modified Cellulose Nanocrystals](#), *ACS Macro. Lett.*, **2**: 236–240 (2013).
<https://doi.org/10.1021/mz400059w>.
- [109] Hackethal K., Döhler D., Tanner S., Binder W.H., [Introducing Polar Monomers into Polyisobutylene by Living Cationic Polymerization: Structural and Kinetic Effects](#). *Macromolecules*, **43**: 1761–1770 (2010).
<https://doi.org/10.1021/ma9025114>.
- [110] Herbst F., Schröter K., Gunkel I., Gröger S., Thurn-Albrecht T., Balbach J., Binder W.H., [Aggregation and Chain Dynamics In Supramolecular Polymers by Dynamic Rheology: Cluster Formation and Self-Aggregation](#), *Macromolecules*, **43**: 10006–10016, (2010).
<https://doi.org/10.1021/ma101962y>.
- [111] Banerjee S., Tripathy R., Cozzens D., Nagy T., Keki S., Zsuga M., Faust R., [Photoinduced Smart, Self-Healing Polymer Sealant for Photovoltaics](#), *ACS Appl. Mater. Interfaces*, **7**: 2064–2072 (2015).
<https://doi.org/10.1021/am508096c>.
- [112] Cordier P., Tourmilhac F., Soulié-Ziakovic C., Leibler L., [Self-Healing and Thermoreversible Rubber from Supramolecular Assembly](#), *Nature*, **451**: 977–980 (2008).
<https://doi.org/10.1038/nature06669>.
- [113] Zhang R., Yan T., Lechner B.D., Schröter K., Liang Y., Li B., Furtado F., Sun p., Saalwachter K., [Heterogeneity, Segmental and Hydrogen Bond Dynamics, and Aging of Supramolecular Self-Healing Rubber](#), *Macromolecules*, **46**: 1841–1850, (2013).
<https://doi.org/10.1021/ma400019m>.
- [114] Montamal D., Tourmilhac F., Hidalgo M., Couturier J.L., Leibler L., [Versatile One-Pot Synthesis of Supramolecular Plastics and Self-Healing Rubbers](#), *J. Am. Chem. Soc.*, **131**: 7966–7967 (2009).
<https://doi.org/10.1021/ja903080c>.
- [115] Tuncaboylu D.C., Sari M., Oppermann W., Okay O., [Tough and Self-Healing Hydrogels Formed via Hydrophobic Interactions](#), *Macromolecules*, **44**: 4997–5005 (2011).
<https://doi.org/10.1021/ma200579v>.
- [116] Burattini S., Colquhoun H.M., Greenland B.W., Hayes W., [A Novel Self-Healing Supramolecular Polymer System](#), *Faraday Discuss*, **143**: 251–264 (2009).
<https://doi.org/10.1039/B900859D>.
- [117] Burattini S., Colquhoun H.M., Fox J.D., Friedmann D., Greenland B.W., Harris P.J.F., Heyes W., Makay M.E., Rowan S.J., [A Self-Repairing, Supramolecular Polymer System: Healability as a Consequence of Donor-Acceptor \$\pi\$ - \$\pi\$ Stacking Interactions](#), *Chem. Commun.*, **44**: 6717–6719 (2009).
<https://doi.org/10.1039/b910648k>.

- [118] Fox J., Wie J.J., Greenland B.W., Burattini S., Hayes W., Colquhoun H.M., Makay M.E., Rowan S.J., **High-Strength, Healable, Supramolecular Polymer Nanocomposites**, *J. Am. Chem. Soc.*, **134**: 5362–5368 (2012).
<https://doi.org/10.1021/ja300050x>.
- [119] Burattini S., Colquhoun H.M., Greenland B.W., Hayes W., Wade M., **Pyrene-Functionalised, Alternating Copolyimide For Sensing Nitroaromatic Compounds**, *Macromol. Rapid Commun.*, **30**: 459–463 (2009).
<https://doi.org/10.1002/marc.200800630>.
- [120] Burattini S., Greenland B.W., Merino D.H., Weng W., Seppala J., Colquhoun H.M., Hayes W., Mackay M.E., Hamley I.W., Rowan S.J., **A Healable Supramolecular Polymer Blend Based on Aromatic π - π Stacking and Hydrogen-Bonding Interactions**, *J. Am. Chem. Soc.*, **132**: 12051–12058 (2010).
<https://doi.org/10.1021/ja104446r>.
- [121] Burattini S., Greenland B.W., Hayes W., MacKay M.E., Rowan S.J., Colquhoun H.M., **A Supramolecular Polymer Based on Tweezer-Type π ? π stacking interactions: Molecular Design For Healability and Enhanced Toughness**, *Chem. Mater.*, **23**: 6–8 (2011).
