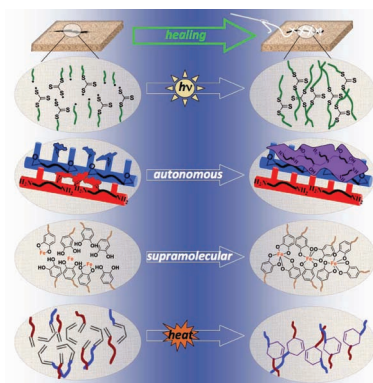


## Trends in Polymer Science

## Current Trends in the Field of Self-Healing Materials

Nathalie K. Guimard, Kim K. Oehlenschlaeger, Jiawen Zhou, Stefan Hilf, Friedrich Georg Schmidt,\* Christopher Barner-Kowollik\*

The evolution of material design has mirrored advancements in the understanding of materials, nature, and the requirements of target applications. Originally, materials were only intended to play a passive role, but with a deepened understanding of material properties and design has come an improved ability to harness these properties to create materials with predetermined response mechanisms. This article has three aims: i) to briefly discuss the origin of and motivation for having materials that are capable of undergoing healing either extrinsically or intrinsically; ii) to present the most recent and promising advancements in the field of self-healing materials; and iii) to discuss important material design and property specifications that should be considered in order to promote the development of optimized self-healing materials.



## 1. Introduction

Advanced functional materials have always been an integral aspect of everyday life. Technological advancements in the area of material development

were initially driven by the need for strong and durable materials that were cheap to produce. These materials were generally comprised of natural resources, subjected to basic processing techniques (e.g., production of alloys and composites), which were intended to simply have structural or passive functions. Later, advancements were also influenced by the desire to generate materials that were optimally tuned to a target application. Efforts to tackle the latter objective have not diminished and, in fact, have been bolstered by a more recent surge in material research geared toward producing “smart” materials. A smart material is a material that has been designed to respond to a selected specific stimulus in a controlled and predetermined fashion. One class of smart materials that has received a great deal

of attention in the last ten to twenty years is that of self-healing materials. The focus of the current Trend Article is to discuss the important aspects of and trends in the relatively new field of self-healing materials and briefly note the most promising and recent advancements in this research area.

## 2. Origin of Self-Healing Materials

Designing smart materials that can withstand environmental stresses, including oxidation, radiation, abrasion, impact, thermal decomposition, and moisture, has become of particular interest. A material that would be capable of healing in a similar fashion to the way animals and plants when they sustain an injury would,

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in principle, provide extra security, have an increased lifetime, reduce the rate of occurrence of system failures, and decrease maintenance and costs requirements. Self-healing materials were first observed as early as the 1970s. For example, hard elastic polypropylene (HPP), just as other viscoelastic polymers, was observed to consist of a stacked lamellar morphology, perpendicular to the axis of polymer extrusion, that was capable of healing interlamellar microvoids formed following stretching (in the perpendicular direction). This deformation recovery process was explained by the energy balance that exists between work, strain energy, viscous dissipation, and damage. In essence, upon polymer stretching, surface energies are converted to strain energy and, subsequently, mechanical work, which gives rise to crack closure.<sup>[1–3]</sup>

Although a limited number of polymers are inherently capable of self-healing, more common materials are incapable of naturally self-healing and, therefore, human intervention is necessary for repairing damage. The most conventional forms of repair are resin injection, reinforcing patch application, and welding; however, in all cases the site of repair generally remains the weakest point in the material. More problematic are cases when the site of damage is inaccessible to repair. Given these limitations, the ultimate goal became to design materials, based on a deeper understanding of (bio)material chemistry and the target applications, which could undergo self-healing at the microscopic or even nanoscopic level, such that crack propagation could be arrested and pristine physico-mechanical properties of the material could be restored.

There are a number of approaches to designing ideal self-healing materials. However, the resulting material can generally be classified as achieving healing either intrinsically by reversible bond formation or extrinsically via the triggered

release of a pre-added healing agent. Other types of materials that can be considered healable that already exist on the market are those with low glass transition temperatures ( $T_g$ ). Heating such a material above its  $T_g$  permits the material to flow and fill into microcracks. For the purposes of this trend article, these materials will not be discussed further unless they also incorporate other healing mechanisms. Regardless of the type of healing, the system must initiate healing in response to a stimulus/trigger. Materials that autonomously heal, whether through intrinsic or extrinsic means, are those that heal in response to a mechanical trigger (i.e., damage). In contrast, there

are also a number of intrinsically and extrinsically healing systems that have been designed to heal in response to a predetermined external trigger, other than damage, such as optical,<sup>[4–11]</sup> thermal,<sup>[12–15]</sup> electrical,<sup>[16,17]</sup> ballistic,<sup>[18,19]</sup> or chemical.<sup>[20,21]</sup> In all cases, a microscopic crack in the material is mended before crack propagation occurs and, therefore, potentially catastrophic failure is circumvented. The first self-healing materials, designed by C. Dry, were based on fiber reinforced concrete. Extrinsically self-healing materials were developed in which fibers, employed for reinforcing the material, were filled with a self-repair fluid. These composite materials would



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autonomously heal (i.e., damage would break the fibers releasing the healing fluid, which would fill microscopic cracks).<sup>[22,23]</sup> Since the development of this first smart self-healing system, many material scientists and engineers have sought to design other self-healing systems for a variety of applications. These efforts have been extensively reviewed in the last five years.<sup>[24–30]</sup>

The last decade has been witness to the development of a diverse array of self-healing materials. A number of extrinsically and some intrinsically self-healing materials have been designed such that they heal autonomously, which is ideal for many applications. For non-autonomously healing materials, human intervention is frequently necessary to trigger the healing process; however, there are some applications where the material may be naturally exposed to the intended self-healing trigger, such as optically sensitive coatings on cars or outdoor equipment that can heal in the presence of sunlight. Consequently, it is important to consider the intended application of the self-healing material. Likewise, in designing the material and determining its applicability, it is important to consider the healing rate, the repeatability of healing at the same fracture point, the extent to which the pristine physico-mechanical properties are restored at the damage site, and the complexity, stability, and cost of the system. Self-healing materials have been designed from a wide variety of materials, including polymers,<sup>[4,6,8,10,12–15,18,24,29–37]</sup> ceramics,<sup>[38]</sup> concretes,<sup>[39–41]</sup> and composites<sup>[42–47]</sup> of any of these. The majority of the discussion to follow will focus on polymeric systems.

