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STRATEGIES FOR SYNTHESIS AND APPLICATIONS OF SELF REPAIRING MATERIALS TO INCREASE DURABILITY OF POLYMERIC MATERIALS

ROLI VERMA*, ASHIMA SRIVASTAVA, PRATIBHA SINGH AND R.S.JAGADISH

DEPARTMENT OF CHEMISTRY, JSS ACADEMY OF TECHNICAL EDUCATION, NOIDA, U.P., INDIA

ABSTRACT

Self-Repairing technology is an autonomic route to repair damage in advanced polymers to extend their lifetime. Self-Repairing has three conceptual approaches: capsule-based repairing systems, vascular healing systems, and intrinsic healing polymers. A variety of self-repairing systems have been developed for mechanical self-healing, protective coatings, and electronic self-healing. These self-repairing systems rely on functional groups within the polymer, microvascular networks, or compartmentalization in capsules and particles. The healing agents become active in the crack plane upon damage, forming new bonds that heal the material. Of these systems, compartmentalization offers a simple and inexpensive means to apply self-healing to current advanced polymer applications. Self-healing can be autonomic, automatic without human intervention, or may require some external energy or pressure. All classes of polymers, from thermosets to thermoplastics to elastomers, have potential for self-healing. The majority of research has focused on the recovery of mechanical integrity following quasi-static fracture.The present article reviews the method of preparation and its possible applications.

KEYWORDS: **Self healing, cracks, smart polymers, polymer composites.**

ROLI VERMA
DEPARTMENT OF CHEMISTRY, JSS ACADEMY OF TECHNICAL EDUCATION, NOIDA, U.P., INDIA

***Corresponding author**

INTRODUCTION

Polymers that respond in a productive fashion to their environment are under active development as they offer significant advantages over traditional materials. The polymers with the ability to self-heal and recover had a significant fraction of their initial properties after being subjected to a damage event. Such Polymers and their composites have been widely used in tremendous engineering fields because of their advantages including light weight, good processibility, chemical stability in any atmospheric conditions, etc. However, long-term durability and reliability of polymeric materials are still problematic when they serve for structural application[1-3.] Exposure to harsh environment would easily leads to degradations of polymeric components. Comparatively, micro-cracking is one of the fatal deteriorations generated in service, which would bring about catastrophic failure of the materials and hence significantly shorten lifetimes of the structures. Since the damages deep inside materials are difficult to be perceived and to repair in particular, the materials had better to have the ability of self-healing. The natural healing in living bodies depends on rapid transportation of repair substance to the injured part and reconstruction of the tissues. Having been inspired by these findings, continuous efforts are now being made to mimic natural materials to integrate self-healing capability into polymers and polymer composites. The progress has opened an era of new intelligent materials. On the whole, researches in this field are still in the infancy. More and more scientists and companies are interested in different aspects of the topic. Innovative measures and new knowledge of the related mechanisms are constantly emerging.Here in this review different types of healing processes are considered. Self healing is only considered as the recovery of mechanical strength through healing of crack. This review also addresses different applications of self repairing materials.

DESIGN STRATEGIES

Different types of materials such as plastic/polymers, paints/coatings, metals/alloys have their own self healing mechanism. Different types of self healing processes are based on their design strategies. The different strategies of designing self healing materials are as follows:

Intrinsic self healing

- Physical interaction
- Chemical interaction (Reversible cross-links) by
  - Diels Alder and Retro Diels Alder reactions

Extrinsic self healing

- Release of healing agent by
  - Microsphere embedment
  - Tube (Hollow fibre) embedment
  - Microvascular system

