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An Overview of Self-Healable Polymers and Recent Advances in the Field

Nadim El Choufi, Samir Mustapha, Ali Tehrani B., and Brian P. Grady*

The search for materials with better performance, longer service life, lower environmental impact, and lower overall cost is at the forefront of polymer science and material engineering. This has led to the development of self-healing polymers with a range of healing mechanisms including capsular-based, vascular, and intrinsic self-healing polymers. The development of self-healable systems has been inspired by the healing of biological systems such as skin wound healing and broken bone reconstruction. The goal of using self-healing polymers in various applications is to extend the service life of polymers without the need for replacement or human intervention especially in restricted access areas such as underwater/underground piping where inspection, intervention, and maintenance are very difficult. Through an industrial and scholarly lens, this paper provides: a) an overview of self-healing polymers; b) classification of different self-healing polymers and polymer-based composites; c) mechanical, thermal, and electrical analysis characterization; d) applications in coating, composites, and electronics; e) modeling and simulation; and f) recent development in the past 20 years. This review highlights the importance of healable polymers for an economically and environmentally sustainable future, the most recent advances in the field, and current limitations in fabrication, manufacturing, and performance.

1. Introduction

The field of polymer science is under continuous development to produce functional polymers with better performance and improved environmental profiles and lower overall costs. Thermoplastic polymers possess many fascinating properties including low density, tactility, and easy processability, in comparison to other materials including metals. Due to such properties, polymers and polymer-based composites have increasingly replaced metal, wood, and ceramic in many applications in the industry.[1,2] Specifically, their resistance to natural degradation and the low manufacturing and transportation cost have made synthetic polymers one of the most versatile derivatives of fossil fuels. From baby feeding bottles to the body of Boeing 787, synthetic polymers are heavily integrated in our modes of living.[3,4]

The majority of synthetic polymers are discarded after reaching the end of their life cycle. Therefore, enhancing the sustainability of fossil fuel-based polymers is crucial and one strategy is to prolong the service life of these products by synthesizing polymers or polymeric systems that have longer service lives as shown schematically in **Figure 1**.[5–8] This development forgoes traditional recycling and reusing techniques for current polymers, and polymers of this type are termed self-healing polymers.

Polymers classified as self-healing can achieve a performance that partially or fully recovers the initial performance of the virgin polymer without the need for significant human intervention, such as manual repair or recovery. The self-healing mechanisms are triggered by damage which is restricted to local sites. Damage is defined by the decreased performance of the studied property in the local region in comparison to the global region.[9] The healing of the self-healing polymer-based systems is usually measured by the healing effi-

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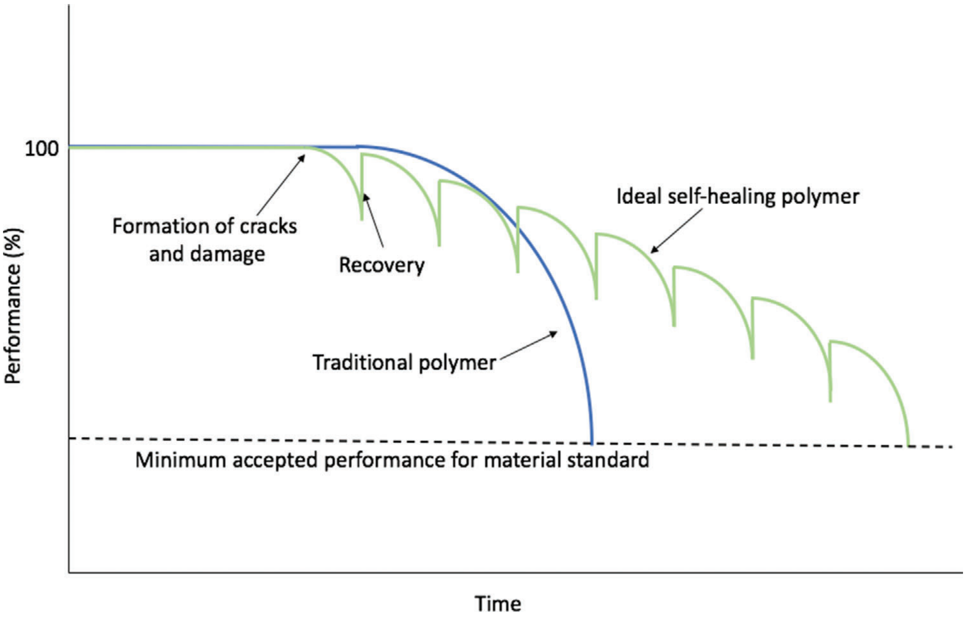

Figure 1. The performance of a traditional polymer versus the performance of self-healing material over time.

ciency which quantifies how much of the original mechanical, thermal, or electrical performance did the healed polymer retain (with a 100% healing efficiency stating that it has retained the performance of an undamaged polymer.)