### 3. Mechanically Triggered Healing

As previously mentioned, the first self-healing materials were those that

healed in response to a mechanical trigger. The earliest design consisted of concrete reinforced with cyanoacrylate-filled fibers.<sup>[23]</sup> This one-part adhesive-filled fiber-reinforced system was later applied to polymer composites.<sup>[44]</sup> In addition to the one-part systems, two other types of self-healing fiber-reinforced polymer (FRP) systems were developed: i) a two-part reagent system, in which a resin (e.g., epoxy) and a hardener (e.g., diamine) are contained within adjacent fibers and ii) a two-part system, where only one component rests within the fibers and the other component is microencapsulated and/or embedded within the polymer matrix.<sup>[47]</sup>

As an alternative to FRPs, White et al. developed self-healing polymers containing a catalyst, originally Grubbs' catalyst, which in later systems was encapsulated, and microcapsules that were filled with a healing agent, typically dicyclopentadiene.<sup>[43]</sup> FRP and microcapsule-polymer composite system parameters, such as fiber or capsule wall thickness,<sup>[45,48,49]</sup> fiber diameter,<sup>[45]</sup> capsule size and concentration,<sup>[50–52]</sup> healing agent,<sup>[43,53,54]</sup> catalyst type (if needed),<sup>[55–57]</sup> and catalyst incorporation method,<sup>[43,53,58]</sup> have all been well studied to optimize the release of the healing agent(s), the mixing of the healing agent with the catalyst (where relevant), and the rate of polymerization/curing following a mechanical trigger. In general, these systems have been moving away from air-sensitive and expensive components, such as Grubbs' catalyst. For instance, a relatively inexpensive, stable, tin-based catalyst has been utilized to catalyze the polycondensation of siloxane-based macromonomers following the mechanically triggered release of these monomers from microspheres.<sup>[56]</sup> Although FRP and microcapsule-based polymeric systems are similar in many ways, the latter system permits finer tuning of the material properties. For instance, careful selection of microcapsule material, size, and concentration has

permitted the preparation of materials with increased toughness of the pristine/undamaged polymer composite<sup>[50,59]</sup> and enhanced healing efficiency and, therefore, increased resistance to bulk material crack formation.<sup>[43]</sup>

Compared to many other self-healing material designs, those that employ a microencapsulated repairing agent are attractive because they allow for autonomous healing, they can be adapted to a number of different polymers (with differing material properties), and they have the potential for quantitative healing. Nonetheless, an ideal system has yet to be developed. In part, this is because the ideal system will depend on the application. Therefore, material scientists are still searching for new, simple, and stable encapsulated healing agent-based systems that result in optimal healing and desirable material properties for a given application. Some recent and notable advances in this area of research have given rise to new polymer healing methods that employ living polymerization chemistry and click chemistry. For example, a poly(isobutylene) matrix was designed to heal upon the release and mixing of encapsulated azide and alkyne linkers.<sup>[60]</sup> Unfortunately, such a click polymerization still relies on the incorporation of an air sensitive copper catalyst. Yao et al. reported on the fabrication of a poly(methyl methacrylate) (PMMA) matrix, synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization, containing microencapsulated glycidyl methacrylate.<sup>[61]</sup> This self-healing system is an improvement over their previous RAFT polymerization-based system that required heat for healing,<sup>[42]</sup> their ATRP-based version of this system,<sup>[62]</sup> and the azide–alkyne click polymerization system mentioned above. In a different approach to microcapsule-based self-healing materials, carbon nanotubes have been proposed as nanoreservoirs for self-healing materials.<sup>[63,64]</sup>



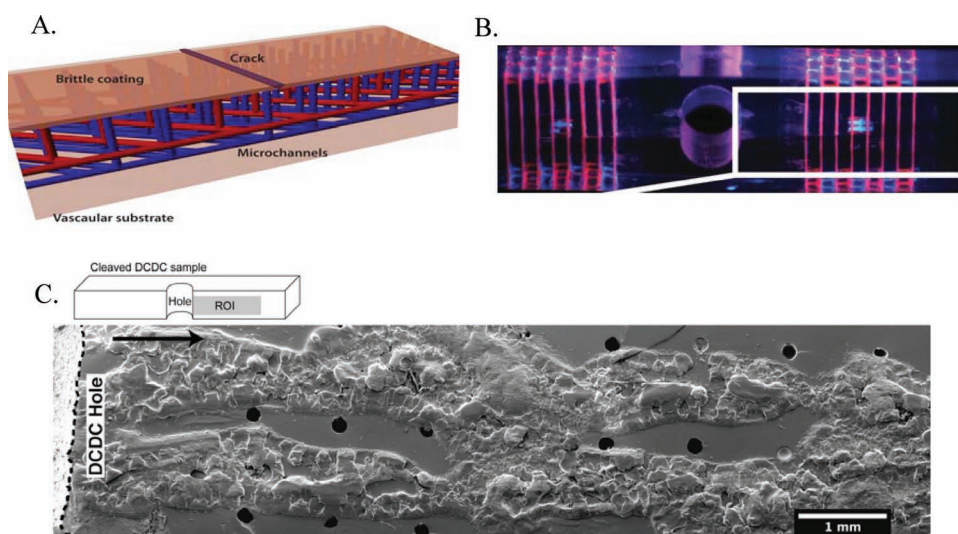
Although carbon nanotube-based self-healing materials have only been explored through modeling, one could imagine that this type of self-healing material would be ideal for applications that require mechanically strong and electroactive materials.