Miscellaneous

- Electrohydrodynamics
- Shape memory effect
- Nanoparticle migration

Co-deposition

Intrinsic self-healing

Intrinsic self-healing materials do not have a sequestered healing agent but possess a latent self-healing functionality that is triggered by damage or by an external stimulus. These materials rely on chain mobility and entanglement, reversible polymerizations, melting of thermoplastic phases, hydrogen bonding, or ionic interactions to initiate self-healing. Because each of these reactions is reversible, multiple healing events are possible.Intrinsic self healing can be either physically or chemically based. Physical self-healing occurs when thermoplastics are heated above their glass transition temperatures and slight pressure is applied (Figure 1). Under such conditions inter-diffusion of polymer chains can occur at the intimate crack surfaces; the degree of recovery can be quite respectable. Importantly for armour applications some polymers can heal through melting caused by frictional heating, for example during ballistic penetration.

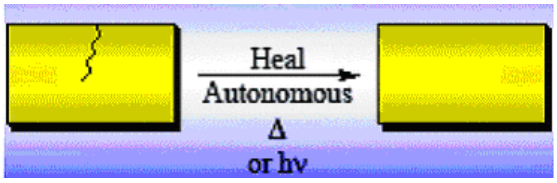
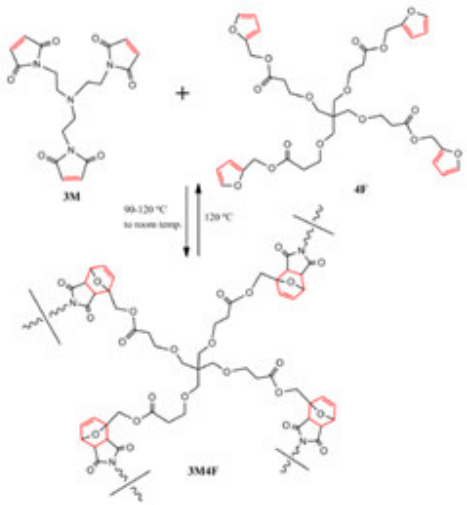


Figure 1
Intrinsic self healing process

Chemical interaction (Reversible cross-links)

Chemically based self healing is based upon thermally reversible cross linking behaviour; at temperatures above ambient the cross-linking is undone and is restored upon cooling. Major classes of thermally reversible polymers are made by using Diels Alder reactions (DA) [4-5]. Examples of this category include crosslinking of furanic polymers with maleimide or polymers containing maleimide pendants at low temperature. Retro Diels-Alder (RDA) reaction occurs at elevated temperatures to debond the chemical linkages of formed networks and to reverse the cross linking process. Wudl and coworkers were the first to implement this strategy to design thermally remendable polymers[6-7]. Liu and co-workers [8] synthesized multifunctional furan and maleimide compounds using epoxy compounds as precursors. The self repairing property of trimaleimide and tetrafuran crosslinked material was investigated by SEM techniques. The cross linked material shows a smooth and planar surface. Later a notch was made on the surface by knife cutting. The cut sample was thermally treated at 120°C for 20 min and at 50°C for 12 hr (Scheme 1).



Scheme 1
Reversible highly crosslinked furan-maleimide base polymer network

At higher temperature, debonding (RDA) occurred and the polymer chains were deformed at this temperature. DA reactions (bonding of polymer chains) take place at lower temperatures and the crosslinked structures.

Extrinsic self-healing

In case of extrinsic self healing, the matrix resin itself is not healable. Healing agent has to be encapsulated or embedded into the material in advance. Liquid active agents such as monomers, dyes, catalyst and hardeners containing microcapsules, hollow fibers or microvascular systems are embedded into polymeric systems during its manufacturing stage. These processes does not need any manual or external intervention, therefore, they are automatic[9]. The following section discusses the different possibilities to explore the concept of designing self healing materials.

Microsphere embedment

Capsule-based self-healing materials (Figure 2a) sequester the healing agent in discrete capsules. When the capsules are ruptured by damage; the self-healing mechanism is triggered through the release and reaction of the healing agent into the crack plane through capillary action. After release, the local healing agent is depleted, leading to only a singular local healing event.