This paper gives an overview of the advancements of self-healing polymers from the year 2000 until 2020 by presenting the classifications, self-healing mechanisms, methods of analysis, and scientific limitations and advantages of different self-healing mechanisms as well as the recent advances and applications of self-healing polymers. Healing is measured differently for different polymer-based systems as it is inextricably linked to the different envisioned applications for self-healing. These applications use mechanical, thermal, and electrical self-healing mechanisms separately or in combination. Based on such applications and recent advances, the review traces the expansion of what is defined as self-healing polymers based on their intended use.

1.1. History of Self-Healing Polymers

Material fatigue, weakening, and damage occur to all materials as they are subjected to stress and long-term use in most applications. Historical engineering techniques to prolong the service life of materials increased the material's strength, which often compromises the elasticity, flexibility, and functionality.[10–14] Examples are strength-ductility trade-offs in metals, and the logic of such material design do not overcome the central issue of the materials being susceptible to damage, where cracks and fractures eventually form and lead to global failure.[15] Alternatively, biological systems tackle damage and fatigue through self-repair rather than relying on an initially high material strength. Biomimicry of healing systems such as blood clotting, wound healing, and bone repair offer knowledge and application transfer to synthetic polymers.[16,17] As shown in **Figure 2**, self-healing polymers and self-healing polymer-based systems aim to heal through similar pathways as biological systems.

The first demonstration of self-healing in synthetic systems occurred in 1993 using a polymer composite embedded with a single hollow fiber filled with a healing agent.[18] When a microcrack occurs on the surface of the fiber and its corresponding polymer composite, the healing agent, which is a non-reacting adhesive or an air curing agent, leaks and closes the crack. Dry et al. expanded the work on hollow fibers to develop a three-part fiber system throughout the 1990s.[19–21] White et al., in 2001, developed a novel encapsulation approach that led to self-healing polymer-based systems and was highly investigated over the past 20 years as shown in **Figure 3**.[22,23] Instead of hollow fibers, the healing agents were embedded into microcapsules within the polymer composites allowing for many healing sites rather than the single hollow fiber. This method allowed the healing agent to be spread out in capsules that cover a larger surface area and are more accessible to different damage locations. The conceptual basis of both the microcapsules and the hollow fibers are derived from a simplified blood vessel network in hopes that future development can employ advanced biomimetic approaches of circulatory networks that allows the recovery damage and degradation of the material over time and prolong its service life.[16,17,24–27] Recovery has mainly focused on mechanical characteristics in scholarly investigation such as elasticity, hardness, tensile stress, and strength limit. Yet in recent years, the notion of self-healing polymers is expanding, and thermal and electrical conductivity recovery are being investigated and coupled with mechanical recovery.[28–31]

1.2. Impact of Self-Healing Polymers

The potential of self-healing polymers lies in increasing service life, their repeated use, decreasing the time and cost of