A major limitation of both self-healing FRPs and micro- or nanocapsule-polymer composite systems is the inability to repeatedly heal the polymer at the same location due to limited healing agent distributed throughout the polymer matrix. This limitation has motivated the development of biomimetic self-healing polymer systems containing a microvascular network that emulates the capillary network of the dermis layer in animals. For instance, a system consisting of hollow, healing-agent-containing channels that are refillable was developed.<sup>[65]</sup> Although repeated healing of this system requires human intervention to refill the microvascular network with healing agent, this type of self-healing system is still considered a step above FRPs and even microcapsule-based self-healing polymers because it can heal multiple times at the same fracture

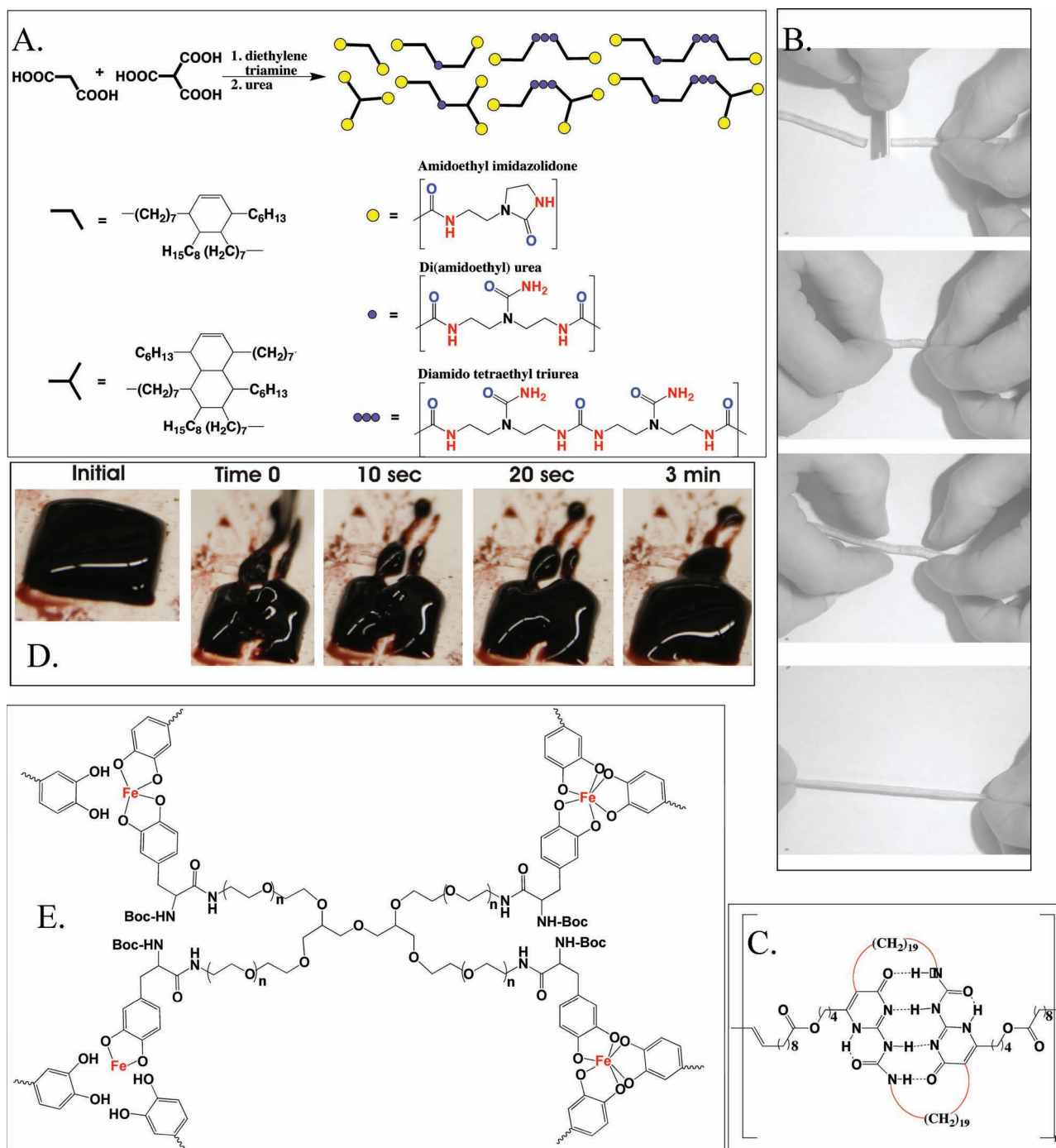
site. For example, thirteen healing cycles have been achieved for a two-part epoxy healing system containing a refillable three-dimensional microvascular network.<sup>[65]</sup> This system has also been modified to eliminate the need for human intervention by including vertical conduits, just below the coating layer, that connect to an interpenetrating microvascular network that is embedded deeper within the polymer.<sup>[66,67]</sup> In such a system, the microvascular network acts like a reservoir and when the surface of the material is fractured the healing agents are delivered to the crack plane by the vertical conduits via capillary forces (Figure 1A–C).

Despite the advantages of such extrinsically self-healing materials for particular applications, developing autonomously, intrinsically healing materials has become increasingly appealing as these materials are composed of dynamically bonding components, which would theoretically be capable of repeatedly healing at the same damage site. Currently, material scientists are still exploring and attempting to understand different reversibly bonded materials, but

eventually the goal would be to design a material with preselected properties for a particular application that employs dynamic, and therefore self-healing bonds. A number of dynamic bonds have been demonstrated to permit healing, but generally only non-covalent, supramolecular interactions, such as hydrogen-bonding (H-bonding)<sup>[36,68–70]</sup> and metal–ligand (M–L) complexation,<sup>[33,71]</sup> are autonomously (i.e., with only a mechanical trigger) self-healing. Although these systems are much simpler than the aforementioned extrinsically self-healing systems and they can undergo repeated healing cycles, the physico-mechanical properties of materials based on supramolecular interactions (instead of 100% covalent bonds) tend to be limited. Unfortunately, the weaker strength of these materials limits their application to the industrial world, but this has motivated further research to address this limitation. One approach explored by Cordier et al.<sup>[68]</sup> was to increase the extent of H-bonding that was possible between all components of the material.<sup>[72]</sup> In this case, a rubber material based on amidoethyl



**Figure 1.** A) Schematic depicting healing of surface damage in a polymer substrate via the release of healing fluids contained inside an interpenetrating microvascular network that is found within the substrate.<sup>[66]</sup> B) Image of the release of healing agents (resin, dyed with perylene, and hardener, dyed with Nile red) into the crack plane (shown in the white rectangle) of a fractured sample.<sup>[65]</sup> C) Scanning electron micrograph of the surface of a sample after 10 cycles of damage and healing.<sup>[65]</sup> Panel (A) reproduced with permission.<sup>[66]</sup> Copyright 2009, Wiley-VCH. Panel (B,C) reproduced with permission.<sup>[65]</sup> Copyright 2010, Wiley-VCH.