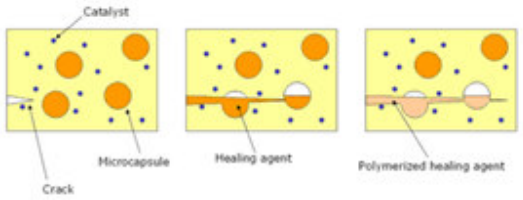
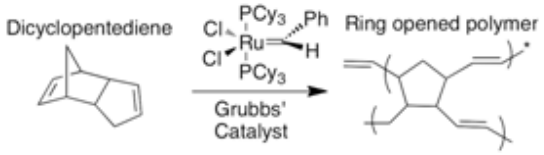


Figure2

Concept of extrinsically self healing polymer based on embedded microcapsules of healing agent, based on the figure from White et al. [9]. From left to right: micro-structure with embedded catalyst and microcapsules of healing agent (polymer precursor), crack ruptures microcapsules and healing agent coats crack surfaces via capillary action, catalyst cross-links healing agent.

White et al. [10] used dicyclopentadiene (DCPD) as the liquid healing agent and Grubbs'catalyst[bis(tricyclohexylphosphine)ben zylidene ruthenium (IV) dichloride] as an internal chemical trigger and it was dispersed in an epoxy matrix. When DCPD comes into contact with the Grubbs' catalyst, ring-opening metathesis polymerization (ROMP) starts (Scheme 2) and a highly cross-linked tough polycyclopendiene is formed that seals the crack. The low viscosity helps it to flow into the crack plane.



Scheme 2

ROMP using DCPD and Grubbs' catalyst

DCPD filled microcapsules (50–200 μm) with a urea-formaldehyde shell was prepared using standard microencapsulation techniques. The microcapsule shell provides a protective barrier between the catalyst and DCPD to prevent polymerization during the preparation of the

composite. Self-healing composites possess great potential for solving some of the most limiting problems of polymeric structural materials: microcracking and hidden damage. Microcracks are the precursors to structural failure and the ability to heal them will enable structures with longer lifetimes and less maintenance. Filling microcracks will also mitigate the deleterious effects of environmentally assisted degradation such as moisture swelling and stress corrosion cracking. Although the potential benefits are quite high, the specific composite described here has some practical limitations on crack-healing kinetics and the stability of the catalyst to environmental conditions.

Encapsulation Technique

There are several requirements to consider in designing a truly self-healing system. These include long shelf-lives of the healing agent and the chemical trigger, low healing agent viscosity and volatility, rapid polymerization upon mixing of the healing agent and the chemical trigger at ambient conditions, low shrinkage upon polymerization, and good mechanical properties of the resulting polymer. Furthermore, since the stoichiometry of the healing chemistry cannot be controlled in the crack plane during a healing event, the initial rate of polymerization and overall degree of monomer conversion must be minimally dependent on the stoichiometric ratios of the reactants. This complex interplay of characteristics also includes the fact that for maximized healing properties to be observed, the monomer released into the crack plane must have sufficient time to cover the entire crack face, prior to the significant increase in viscosity due to the polymerization process, in order to have a continuous polymer layer that bonds the crack faces together. A comprehensive summary of the requirements for the design of microencapsulation-based self-healing systems is given in Table 1.

Table 1
Characteristics Required for Designing Microencapsulation-Based Self-Healing Polymeric Materials (11, 12)