<https://doi.org/10.1021/cm102963k>.
- [122] Xu Z., Peng J., Yan N., Yu H., Zhang S., Liu K., Fang Y., **Simple Design but Marvelous Performances: Molecular Gels of Superior Strength and Self-Healing Properties**, *Soft. Matter*, **9**: 1091–1099 (2013).
<https://doi.org/10.1039/C2SM27208C>.
- [123] Wool R.P., O'Connor K.M., **A Theory Crack Healing In Polymers**, *J. Appl. Phys.*, **52**: 5953 (1981).
<https://doi.org/10.1063/1.328526>.
- [124] Kalista S.J., Ward T.C., Oyetunji Z., **Self-Healing of Poly(Ethylene-co-Methacrylic Acid) Copolymers Following Projectile Puncture**, *Mech. Adv. Mater. Struct.*, **14**: 391–397 (2007).
<https://doi.org/10.1080/15376490701298819>.
- [125] Coulibaly S., Roulin A., Balog S., Biyani M.V., Foster E.J., Rowan S.J., Fiore J.L., Weder C., **Reinforcement of Optically Healable Supramolecular Polymers with Cellulose Nanocrystals**, *Macromolecules*, **47(1)**: 152–160 (2014).
<https://doi.org/10.1021/ma402143c>.
- [126] Kalista S.J., Ward T.C., **Thermal Characteristics of the Self-Healing Response in Poly(ethylene-co-methacrylic acid) Copolymers**, *J. R. Soc. Interface.*, **4**: 405–411 (2007).
<https://doi.org/10.1098/rsif.2006.0169>.
- [127] Pan C., Liu L., Chen Q., Zhang Q., Guo G., **Tough, Stretchable, Compressive Novel Polymer/Graphene Oxide Nanocomposite Hydrogels with Excellent Self-Healing Performance**, *ACS Appl. Mater. Interfaces*, **9(43)**: 38052–38061 (2017).
<https://doi.org/10.1021/acsami.7b12932>.
- [128] Jia H., Gu S.Y., **A Near Infrared Induced Self-Healable Composite Based on Disulfide Bonds for Flexible Electronics**, *J. Polym. Res.*, **27**: 1–13 (2020).
<https://doi.org/10.1007/s10965-020-02186-2>.
- [129] Zhao L., Huang J., Wang T., Sun W., Tong Z., **Multiple Shape Memory, Self-Healable, and Supertough PAA-GO-Fe³⁺ Hydrogel**, *Macromol. Mater. Eng.*, **302(2)**: 1600359 (2017).
<https://doi.org/10.1002/mame.201600359>.
- [130] Gunckel R., Koo B., Xu Y., Pauley B., Hall A., Chattopadhyay A., Dai L., **Grafted Cinnamoyl-Based Mechanophores for Self-Sensing and Photochemical Healing Capabilities in Epoxy**, *ACS Appl. Polym. Mater.*, **2(9)**: 3916–3928 (2020).
<https://doi.org/10.1021/acsapm.0c00599>.
- [131] Valentini L., Bittolo Bon S., Pugno N.M., **Severe Graphene Nanoplatelets Aggregation as Building Block For The Preparation of Negative Temperature Coefficient and Healable Silicone Rubber Composites**, *Compos. Sci. Technol.*, **134**: 125–131 (2016).
<https://doi.org/10.1016/j.compscitech.2016.08.005>.
- [132] Wu S., Li J., Zhang G., Yao Y., Li G., Sun R., Wong C., **Ultrafast Self-Healing Nanocomposites Via Infrared Laser and their Application in Flexible Electronics**, *ACS Appl. Mater. Interfaces*, **9(3)**: 3040–3049 (2017).
<https://doi.org/10.1021/acsami.6b15476>.
- [133] Jing X., Mi H.Y., Napiwocki B.N., Peng X.F., Turng L.S., **Mussel-Inspired Electroactive Chitosan/Graphene Oxide Composite Hydrogel with Rapid Self-Healing and Recovery Behavior for Tissue Engineering**, *Carbon*, **129**: 674–687 (2017).
<https://doi.org/10.1016/j.carbon.2017.09.071>.

- [134] Li J., Zhang G., Sun R., Wong C.P., A Covalently Cross-Linked Reduced Functionalized Graphene Oxide/Polyurethane Composite Based on Diels-Alder Chemistry and its Potential Application in Healable Flexible Electronics, *J. Mater. Chem. C*, **5**: 220-228 (2017).
<https://doi.org/10.1039/C6TC04715G>.