**Figure 2.** A) Fatty acids condensed with diethylene triamine and subsequently reacted with urea to give a mixture of oligomers that interact via hydrogen bonding.<sup>[68]</sup> B) Photographs of the cutting and self-healing of the hydrogen-bonded polymer depicted in panel A. The sequence of images shows the material after cutting, pressing the cut ends together, and after stretching (to demonstrate complete material mending).<sup>[68,72]</sup> C) A linear polymer consisting of the quadruple hydrogen bonding 2-ureido-4[1H]-pyrimidone (UPy) dimer constrained within a macrocycle proves to be strong and elastic.<sup>[32]</sup> D) Images showing the recovery over 3 min of cohesiveness and stiffness of tris-catechol-Fe<sup>3+</sup> gel (chemical structure shown in panel E).<sup>[33]</sup> E) Mussel inspired DOPA-modified poly(ethylene glycol) cross-linked with Fe<sup>3+</sup>. The three possible metal-binding complexes are shown. The complexation with Fe<sup>3+</sup> increases as pH increases.<sup>[33]</sup> Panel (B) reproduced with permission.<sup>[68]</sup> Copyright 2008, Nature Publishing Group. Panel (D) reproduced with permission.<sup>[33]</sup> Copyright 2011, National Academy of Sciences.

imidazolidone, di(amidoethyl) urea, and diamidotetraethyl triurea was able to be cut and completely healed

at ambient temperature (Figure 2A and B). In a different approach, Guan and co-workers<sup>[32]</sup> recently developed

a very promising titin-mimicking polymer, which consisted of H-bonding domains that were also connected by

long linkers (Figure 2C). Under stress the H-bonding domains of the polymer break, preventing the breaking of the covalent bonds. After the stress is removed, this elastic polymer recovers its original form because the covalently linked H-bonding domains are able to redimerize. Another supramolecular self-healing system modeled after a natural product is the mussel tissue-mimicking catechol-iron complex-based polymer developed by Holten-Anderson et al.<sup>[33]</sup> (Figure 2D and E). This polymer demonstrated near-covalent elastic moduli as well as 100% self-healing. Although the material must be at basic pH values to undergo healing, as long as the material is initially prepared under basic pH conditions it is not necessary to stimulate healing. Even considering the potential of these supramolecular-based self-healing materials, it is still necessary to further improve the strength of such supramolecular materials in order to expand the possible applications for these types of intrinsically healable materials.

There are many other dynamic bonds, both covalent and non-covalent, which could be used to create self-healing materials, but materials based on these bonds are not autonomously self-healing, but rather require heat, light, or a chemical to trigger healing. Therefore, these will be discussed in the following sections.

## 4. Thermally Triggered Healing

As mentioned in the previous section, there are many types of dynamic bonds that have been incorporated into materials to render them intrinsically self-healing. With only a few exceptions, materials based on non-covalent reversibly formed bonds tend to heal without any addition of energy following mechanical damage/stress, whereas ruptured covalent dynamic bonds require input of some form of energy in order for healing (bond

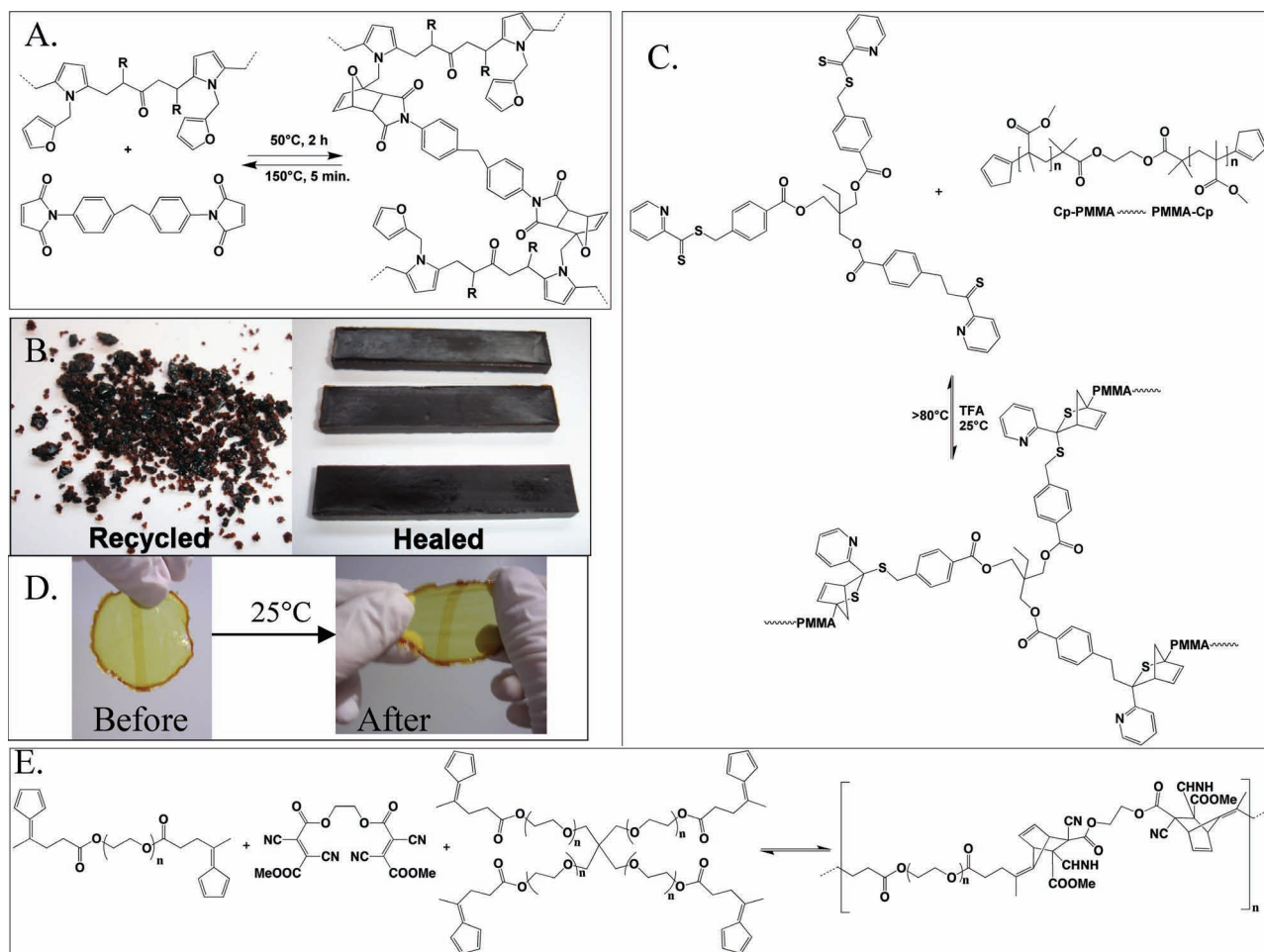
reformation) to occur. Although the self-healing systems based on covalent bonds would no longer be capable of autonomous healing, these materials would benefit from improved mechanical properties, which may be necessary for certain applications. For this reason, many material chemists have invested time into designing self-healing materials from thermally controllable covalent dynamic bonds, such as bonds formed from Diels–Alder (DA) cycloaddition,<sup>[12,15,31,73–76]</sup> disulfide bonds,<sup>[77]</sup> alkoxyamine bonds,<sup>[13,34,78,79]</sup> and imine bonds.<sup>[29]</sup>