Liquid healing agent Stability and shelf-life	Must be stable enough to be encapsulated without reaction and must be stable within the microcapsule for long periods until it is released during a healing event
Deliverablity:	Must flow into the site of damage by capillary action, so it cannot be a highly viscous liquid. It must also remain in the site of damage long enough to react, so a highly volatile liquid is not desirable.
Reactivity:	Once the healing agent comes in contact with the catalyst or second reactant, it must react quickly enough to provide healing in a reasonable time frame and to compete with nonproductive processes like evaporation,absorption into the matrix and side reactions.
Shrinkage	The resulting polymer should exhibit good adhesive characteristics to rebond the crack planes. Any volume shrinkage could result in the polymerized healing agent pulling away from the crack faces as it is being cured.
Physical and mechanical properties	The incorporation of the healing agent in its encapsulated form should not introduce any deleterious effects to the matrix. Additionally the healing agent must demonstrate mechanical properties equal to or surpassing that of the matrix in its polymerized form
Thermal stability	Must have a low freezing point and a high boiling point to minimize the likelihood of phase changes at various application or use-temperatures
Microcapsule shell wall Chemical compatibility:	Material must be chemically inert both to the core material within as well as the surrounding matrix chemistry
Mechanical properties:	To facilitate rupture during a healing event, the fracture toughness of the capsule shell wall material should be less than that of the matrix, but high enough to survive standard processing conditions
Dispersion:	Must facilitate or at the very least not create a hindrance to dispersion in the desired matrix
Thermal stability:	Must be thermally stable over a wide range of temperatures for a wider scope of applications
Solubility	The catalyst, curing agent or reaction initiator must dissolve rapidly in the liquid healing agent
Chemical compatibility	Must be chemically stable to the matrix in which it is being incorporated to ensure activity when it is needed during a healing event
Reactivity	Must promote rapid reaction with the healing agent. However, the reaction kinetics must not be faster than the dissolution kinetics as that would lead to self-limiting polymerization and inefficient use of the catalyst, curing agent or reaction initiator
Dispersion:	Must be well-dispersed throughout the matrix in order to ensure proximity to the microcapsules and efficient use of catalyst
Healing chemistry Stoichiometry:	Must be forgiving since it cannot be controlled in the crack plane during a healing Event.

A variety of techniques exist for encapsulation of reactive materials. These techniques can be classified as interfacial, in situ, coacervation, meltable dispersion, or physical on the basis of the mechanism of wall formation. The encapsulation techniques can be sited in literature for food science, medical, industrial, and agricultural applications [13–15.]

Tube (Hollow fiber) embedment

Bio-inspired self-healing using hollow fibers embedded within a structure has been investigated at different length-scales in several materials by various authors, e.g. bulk concrete, bulk polymers and polymer composites[16-17]. The latter has seen exciting developments in recent years, e.g. [18-20] using the inspiration of biological self-healing applied with broadly traditional engineering approaches[21-22]. Hollow glass fibers (HGFs) [23] are used in preference to embedded microcapsules because they offer the advantage of being able to store functional agents for self-repair as well as integrating easily with and acting as a reinforcement. A typical hollow fiber self healing approach used within composite laminates could take the form of fibers containing a one-part resin system, a two-part resin and hardener system, or a resin system with a catalyst or hardener contained within the matrix material[19]. A schematic of these approaches is shown in Figure 3.

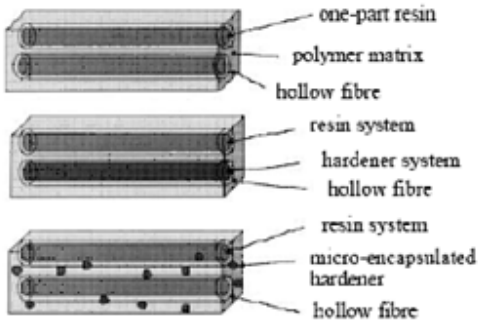


Figure 3
Different hollow fiber self healing approaches

A bespoke HGF making facility[24] has been used to produce HGF between 30-100 μm diameters with a hollowness of approximately 50% Figure 4a. A fiber spacing of 70 μm Figure 4b ensures that the HGF were in close proximity and thereby facilitating a high degree of healing efficiency. These are then embedded within either glass fiber-reinforced plastic (GFRP) or carbon reinforced plastic (CFRP) and infused with uncured resin to impart self healing functionality to the laminate. During a damage event, some of these hollow fibers will fracture, thus initiating the recovery of properties by 'healing' whereby repair agent passes from within any broken hollow fibers to infiltrate the damage zone, and acts to ameliorate the critical effects of matrix cracking and delamination between plies and, most importantly, prevent further damage propagation. This release of repair agent mimics the bleeding mechanism in biological organisms.