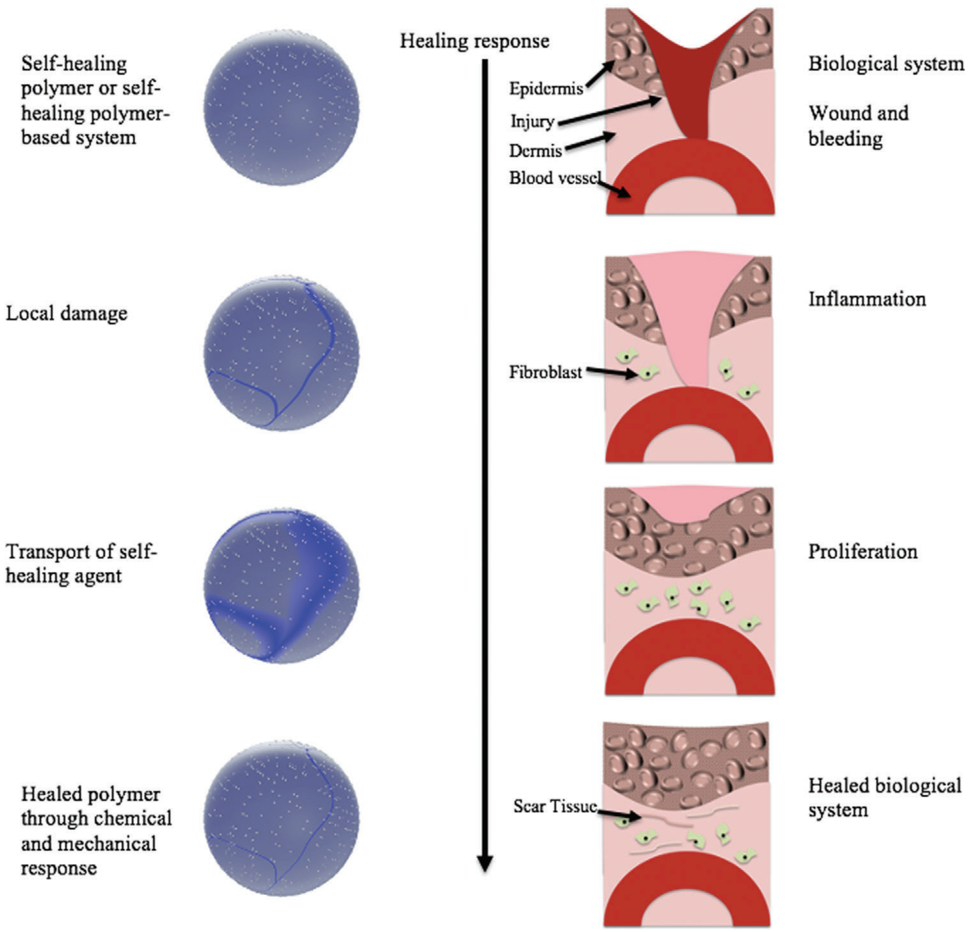

Figure 2. Healing response by self-healing polymers in comparison to self-healing found in biological systems.

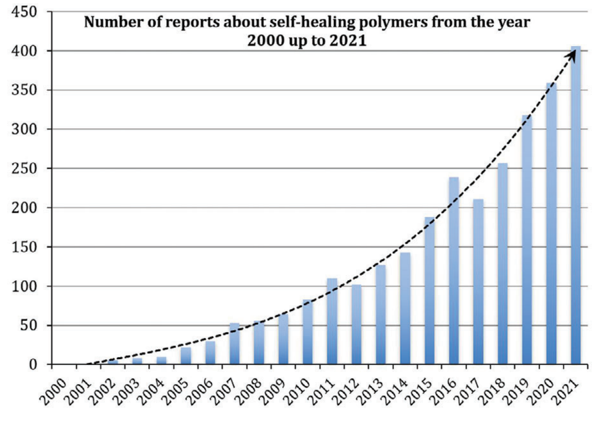

Figure 3. Number of articles indexed by Scopus whose titles, abstracts, or keywords include the following terms ("self-healing polymer") or ("self-healing coating") or ("healable polymer") or ("autonomic self-healing") or ("Self-healing composite") or ("self-healing" AND "ionomer") or ("self-healing" AND "microcapsule") or ("self-healing polymeric") or ("vascular self-healing") or ("self-healing" AND "polymer composite").

maintenance, increasing overall safety, as well as enabling the autonomous healing of parts in remote locations.[32] Furthermore, self-healing polymers can play a crucial role in lowering environmental pollution associated with the use of polymers, as the polymers can regain their functionality after being damaged instead of being replaced.[33] In a future dictated by global health and climate crises attributed to industrial production along with finite resources, self-healing polymers have a far-reaching scientific and social consequence on how we produce, use, and introduce synthetic polymers into our lives.

2. . Self-Healing Polymers: Classifications, Production, and Self-Healing Mechanisms

Self-healing polymers are classified into three main categories: capsular-based, vascular, and intrinsic.[34–36] This section provides an overview of the self-healing mechanisms within each classification and the polymers and healing agents that are incorporated to design self-healing polymers.

2.1. Capsular-Based Self-Healing Polymers

Capsular-based materials incorporate healing agents in microcapsules. Upon damage, the local microcapsules burst, and the

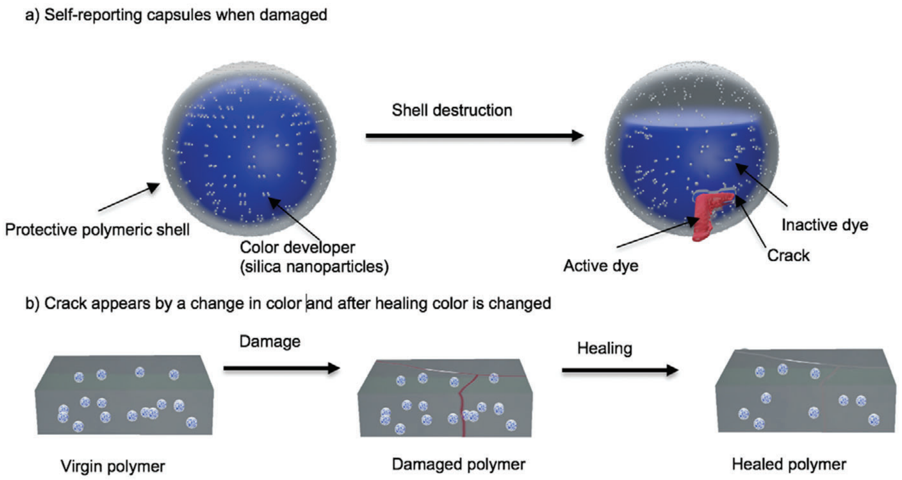

Figure 4. a) Scheme of damage self-reporting capsule through shell destruction and sequestering dye and b) indication of the healing scheme through color development.