DA chemistry is a highly promising technique for generating polymeric systems with thermally triggered self-healing.<sup>[26,28,30]</sup> The first study about thermally reversible polymeric networks containing DA functionalities was reported by Craven<sup>[80]</sup> in 1969. A few different strategies for generating self-healing materials from DA polymer networks have, since, been investigated. One strategy consists of polymerizing di- or multifunctional monomers (e.g., a bis- or multifuran functionalized monomer with a bis- or multimaleimide functionalized monomer). Chen et al.<sup>[14]</sup> were among the first to utilize this technique to generate a cross-linked material from a furan tetra-linker (diene) and a maleimide tri-linker (dienophile), which healed above 120 °C. Since then, a wide variety of mendable materials have been synthesized employing the same diene–dienophile pairing<sup>[76,81–90]</sup> in an effort to improve the rate of the DA and retroDA (rDA) reactions, decrease the rDA temperature, and increase the applications for this type of self-healing material. For instance, recently Ghezzi et al. developed carbon FRP laminates consisting of a self-healing bismaleimide/tetra-furan cross-linked polymer.<sup>[91]</sup> The carbon fiber reinforcement improved the mechanical properties of the material, such that this self-healing material could potentially be used for applications demanding stronger materials.

Another strategy that has been explored for creating self-healing DA-cross-linked polymers is that which involves cross-linking a linear thermoplastic bearing pendant furan or maleimide groups with either a di-linker or another linear polymer with pendant functional groups.<sup>[92,93]</sup> For instance, Zhang et al. recently developed a recyclable material from a furan-functionalized thermosetting polyketone cross-linked with bismaleimide (Figure 3A and B).<sup>[12]</sup> The cross-linking reaction was performed at 50 °C for 2–24 h, while the dissociation of the polymer network was accomplished by the rDA reaction at 120 °C after 20 min (or at 150 °C for 5–10 min). Other recent contributions include, a furan functionalized epoxy-amine thermoset reinforced with glass fibers that heals in the presence of a bismaleimide healing agent<sup>[94]</sup> and the thermally reversible polymerization of furfuryl functionalized ABA triblock copolymer with a bismaleimide.<sup>[81,95]</sup>

Other dienes and dienophiles have been explored for their DA reactivity and self-healing potential.<sup>[73,74]</sup> For instance, recently, Barner-Kowollik and colleagues reported the synthesis of a reversibly cross-linked polymer formed by the hetero-DA reaction of biscyclopentadiene end-functionalized PMMA with a trifunctional pyridinyl dithioformate cross-linker (Figure 3C).<sup>[15]</sup> In addition, a cyanfumarate di-linker cross-linked with a fulvene functionalized polymer resulted in an ambient temperature healable polymer film (Figure 3D and E) in work by Lehn and co-workers.<sup>[31]</sup> Although this system could be considered autonomously healing at ambient temperatures (i.e., requiring no external stimulus to initiate healing), it is still classified as a heat-triggered healing system because at lower temperatures heat would presumably be required to stimulate healing. Regardless, the above evidences that careful selection of the dienophile and diene pairs can drastically improve the self-healing properties of the resulting material.





**Figure 3.** A) The reversible cross-linking of a furan functionalized polyketone (PK-furan) with a bismaleimide using Diels-Alder chemistry.<sup>[12]</sup> B) Photographs depicting the complete healing of small granules of PK-furan after heating at 110–150 °C for 30–40 min.<sup>[12]</sup> C) The reversible polymerization (via hetero-Diels-Alder chemistry) of a pyridyl dithioester tri-linker with a bis(cyclopentadienyl) poly(methyl methacrylate) di-linker (TFA = trifluoroacetic acid).<sup>[15]</sup> D) Photographs of a fulvene-based cross-linked polymer film that has been cut in half before pressing the edges of the two film halves together at room temperature to allow for healing (see panel E for chemistry).<sup>[31]</sup> E) Diels-Alder chemistry used to reversibly cross-link fulvene functionalized glycol-based polymers with a cyanofumarate di-linker at room temperature.<sup>[31]</sup> Panel (B) reproduced with permission.<sup>[12]</sup> Copyright 2009, American Chemical Society. Panel (D) reproduced with permission.<sup>[31]</sup> Copyright 2009, Wiley-VCH.

As mentioned above, bond formation via Diels-Alder chemistry is not the only thermally reversible dynamic bond formation method. There has been an enormous amount of effort spent attempting to discover and characterize other thermally reversible linkages. Particularly promising is the research by Klumperman and co-workers,<sup>[77]</sup> which demonstrates that an epoxy resin cross-linked with disulfide bonds is capable of healing at 60 °C after 1 h due to the dynamic nature of the disulfide bonds and the low  $T_g$  of polyesters.