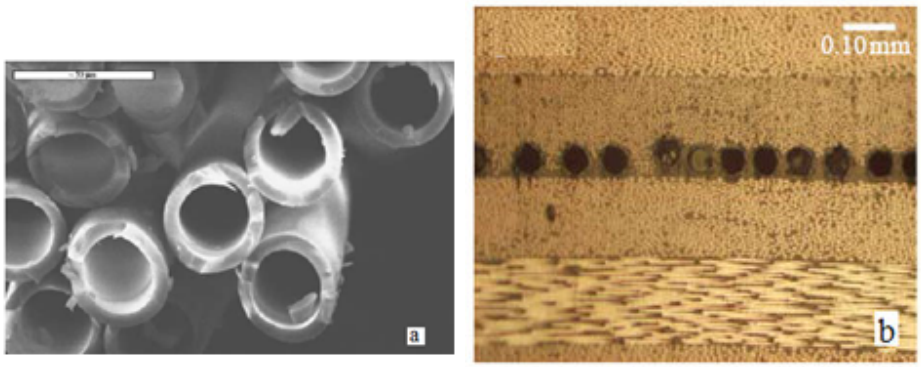


Figure 4
a. SEM of Typical HGF (35 mm external diameter with 55% hollowness fraction).
b. HGF spaced at 70μm showing good embedment

Microvascular system

Vascular self-healing materials (sequester the healing agent in a network in the form of capillaries or hollow channels, which may be interconnected one-dimensionally (1D), two-dimensionally (2D), or three-dimensionally (3D), until damage triggers self-healing. After the vasculature is damaged and the first delivery of healing agent occurs, the network may be refilled by an external source or from an undamaged but connected region of the vasculature. This refilling action allows for multiple local healing events. In conventional extrinsic self healing composites it is hard to perform repeated healing, because rupture of the embedded healant- loaded containers would lead to depletion of the healing agent after the first damage. To overcome this difficulty, Toohey et al. [25-26] proposed a self healing system consisting a three dimensional microvascular network capable of autonomously repairing repeated damage events.The design cycle for vascular networks can be partitioned in a manner similar to capsule-based healing systems. Many of the same issues must be considered with regard to mechanical characterization, the triggering mechanism, and the healing performance. Where the two systems differ is with respect to fabrication and integration within a matrix material. Depending on the fabrication method, the interactions between the matrix materials, the healing agents, and the network materials play a crucial role in the effective development of a self-healing system.This approach opens new avenues for continuous delivery of healing agents for self-repair as well as other active species for additional functionality.Their work mimicked the architecture of human skin. When a cut in the skin triggers blood flow from the capillary network in the dermal layer to the wound site, clot would rapidly form, which serves as a matrix through which cells and growth factors migrates as healing ensues.In this process, organic inks are deposited following the 3D-array and the interstitial pores between the printed lines are infiltrated with an epoxy resin. Once the polymer is cured, the fugitive ink is removed leaving behind the 3D-microvascular channel with well defined connectivity. Polymeric systems with microvascular systems were prepared by incorporating chemical catalyst in the polymer used to infiltrate the organic ink scaffold Figure 5. Upon curing, the