healing agent flows out to react with a catalyst that is embedded in the polymer to fill and heal in the crack.[22,37,38] Capsules allow a self-healing polymer to initiate and perform self-repair autonomously since the capsules provide a dual function of storing the healing agent as well as attracting the crack to the capsule as the interfacial area between the capsule and the polymer will be a weak point in the polymer-based system.[22]

2.1.1. Capsular-Based Self-Healing Models

White et al. presented the first capsular-based self-healing polymer of dicyclopentadiene (DCPD) filled microcapsules in a urea-formaldehyde shell.[22] The composite matrix contained a Grubbs catalyst which polymerizes DCPD at room temperature into a tough cross-linked polymer network.[21] When a crack occurs at a locally damaged site, the DCPD leaks out and begins polymerization when it is in contact with the catalyst, eventually closing the crack surface. After the success of DCPD filled microcapsules, several other research groups followed the same approach.[39–43] The healing cycle of capsular-based self-healing polymers was observed by adding a colorant like crystal violet lactone (CVL) to the capsule to monitor the entire cycle as shown in **Figure 4**.[44] When damage occurs and the capsules break, initially colorless CVL comes in contact with silica particles on the outer region of the capsule and color emerges due to the reversible opening of the lactone rings through a reaction with silica. The colored damaged spots can be erased using different self-healing polymers that heal the polymer and also restores the dye to its original colorless property. Color changing allows the healing process to be monitored and the condition of the material over time can be assessed. As shown in Figure 4b) the reversibility of the dye from its inactive (not colored) form to active (colored) form is vital to track both the damage and the healing process; this is achieved by the dye interacting with the color developer when the capsule is broken and changing color while its color is deactivated by the healing process.

The following generations of the capsular-based polymer systems have been enhanced by different capsulation approaches. A dual capsular-based self-healing polymer with separate mercaptan and epoxy-loaded capsules was achieved.[39,45] The dual capsule system has become particularly useful for liquid–liquid self-healing mechanisms. Single capsule systems were compared to a dual liquid–liquid phase of the healing agent and the hardener where the latter facilitated an easier reaction at the crack surface and exhibited better healing efficiencies.[46] The self-healing material was affected by the quantity of microcapsule with a maximum tensile strength recovery obtained at 5 wt%.[46] Multilayered capsules have also been investigated for strengthening the wall thickness of the shell by synthesizing double-walled shells or to forgo the embedment process of the catalyst into the polymer and synthesizing one capsule that contains both the healing agent and its catalyst.[47–49]

McDonald et al. used, for the first time, time-lapse synchrotron X-ray phase-contrast computed tomography to study and monitor the capsule activation.[37] This measurement correlated the discharge amount of the capsules to two parameters: crack growth propagation process and the distance from the crack plane. Solid-state nuclear magnetic resonance (NMR) measurements directly correlated capsule size to healing efficiency and the reduction of mechanical properties after self-healing capsule incorporation.[50] Healing efficiency is directly proportional to capsule size with a 68% maximum load recovery while smaller capsules lead to a lower reduction in properties in the initial material versus the polymer with no capsules. While healing properties are enhanced by a larger capsule size, the capsule size was also shown to be inversely proportional with the reduction of mechanical performance in the virgin material. This result demonstrates that there is a clear optimal capsule size to attain both properties.

2.1.2. Microencapsulation Techniques

Encapsulation techniques are often used and extensively researched in the food and pharmaceutical fields. In the food sector, encapsulation plays an important role in containing and discharging flavors for longer sensory times.[51–53] In pharmaceuticals, encapsulation is used to sustain or control the delivery of a drug for a specific duration usually coinciding with the time required for the drug to reach the required site.[54] The two most common techniques for encapsulation are in situ polymerization and interfacial polymerization. The deciding factor to use one technique over the other is the stability and reactivity of the monomer in different phases, such as oil-based or water-based phases. Many unstable oligomers can only be encapsulated in situ and not through interfacial polymerization.

Interfacial polymerization uses two reactive monomers with opposite solvent polarity in immiscible phases (e.g., water and oil).[55] Through constant stirring, the oil phase is emulsified in the water phase (or vice-versa) and within the emulsification process, a polymer is formed at the droplet interface and encapsulates the active compound.[56] The solubility of the healing agent determines whether the droplets should be oil or water, and emulsifying agents as well as the oil–water ratio are used to force the appropriate drop to occur. Using interfacial encapsulation with Pickering emulsion templates, multilayer microcapsules were successfully synthesized.[57] Capsules made using Pickering emulsion templates has solid particles adsorbed at the liquid–liquid interface providing interfacial stabilization.[58] In this case, inexpensive, environmentally friendly lignin nanoparticles form the Pickering emulsion templates. The oil phase already contains the healing agent, and the hydroxyl of the lignin interacts with the isocyanate group at the interface of an emulsion droplet and forms a thin membrane followed by microencapsulation through interfacial encapsulation.[57]