Another class of thermally triggered self-healing materials is that

comprised of materials which are based on  $\pi$ - $\pi$  stacking. Although such materials are composed of non-covalent dynamic bonds, it has been demonstrated that a robust free standing film that heals at 80 °C within seconds can be formed from a mixture of a diimide-containing polymer and a pyrene end-capped polymer.<sup>[36,37]</sup>

## 5. Optically Triggered Healing

In addition to heat and mechanical triggers, other stimuli, such as light, have been explored for their ability to

control dynamic bond (de)formation.<sup>[96]</sup> The first optically triggered self-healing systems were based on reversible cycloaddition reactions, which could be cycled back and forth to open and close cross-links in a polymer network. Typical examples for such optically triggered, reversible reactions are the [2 + 2] cycloaddition of coumarin<sup>[4]</sup> and cinnamoyl groups,<sup>[8,97]</sup> as well as the [4 + 4] cycloaddition of anthracene.<sup>[9]</sup> The latter type of pericyclic reaction has become more important to chemists due to the longer wavelength at which the forward and backward dynamic bond reactions proceed. Anthracene

cycloaddition occurs under irradiation at 340 nm, which is a wavelength that is tolerated by most functional groups and is even close to the wavelength of sunlight. As a result, an anthracene-based system is potentially attractive for its application to environmentally exposed surfaces.<sup>[7,9,97]</sup> Although the linkages formed by the cycloaddition of cumarins, cinnamic acids, or anthracenes are hypothesized to be the first to cleave under mechanical stress/damage<sup>[8,98]</sup> (in which case material healing can be achieved after the material is exposed to the relevant wavelength), if one desires to controllably cleave the network to allow for polymer network rearrangement, a different wavelength is required than that needed to (re)form/heal the network. This property may or may not be considered a disadvantage, but in any case it has motivated material scientists to develop optically triggered self-healing materials that require the same wavelength to trigger both bond cleavage and formation.

Most recently developed optically triggered self-healing systems are designed to require irradiation by only one wavelength in order to undergo healing. Metathesis is the key mechanism involved in the healing of this type of system. Exposing bonds that are susceptible to metathesis to irradiation results in the homolytic cleavage of these bonds, yielding highly reactive radicals, which subsequently recombine. Through this dynamic bond exchange, the network is able to accommodate and repair damage and, therefore, mend itself. Examples of bonds that can undergo light triggered metathesis are disulfide bonds, as demonstrated by Otsuka et al.,<sup>[6]</sup> and allyl sulfide bonds.<sup>[99]</sup> Although both systems are capable of optically triggered healing, the metathesis (and therefore healing) of allyl sulfides is limited by the addition of an extra reagent, a photoinitiator, whereas disulfide bond exchange is not. Fortunately,

allyl sulfide groups are preserved in the polymer network regardless of whether the photoinitiator has been consumed, which means that after adding more photoinitiator, self-healing is again possible. Trithiocarbonates are also known to undergo metathesis-based reversible bond cleavage following irradiation at 330 nm at ambient temperature, and without needing a photoinitiator (Figure 4A and B).<sup>[100]</sup> Moreover, since trithiocarbonates are RAFT agents they offer the additional advantages associated with such reactive centers. In particular, polymer branches of a preselected molecular weight could be synthesized from the trithiocarbonate center using living radical polymerization.<sup>[10]</sup>

A different, interesting approach to creating self-healing materials consists of modifying a natural polysaccharide, chitosan, with urea cross-links and oxetan.<sup>[11]</sup> Under mechanical stress the urea linkages and chitosan ether bonds were found to break; however, in the presence of visible light the oxetan rings opened, forming radical species that cross-linked with the chitosan network to achieve healing. Therefore, such a material could self-heal in the sunlight without any human intervention. The fact that the system is sensitive to sunlight is a considerable advantage, yet at the same time the lifetime of the system is limited to the presence of the oxetan functional groups.

A last example of metathesis-based healing materials is a material comprised of M-L complexes that can dynamically de-bond and re-bond. For instance, Burnworth et al. recently developed a metal complex-based polymer that relies on M-L bond exchange to repair scratches in the polymer.<sup>[101]</sup> When exposed to light between 340 and 390 nm, the metal complexes absorbed light. This energy was transferred into heat, causing M-L bond cleavage, which allowed for M-L exchange and

rebonding, resulting in the healed material.

## 6. Other Methods for Triggering Healing

Many intrinsically self-healing materials are designed to undergo reversible bond formation in the presence of a chemical trigger. Specifically, most of these reversible systems are sensitive to pH value<sup>[20,21,46,102–104]</sup> or the presence of redox agents.<sup>[9,105,106]</sup> Attractive examples of pH-sensitive systems are those based on boronic-acid-salicylhydroxy complexation,<sup>[103]</sup> hydrazone formation of acylhydrazines (Figure 4C),<sup>[102]</sup> and crown ether-benzylammonium salt ionic interactions.<sup>[107]</sup> A typical example of redox agent triggered self-healing systems, is that which incorporates disulfide linkages.<sup>[9,105]</sup> It is no surprise that polymers containing disulfide linkages have become increasingly attractive for self-healing material applications given the fact that healing can be stimulated and controlled by redox agents, in addition to heat<sup>[77]</sup> and irradiation.<sup>[6]</sup> All chemically triggered self-healing materials offer the user the advantage of total control over the extent of bonding of the chemically sensitive bonds and, therefore, over the healing process, as well as the disadvantage of non-autonomous healing.