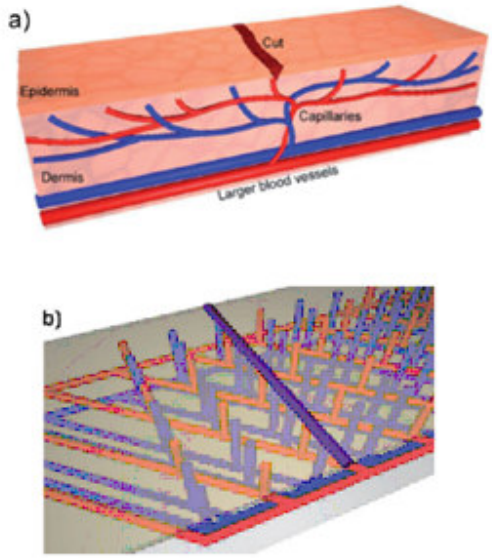


Figure 5
a. Schematic view of a cut in the epidermis layer of skin and the capillary network in the dermis layer. b. Schematic view of an interpenetrating microvascular network that supplies two fluids to a crack plane, where mixing occurs.

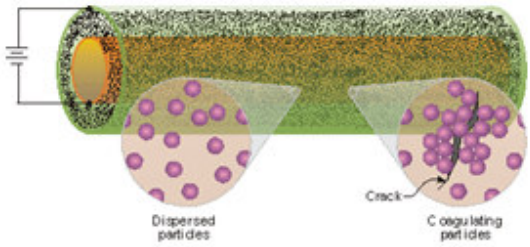


Figure 6
A schematic for a self-healing system that uses the electrohydrodynamic coagulation of particles to close a defect in a cylinder wall

The defect is not completely repaired because the voids between the colloids prevent the formation of a completely dense surface. To fill in these interstitial spaces, simultaneous metal electrodeposition within the void spaces by dissolving and electroplating of the anodic metal electrode (sacrificial anode) ultimately fills the void [30]. This process produces a coating of a ceramic/metal composite at the site of the initial defect.

Shape memory effect

Certain strongly ordered intermetallic systems show the well known shape memory effect[31], in which plastic deformation imparted to the low-temperature marten site phase can be reversed almost completely during transformation to the high temperature austenite phase. The shape memory alloys (SMAs) viz., NiTi, NiTiCu, CuAlNi, can be used as self healing materials. Example nitinol (nickel-titanium alloy) which exhibits self healing effect on heating [32-33]. If they are permanently deformed and heated above certain temperatures they will return to their original shape[34]. Shape memory polymer (nickel-titanium alloy) when mixed with carbon nanotubes, which are highly conductive materials, develops self-healing capability. The

developed polymeric material is applied to carbon fiber reinforced composites to automatically heal the delamination between different layers. Experimental results showed that the developed composite materials are capable of healing the matrix cracks and delaminations in the bonded areas of the test specimens. The developed self-healing material has the potential to be used as a novel structural material in mechanical, civil, aerospace applications[35].

Nanoparticle migration

Balazs and coworkers have demonstrated that nanoparticles in a polymer fluid can segregate into cracks due to the polymer induced depletion attraction between the particles and the surface [36-37]. Self healing materials based on this approach are yet to be demonstrated. Incorporation of nanoparticles into polymeric systems has two fold benefits: (i) it increases the mechanical strength of the system (ii) segregates to the crack surface. Carbon nanotubes (CNTs) are considered to be an ideal filler material for mechanical reinforcement as well as best molecular storage devices. This is owing to the fact that CNTs are very small, thus they have an enormously large interfacial area. CNTs have a hollow tubular structure and remarkable chemical and mechanical properties. Recently, C60 [38], Hydrogen[39], metal carbide[40], CH_4 [41], and DNA [42] have been effectively planted inside CNT.

Co-deposition

Electro co-deposition can also be employed to design self healing anti-corrosive coatings. Microcapsules containing corrosion inhibitors can be added to composite plating coatings by this method [43-44]. The capsules can be deposited with metallic ions to form composite metallic coatings. When the crack is formed in the composite, the capsule releases its contents to heal the crack.