In situ polymerization differs from interfacial polymerization encapsulation where encapsulation occurs in the continuous phase rather than at the interface.[59,60] Urea-formaldehyde shell, which has been extensively used in self-healable polymers, are produced in-situ where the oil-phase is emulsified in a premixed solution of urea, formaldehyde, and deionized water. Mixing occurs at high shear levels to create droplets and lowering pH causes polycondensation at the interface resulting in capsules at the required size.[41,48,59]

2.1.3. Advantages and Limitations of Capsular-Based Self-Healing Polymer

The main advantage of the capsular-based system is that capsules are easily integrated into polymers.[61] The current state of capsular-based self-healing polymers is promising, as it is the most used self-healing mechanism in engineering applications, particularly in coating applications, and can be industrially produced on a large scale.[62–64]

The major limitation of capsular-based self-healing polymers is one-time healing at the same local zone since the microcapsules cannot be refilled. Thus, capsular-based self-healing polymers have been mainly used as coatings, where the structural dependence of the product does not depend on the repetition of their healing ability due to the low probability of damage and scratches occurring on the same zone repeatedly. Other limitations are that the capsules can have a negative effect on the coatings' mechanical properties and that dual microcapsule systems can be ineffective if not properly mixed. The weight percent and volume of microcapsules play a critical role in the extent of healing, and there are size limitations for microencapsulation based on use temperature.[65,66]

Further studies focusing on fine-tuning parameters are needed such as the thickness of capsular walls, amount and kind of healing agent, the reactivity of the healing agent, and the size of the capsule. Problems that should be addressed are to inhibit undesirable release before the crack formation, and to increase service life.[67] Lastly, microcapsule synthesis through in situ polymerization or interfacial polymerization encapsulation relies on the use of synthetic and non-biodegradable polymers. In the long run, while current self-healing polymers prolong the service life, there is a demand to use biodegradable coatings and biodegradable encapsulation materials which have recently become an interest in scholarly research.[68]

2.2. Vascular Self-Healing Polymers

Using the design framework of vessels, vascular self-healing systems incorporate hollow microchannels filled with healing agents. The hollow microchannels can be fabricated to flow in one, two, or three axes respectively termed 1D, 2D, or 3D.[69,70] The interconnection depends on the fabrication and organization of the vessels within the composite matrix. They function similarly to capsular-based systems where the vessels break at locally damaged zones and the healing agent is carried into the crack or fracture and polymerized.[71]

2.2.1. . Techniques and Fabrication

Vascular structures that only orient in one straight direction are called 1D vascular systems. They are based on studies by Dry et al. who investigated the prefilled hollow glass tubes filled with healing agents.[19–21] When the hollow glass fibers are aligned parallel to the loading direction, tension and compression strengths are not changed, however, if they are placed perpendicularly the strength properties are reduced.[72]

While 1D vascular networks were foundational for the advancements of the field, they do not cover a large surface area of the polymer-based systems they are placed into, which led to the fabrication of 2D and 3D networks. In 2D networks, stacking occurs in unidirectional plies while the use of different technologies of sacrificial scaffolds is employed in 3D networks. Optimized 2D networks were tested for various channel ratios and diameters by mimicking tree structures such as blood vessels. This work has been influential, and a novel evolution parameter (*Ev*) was developed based on the constructal law of organization in vascular architecture to quantify the flow capacity of vascular structures.[73–76] *Ev* quantifies the flow capacity of vascular structures and is the ratio of the flow conductance in a structure with imperfections to the flow conductance in a structure with the least imperfection.[77] A higher *Ev* means the structure can enable flow circulation with less energy dissipation. Another fabrication method for 2D networks utilized composite sandwich structures in a two-part epoxy system. The vascular system of pre-mixed epoxy resin was embedded by placing polyvinyl chloride tubes in the mid-plane and smaller channels extending through the foam core.[78,79] This set-up was expanded by having a two-part vascular

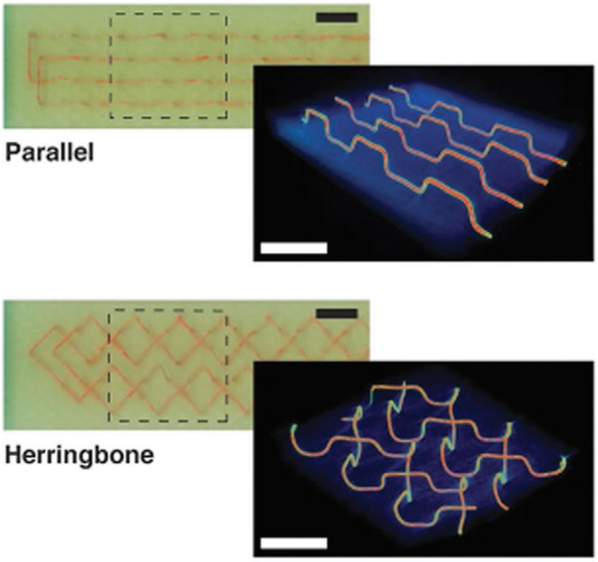

Figure 5. Two sacrificial PLA stitching patterns, the parallel architecture (above), and the herringbone architecture (below) in a thermoset epoxy matrix (scale bars = 10 mm). Reproducedwith permission.[81] Copyright 2014, Wiley-VCH GmbH.