- [135] Pepels M., Filot I., Klumperman B., Goossens H., Self-Healing Systems Based on Disulfide-Thiol Exchange Reactions, *Polym. Chem.*, **4**(18): 4955-4965 (2013).
<https://doi.org/10.1039/c3py00087g>.
- [136] Yuan C., Rong M.Z., Zhang M.Q., Self-Healing Polyurethane Elastomer with Thermally Reversible Alkoxyamines as Crosslinkages, *Polymer*, **55**(7): 1782-1791 (2014).
<https://doi.org/10.1016/j.polymer.2014.02.033>.
- [137] Erice A., Ruiz de Luzuriaga A., Azcune I., Fernandez M., Calafel I., Grande H.J., Rekondo A., New injectable and Self-Healable Thermoset Polythiourethane Based on S-Aromatic Thiourethane Dissociative Exchange Mechanism, *Polymer*, **196**: 122461 (2020).
<https://doi.org/10.1016/j.polymer.2020.122461>.
- [138] Panda P., Dutta A., Ganguly D., Chattopadhyay S., Das R.K., Engineering Hydrophobically Associated Hydrogels with Rapid Self-Recovery and Tunable Mechanical Properties Using Metal-Ligand Interactions, *J. Appl. Polym. Sci.*, **137**(48): 49590 (2020).
<https://doi.org/10.1002/app.49590>.
- [139] Park J., Murayama S., Osaki M., Yamaguchi H., Harada A., Matsuba G., Wu J., Zahang J., He J.S., Extremely Rapid Self-Healable and Recyclable Supramolecular Materials through Planetary Ball Milling and Host-Guest Interactions, *Adv Mater*, **19**(5): 698-704 (2020).
<https://doi.org/10.1002/adma.202002008>.
- [140] Seyed Shahabadi S.I., Kong Lu J.X., Aqueous-Only, Green Route to Self-Healable, UV-Resistant, and Electrically Conductive Polyurethane/Graphene/Lignin Nanocomposite Coatings, *ACS Sustain. Chem. Eng.*, **5**(4): 3148-3157 (2017).
<https://doi.org/10.1021/acssuschemeng.6b02941>.
- [141] Chen Z., Sun Y.C., Wang J., Qi H.J., Wang T., Naguib H.E., Flexible, Reconfigurable, and Self-Healing TPU/Vitrimer Polymer Blend with Copolymerization Triggered by Bond Exchange Reaction, *ACS Appl. Mater. Interfaces*, **12**(7): 8740-8750 (2020).
<https://doi.org/10.1021/acsami.9b21411>.
- [142] Bai Y., Zhang J., Wen D., Gong P., Liu J., Ju J., Chen X., A Reconfigurable, Self-Healing and Near Infrared Light Responsive Thermoset Shape Memory Polymer, *Compos. Sci. Technol.*, **187**: 107940 (2020).
<https://doi.org/10.1016/j.compscitech.2019.107940>.
- [143] Jia H., Gu S.Y., Remote and Efficient Infrared Induced Self-Healable Stretchable Substrate for Wearable Electronics, *Eur. Polym. J.*, **126**: 109542 (2020).
<https://doi.org/10.1016/j.eurpolymj.2020.109542>.
- [144] Ebrahimnezhad-Khaljiri H., Eslami-Farsani R., The Tensile Properties and Interlaminar Shear Strength of Microcapsules-Glass Fibers/Epoxy Self-Healable Composites, *Eng. Fract. Mech.*, **230**: 106937 (2020).
<https://doi.org/10.1016/j.engfracmech.2020.106937>.
- [145] Li Z., Souza L.R. de., Litina C., Markaki A.E., Al-Tabbaa A., A Novel Biomimetic Design of a 3D Vascular Structure for Self-Healing in Cementitious Materials Using Murray's Law, *Mater. Des.*, **190**: 108572 (2020).
<https://doi.org/10.1016/j.matdes.2020.108572>.
- [146] Konlan J., Mensah P., Ibekwe S., Crosby K., Li G., Vitrimer Based Composite Laminates with Shape Memory Alloy Z-Pins for Repeated Healing of Impact-Induced Delamination, *Compos. Part B Eng.*, **200**: 108324 (2020).
<https://doi.org/10.1016/j.compositesb.2020.108324>.
- [147] Abedinzadeh R., Faraji Nejad M., Effect of Embedded Shape Memory Alloy Wires on the Mechanical Behavior of Self-Healing Graphene-Glass Fiber-Reinforced Polymer Nanocomposites, *Polym. Bull.*, **78**: 3009-3022 (2021).
<https://doi.org/10.1007/s00289-020-03253-w>