Applications

The uses for these self-healing polymer composites[45] are virtually endless. This technology can be used in nearly any plastic or composite part that is subject to microcracking. Below are just a few examples.

- **Transportation**: Cracks in the structure or components of automobiles, airplanes, and spacecraft shorten vehicle life and can compromise passenger safety. This self-healing technology would repair these cracks before they grow to dangerous levels.
- **Sporting Goods**: Many consumers are willing to pay top dollar for high-quality fishing equipment, tennis rackets, helmets and other protective gear, boats and surfboards, skis, and other sports equipment. This self-healing technology would improve the quality of these products.
- **Medicine**: Once implanted in the body, prosthetics and other medical devices are difficult to monitor and access for repair. This self-healing technology could prevent problems caused by damaged pacemakers, hip and knee replacements, dental materials, and other medical devices.
- **Electronics**: Polymer composite circuit boards and electronic components can suffer from mechanical and electrical failures if microcracks progress unabated. This self-healing technology would help to prevent such failures.
- **Paints, Coatings, and Adhesives**: Used in a wide variety of products, paints, coatings, and adhesives are subject to scratches, cracks, and deterioration. This self-healing technology would repair this damage, maintaining protection from environmental conditions and/or a long lasting seal.

FUTURES OUTLOOKS

In summary, the material deprivation can occur for a large assortment of reasons, such as fatigue loadings, thermal effects, corrosion, or, in general, for environmental effects of all kinds. However, the materials strength is most likely one of the main challenges encountered today for structural applications. The failure of materials in general starts at the nanoscale level and is then augmented to the micro- up to

the macro-scale level until disastrous failure occurs, the best solution would be to block and/or eliminate damage as it occurs at the nano/microscale and restore the original material properties.So far, all the operational techniques are limited by the container size. Containers must be in the nanoscale range since larger ones could lead to large hollow cavities that could pacification the mechanical properties of the hosting structural material [46]. Moreover, the advanced materials are designed so for to be either tough or self-healing, but typically not both. It would be best to have a material which could be at the same time tougher and self-repairable, and this is still unattainable with existing technologies.Even though an enormous work has been done with CNTs as self-storage devices, still CNTs yet to be explored as nanoreservoirs for self-healing applications[47].The key challenges related with this application are how to insert molecules into the carbon nanotubes, whether crack can form on the sidewall of a carbon nanotube at some stage in its propagation, and if the healing agent will come out of the carbon nanotube when the crack forms. In recent times, Lanzara et al. have investigated the use of CNTs as nanoreservoirs for automatic repairing applications, through a molecular dynamics (MD) study with particular focus on the CNTs capacity of delivering a healing agent. Of late authors have shown that the CNTs were not only able to carry the catalytic healing agent for local repair but also can simultaneously play the role of filler material for mechanical reinforcement prior and after the delivery of the active material.

CONCLUSION

During the last decades, constant improvements have been made on composite materials, manufacturing processes and structural design. Self-healing polymeric and composite materials are subject to weakening due to fatigue cracking. A self-healing composite has the potential to defend against material failure due to fatigue and to greatly improve product safety and reliability and to extend product lifetimes. Addition of microcapsules to the resin and later initiating the self-healing process increases the toughness of the resin.Self-healing polymers are extremely attractive materials, but creating the "ideal" polymer is far from easy, and compromises are in order. So far, scientists have mainly approached the problem from two angles: they've either used a network of embedded microcapsules containing a healing agent (which can only heal the material a limited number of times), or materials that can heal indefinitely because they are bound together by reversible chemical reactions (but need a large amount of energy as a catalyst). Their exploitation will require extensive multidisciplinary research because many natural systems have evolved to be enormously complex but robust systems. In recent years, interesting perspectives have opened for the design of innovative self -healing nano systems. The key engineering challenge is to understand and extract the key functional aspects of natural systems in order to produce systems that can feasibly and cost-effectively be applied to engineering structures.

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