system where the epoxy and the hardener are placed in two separate vascular systems allowing the shelf-life of the self-healing mechanism to match the shelf-life of the polymer-based system it is placed in.

For 3D networks, the most common yet diverse method of achieving complex networks is through the use of sacrificial scaffolds. The scaffolds are integrated into the composite matrix and then dissolved, manually removed, or heated until they are in a liquid state. The result is complex hollow networks based on the researchers' designs.[80] The melting point and viscosity of the scaffold material are vital parameters to study and ensure a successful hollow network as they can contribute to a partially closed network. The healing agents are then added to the hollow network. The traditional fugitive wax scaffolds in 3D neat polymers were advanced by stitching sacrificial poly(lactic acid) (PLA) monofilament in precise locations while testing two 3D architectural fabrications of "herringbone" and "parallel" as shown in **Figure 5**.[81,82] Diglycidyl ether of bisphenol A (DGEBA) based epoxy resin and aliphatic triethylenetetramine (TETA) based hardener placed in separate channels were selected as healing agents due to their low viscosity and ability to polymerize at room temperature. DGEBA and TETA possess low viscosity and hence minute pressure changes can begin polymerization at room temperature. For both architectures, there was no significant change in the fracture properties of the matrix. Yet the herringbone placement showed remarkable results that required a higher load to propagate the crack after each healing sequence reaching a healing efficiency over 100% by the healed specimen having a higher fracture toughness than the underlying matrix.

While PLA) is a good sacrificial material, typically removed by heating to 200 °C, such temperatures can also damage the composite matrix hosting the network, which has led researchers to extensively study other scaffold materials.[83,84] Fugitive organic ink developed through a direct-write assembly by Therriault et al. addressed these concerns as the fugitive scaffolds were removed by heating at 60 °C.[82] The direct-write assembly consists of three steps where the scaffold is fabricated using fugitive ink, followed by infiltrating the scaffold with epoxy resin and allowing it to cure. Next, the fugitive ink is extracted and replaced with a healing agent.[81,82] Besides, the assembly through robotic disposition granted them the ability to manufacture complex architecture where the vertical towers allow the 3D networks to be far more advantageous than simple 1D and 2D networks, yet the process is time-consuming. With the increase in connectivity, the technology also allowed precise control over the thickness of the channels, as they were able to produce the network in a range of 10–300 μm.

Besides 3D printing, melt-spinning and electrospinning have been utilized to generate fibers for a sacrificial scaffold. Bellan et al. used a sugar fiber that was placed in resin and the latter cured for 24 h.[85,86] The resulting composite matrix was placed in water and ethanol to dissolve the sugar and leave a hollow network. Similar conceptual plans are implemented with other materials such as pullulan that is a water-soluble polysaccharide and degrades at 250 °C.[87]

2.2.2. Limitations and Analysis of Vascular-Based Self-Healing Polymer

An advantage of vascular self-healing systems is that they can be refilled from an outside source.[88] However, refilling does require human involvement. In addition, fabrication and production have major challenges. Qamar et al. highlights six major challenges in vascular-based self-healing systems; structural integrity, network junctions, material properties, size limitation, and design accuracy.[89] In capsular-based and intrinsic self-healing material, structural integrity does not pose as much of a threat as in vascular self-healing composites because vascular networks occupy much more space and, in turn, compromise the integral structural properties to a larger degree. The fabrication techniques in vascular-based composites generate a hollow, liquid-filled, network which can lead to an inferior polymer structure. The self-healing polymer-based system cannot increase the original mechanical performance if comprised of a vascular network. Network junctions in vascular 3D networks play a major role in the self-healing capabilities of the material as they are regions where blocking and thinning of the network have a high risk of occurring during production.[90] The complexity of vascular self-healing systems is also linked directly to the software whose limitations in addressing complex geometries, substructures, and the ability to process multiple materials simultaneously (such as a three-part system of a healing agent, material needed for vascular network formation, and the matrix polymer) effect the advancement of vascular network building.