More recently, some self-healing materials have been designed to heal when electrochemically stimulated. For instance, conducting polymers have been used to coat metal surfaces to protect them from corrosion by releasing healing ions and reforming the damaged coating at the surface following damage.<sup>[108]</sup> In addition, another electrically conductive material, *N*-heterocyclic carbenes (NHCs), has been found to heal when a crack is formed after a current is passed through the system.<sup>[17,109]</sup> Although these self-healing systems are



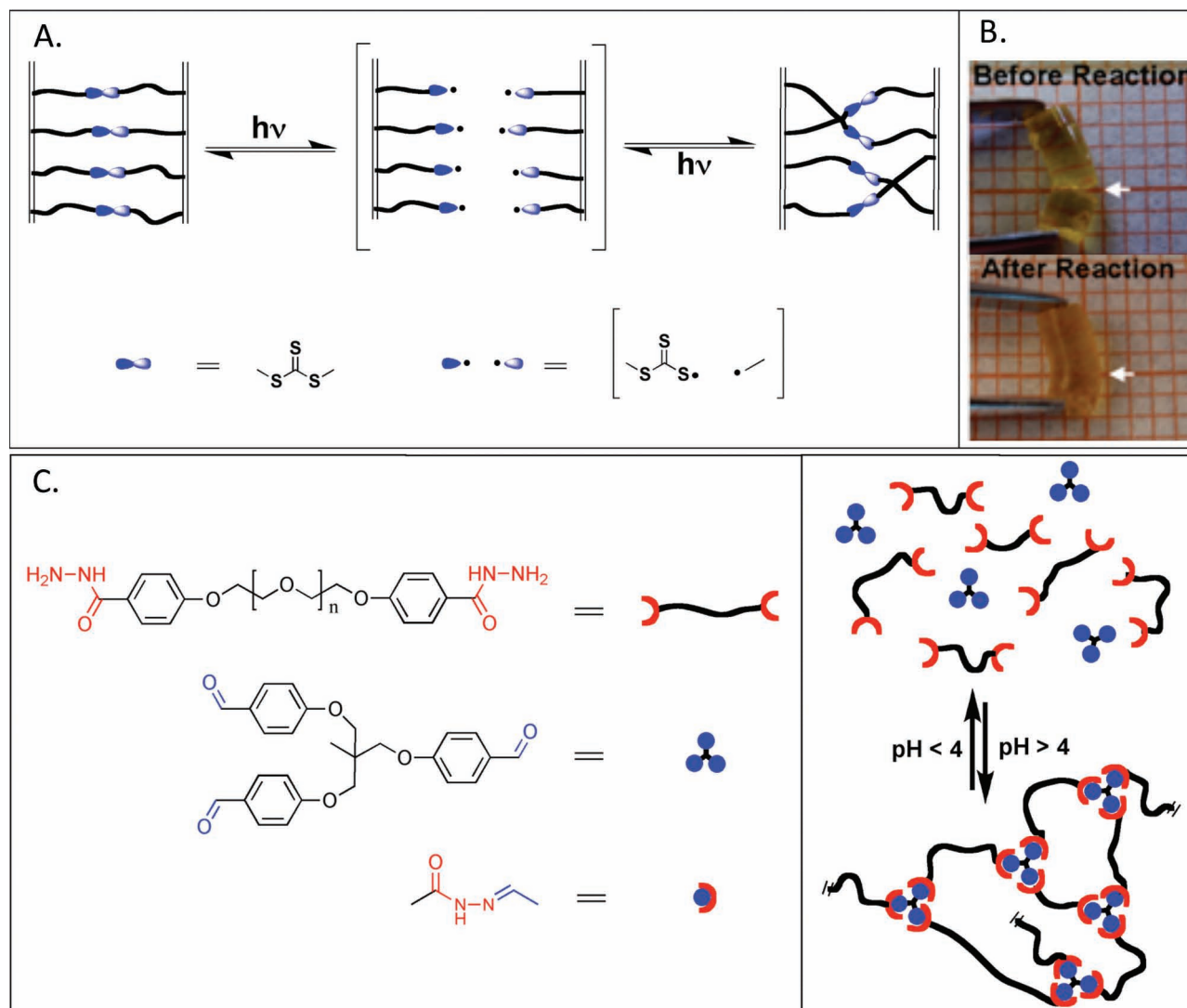


Figure 4. A) Metathesis of trithiocarbonate bonds in a polymer following photoirradiation (330 nm).<sup>[10]</sup> B) A photograph of a trithiocarbonate-based polymer in bulk after sustaining damage and before (top) and after (bottom) UV irradiation under nitrogen.<sup>[10]</sup> C) Schematic of the pH-sensitive reversible polymerization of a bisacylhydrazone functionalized poly(ethylene glycol) with an acylhydrazone tri-linker.<sup>[20]</sup> Panel (B) Reproduced with permission.<sup>[10]</sup> Copyright 2011, Wiley-VCH.

particularly advantageous for applications employing conductive materials, these systems have yet to be optimized.

## 7. Trends and Future Directions

As is evidenced by the extensive amount of research that has been conducted on healable systems, the concept of self-healing materials, as applied to anything from biomaterials

to protective coatings to architectural integrity, is very attractive. This is, of course, due to the fact that over the lifetime of a material, synthetic or natural, damage inevitably occurs by handling, use, and/or environmental stresses. When the crazes, cracks, or scratches propagate to form larger defects, the affected material will lose its mechanical integrity or protective properties, sometimes with critical effects (e.g., corrosion or catastrophic failure). Initially, material researchers sought to improve their

understanding of material properties, including natural self-healing (an ability possessed by a few materials) and damage formation and propagation. Subsequently, efforts were made to harness our understanding of nature and dynamic bond chemistry to produce artificial self-healing materials. As discussed above, there are several approaches to designing such a self-healing material. We are now at the point where our understanding of material chemistry is sufficiently advanced enough to allow us

to intelligently design materials. In order to do this, the intended application must, first and foremost, be considered.

Ultimately, an autonomously healing material would be ideal. Self-healing coatings that mend without an external stimulus/trigger would be particularly important for preventing corrosion in hard-to-reach places, especially when hardware replacement or surface reparation is a major undertaking. For instance, if one considers the costs of replacing the rotor blade of an offshore wind-mill due to little cracks, which could cause the whole system to fail, or repairing deep-sea oil well platform coatings that stave off corrosion, it would be much more favorable to utilize materials with autonomous self-healing properties to extend material lifetime. Alternatively, materials found in applications that are frequently or always exposed to UV light or heat could be designed to heal in the presence of the available external stimulus. Although these materials are not autonomously self-healing, in the absolute sense of the definition, human intervention would be unnecessary to initiate healing, as the material would be naturally exposed to the external stimulus necessary to trigger repair. For example, a cost-effective application of such self-healing materials would be corrosion protective automotive coatings, which would be capable of UV, heat, or mechanically triggered healing to repair little scratches caused by wear and tear (e.g., stone chipping or car wash bruises).