Currently, the production of vascular-based self-healing polymers is an expensive and unsustainable method for manufacturing and limits the scaling of network scaffolds for mass production.[91] While vascular-based self-healing polymers attempt to translate the promises found in the vascular systems of organisms, there are many challenges to overcome in the introduction of a complex vascular system without undermining the original properties of the material. To reach a stage of com-

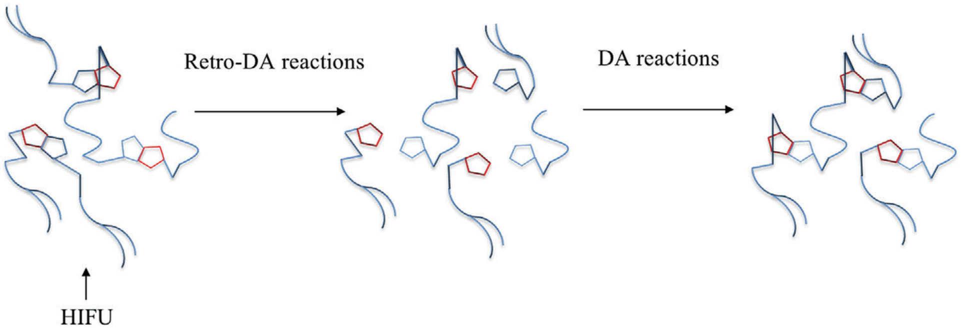

Figure 6. Schematic illustration of the concept for memory-assisted healing via ultrasound.[104]

mercial output for vascular-based self-healing polymers, network fabrication and optimization need to be adaptable to design requirements and higher or lower density vascular areas must be used based on the risk assessment of the global structure itself.

2.3. Intrinsic Self-Healing Polymers

Intrinsic self-healing materials do not require the addition of healing agents since healing occurs through their bond reversibility in the polymer.[92,93] The reversible nature differs between each material and the intrinsic self-healing mechanism has been classified into five different categories: reversible reactions, dispersed thermoplastic, ionomers, supramolecular material, and molecular diffusion.[34]

2.3.1. Intrinsic Self-Healing Mechanisms

Intrinsic self-healing mechanism can be stimulated in various ways including ultraviolet (UV) light, temperature, or static load followed by a process of restoration of the chemical or physical bond strength upon stimulus removal.[94]

Intrinsic Healing Based on Reversible Reactions: The reversible transformation from the monomeric state to the cross-linked polymer state through the addition of energy allows a self-healing mechanism to occur. The first developed polymer composite matrix in 2002 incorporated the Diels-Alder (DA) and retro-Diels-Alder (rDA) reactions and since then the thermally aided DA reaction has been one of the most extensively studied intrinsic self-healing systems.[95] Reversible reactions in self-healing polymers, including the DA reaction, occur through dynamic covalent bonds. Even after polymerization, dynamic covalent polymers can reform their chemical structure under certain stimuli. Such reversible reactions allow self-healing and often exhibit shape memory abilities as well.[96–99] The main advantage of this reversibility is the theoretically infinite cycles of healing sequences.[100–103] An advancement in this field was the presentation of novel polymers of poly(ϵ-caprolactone) (PCL) based polyurethane (PU) networks with DA bonds that exhibit shape memory and self-healing mechanisms in response to the ultrasound as shown in **Figure 6** using high intensity focused ultrasound (HIFU).[104]

Intrinsic Healing Based on Thermoplastic Dispersion: Thermoplastic inserted or integrated into thermoset can achieve a self-healing polymer as the thermoplastics can melt and disperse into the crack or fracture and connect the surrounding composite surfaces.[92] Thermoplastics in shapes such as fibers, particles, or spheres are used by heating to a temperature at or above the thermoplastic's melting point, then cooling of the material. These compositions can not only close macroscopic defects but also can do so repeatedly if another damage occurs in a previously healed area.[92] Hayes et al., have worked extensively on this topic and the selected thermoplastic poly(bisphenol-A-co-epichlorohydrin) in epoxy resin would regain 70% of its virgin properties.[105] This mechanism has extended beyond the thermoset with thermoplastic dispersion and has been used widely in other fields. Most recently it was incorporated in glass fiber reinforced polymer (FRP)-dispersed with magnetic polyamide-6 (PA-6) nanocomposite (PNC) that yielded 84% tensile recovery.[106] A polymer fabricated from Veriflex polystyrene with dispersed thermoplastic particles leads to healable repeatability of up to 5 cycles before becoming inefficient and a near-total recovery of 65% of the bending load.[107] Another study enhanced few-layered graphene (FG) with dispersed thermoplastic polyurethane (TPU).[108] Due to graphene's capacity to absorb Infrared radiation (IR) and electromagnetic waves, the FG-TPU self-healing material was able to heal repeatedly through IR light, electromagnetic waves, and electricity with healing efficiencies higher than 98%.[109–111]