Regardless of the type of self-healing material, the intelligent application of these materials would likely result in a reduction of, hitherto necessary, safety margins for the constructive geometry of mechanically, thermally, and corrosively exposed components that are found in almost all technical areas. Consequently, substantial resource and energy savings could be anticipated. It follows

that the improvement in material reliability that would be achieved if self-healing materials were employed could revolutionize the construction and design of critical parts and components.<sup>[41]</sup>

Today most self-healing materials are developed in scientific laboratories. Nevertheless, the application potential of laboratory-based materials has been recognized by industries, as is evidenced by the recently initiated production of self-healing coatings by companies such as Autonomic Materials or Akzo Nobel, and the production of self-healing elastomers by Arkema. More specifically, Akzo Nobel promotes a high gloss clear-coat (Sikkens Autoclear LV Exclusive) for cars, which features self-healing properties when exposed to heat.

The different types of self-healing products that already exist on the market correctly reflect the technological approaches that are best suited for different applications. For instance, utilization of a microencapsulated healing agent within a material automatically results in an inhomogeneous material that requires a certain amount of microcapsules and a material thickness that far exceeds the microcapsule diameter. The application of such a material to clear coatings or thin layer lacquers would, therefore, not be ideal, but instead this material could be valuable for thick-layer coatings, such as those typically used for corrosion protection or adhesives. An autonomously healing material would also be valuable for coatings on surfaces that are difficult to reach. However, materials based on dynamic bonds that require an external trigger to induce healing are particularly well suited for thin protective coatings, which are naturally exposed to an external source of energy, such as light or heat. To date, most “self-healing” coatings do not, yet, rely on dynamic bonds to heal. The typical healing process of a self-healing coating material

still requires a material designed to have a precisely selected  $T_g$ . Heating the material above its  $T_g$  allows the material to reflow and mend. Once the material is cooled below the  $T_g$ , it regains gloss and hardness.

It is still a significant challenge to develop intrinsically (i.e., based on dynamic bonds) self-healing materials and coatings in a cost-effective way without changing the overall material performance. Overcoming this challenge is especially important for the aerospace and automotive industries. The future of self-healing materials in industrial/commercial/medicinal applications has yet to be fully established; however, the potential of these materials is likely to expand rapidly in the coming years. We expect, as mentioned in most of the related literature, that self-healing materials will, at least, find an application in parts/products:

- that are inaccessible or challenging to reach for repair, such as those found in high-rise buildings, marine equipment, underground piping, and wind turbines;
- where an undamaged surface is important, such as some high-price decorative coatings, corrosion protective coatings, or thermal barrier coatings;
- used in the aerospace industry, where part reliability, even under circumstances of overload or unforeseen loading, is of crucial importance;
- requiring long life cycles, including those found in flood barriers, tunnels, and piping networks;
- necessary for the long-term storage of nuclear waste;
- and utilized in biomedical applications.

Aside from considering the trigger mechanism for healing that would be ideal for a material given the target application, the material properties that are required must be taken into account. As mentioned above, it

is difficult to integrate self-healing properties into a material without significantly changing the physico-mechanical properties of the material. For instance, addition of fibers, microcapsules, or microvascular networks may drastically change the elasticity or toughness of the original material. Given this, one might favor an intrinsically healing material over an extrinsically healing material. However, in the case of intrinsically healing materials there are other limitations to consider. For example, certain dynamic bond-based self-healing mechanisms can only be applied to a particular polymer, whether it is a polymer with a low  $T_g$ , a thermoset, a polymer at basic pH values, or an ionic polymer. Another drawback of materials based on dynamic bonds, whether covalent or non-covalent bonds, is that damage on the nanoscopic scale must cleave only the dynamic bonds in order to permit 100% healing and recovery of mechanical properties. Unfortunately, the healing promoted by the dynamic bonds can only accommodate so much of the damage that is sustained by non-dynamic bonds before the mechanical strength of the material diminishes.

In addition to considering material properties and the limitations that each healing mechanism imposes on these properties, the material design needs to be kept simple and cost effective. In order to industrialize any material, reagents must be relatively cheap and stable and the design must be easy to reproduce. Given this, avoiding expensive or unstable catalysts and metal ions may prove to be advantageous in the long term.

Although one approach to developing self-healing materials is to design every material from the bottom-up, such that one starts from square one for every application, another more top-down approach would be to identify dynamic bonds that could be readily integrated into any number of polymeric systems in order to generate self-healing

polymers with properties belonging to the selected polymeric system. In other words, tunable materials could be designed that can be targeted to any selected application. It is clear that dynamic bonds, such as H-bonds, bonds formed from Diels–Alder chemistry, disulfide bonds, allyl sulfide bonds, and trithiocarbonate bonds have the potential to be incorporated into a number of different polymeric systems. Therefore, integrating these systems into materials and then tuning the material properties according to the desired application should be possible. One potentially promising means for accomplishing this would be to combine more than one type of dynamic bond into a polymeric network, such that self-healing, and possibly other material properties, could be controlled by more than one trigger.

A completely orthogonal approach that could be used to design self-healing systems more intelligently (and less randomly) would be the utilization of quantum chemistry prediction methods to predict the energy (e.g., temperature) at which a dynamic bond forms and breaks based on the chemical environment around the bonds (i.e., the polymer backbone that the dynamic bond is integrated into).<sup>[110]</sup> Taking advantage of such prediction/modeling methods should ultimately be more time and cost efficient. It is clear that material scientists should seek to integrate concepts and methods from a wide range of disciplines, including, but not limited to, biology, organic and quantum chemistry, and chemical and mechanical engineering to intelligently create materials that both serve a purpose and self-heal.

## 8. Conclusions

In only 20 years, material scientists have gone from conceiving the notion of self-healing materials to generating self-healing materials

with improved mechanical properties that are capable of repeated healing cycles. Many of the most promising self-healing materials have been designed to emulate nature and thus it appears that it continues to be worthwhile to invest time into the development of biomimetic materials. In addition, it is clear that the optimal self-healing material design depends on the targeted application and, therefore, required material properties. However, in nearly all cases it would be ideal to employ a healing system that is cost efficient, ultimately capable of infinite healing cycles, and autonomously healing or healing in response to a trigger that is naturally present for the desired material application. In the end, the successful application of self-healing materials promises to improve our way of life and reduce expenses.

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