Supramolecular Polymers: Supramolecular polymers differ from the traditional polymer typically connected by covalent bonds; in supramolecular polymers only reversible, noncovalent bonds connect monomeric units.[112–114] Interactions in supramolecular polymers include van der Waal forces, hydrogen bonding, π–π interaction, metal coordination, and host–guest interactions. These interactions allow supramolecular polymers to exhibit self-healing properties, leading to the advancement of supramolecular chemistry and its integration in nanocomposite materials.[115] The interplay between all the interactions and their strengths greatly influence the mechanical characteristics of the supramolecular polymers and in turn their efficiency at self-healing. The challenge in assessing how the individual strengths of each interaction factor into the overall mechanical properties is particularly challenging for solid state supramolecular polymers as arrangement, crystallization, and segregation also play a major role.[116] In the majority of cases, carboxyl groups on the polymer side chain play a very important role in forming supramolecular self-healing materials. Carboxylic groups can participate in hydrogen bonding, electrostatic interactions, and the formation of metal complexes and the hydroxyl and carbonyl groups form carboxyl cyclic dimers that act as both proton donors and acceptors simultaneously. This complexity is exemplified in the formation of a polyelectrolyte comprising polyacrylic acid (PAA) dual crosslinked by hydrogen bonds and vinyl hybrid silica nanoparticles (VSNP) resulting in high stretchability, self-healability, and ionic conductivity. The films showed nearly ≈100% efficiency in self-healing mechanical requirements during all 20 healing cycles.[117]

Intrinsic Healing by Molecular Diffusion: Intrinsic self-healing can also occur by molecular inter-diffusion leading to polymer–polymer chain entanglement at the crack surface. Dangling chains, mainly seen in weak gels, become the sites of entanglement as they are able to diffuse over longer distances compared to chains in permanent networks that do not allow macroscopic rearrangement.[118] The backbone of self-healing through interdiffusion is based on Prager et al.'s 1981 work that developed an analysis for the welding process, which occurs when two pieces of the same amorphous polymer are brought into contact at a temperature above the glass transition.[119] The junction surface gradually heals until, at very long contact times, it is indistinguishable from bulk polymer. While most thermoplastics show such behavior it is not considered efficient self-healing due to the long period and the need to reach the glass temperature phase. Yamaguchi et al. furthered this research by linking the healing efficiency through the interdiffusion of dangling chains to time and temperature.[120]

Intrinsic Ionomeric Healing: An ionomer is an ion-containing co-polymer with repeat units of both electrically neutral molecules and a fraction of ionized molecules.[121] The ionic groups are typically lower than 15% by mol. Ionomers are typically synthesized in a two-step process; first the non-ionic monomer is copolymerized with the acid-containing monomer. Second, metal salts are introduced, either in solution or added to a polymer melt, and ionic pairs form with the metal cations. The polar ionic pairs attract each other, and form aggregates rich in ionic material.[122,123] Due to this formation, ionomers acquire interesting structures and properties.

The effective crosslinks caused by aggregate formation lose attraction when heated and the chains can move, and self-heal cracks and local damage points as shown in **Figure 7**. At room temperature, ionomers behave similarly to elastomers while at elevated temperatures, ionomers are able to flow thereby behaving as thermoplastics.

Poly(ethylene methacrylic acid) (EMAA) neutralized with various cations was tested as an intrinsic self-healing polymer by conducting multiple types of damages including sawing, cutting, and puncturing.[124,125] For various film thicknesses, cutting by a razor blade and puncturing by a nail driven through the films yielded no observable healing. However, sawing generated a sizeable amount of heat and following cutting, the two halves self-bonded to each other. In addition, successful healing exhibited during projectile testing proved that the healing mechanism has a positive correlation with heat. The proposed self-healing mechanism of ionomers subjected to projectile testing relies on the pellet heating the specimen during puncturing. The increase in temperatures allows a reordering of ionic clusters and their potential rearrangement which can seal the damaged site.[125] While ionomers have been studied as self-healing polymers, they have also been incorporated with non-healing polymers into polymer blends and polymer composites to create new polymer-based systems with the ability to self-heal.[126,127]

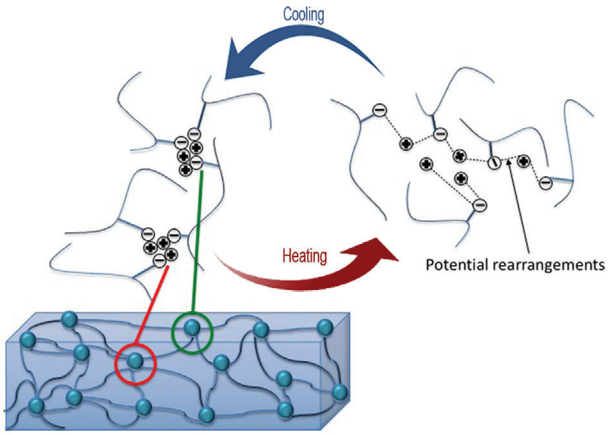

Figure 7. On the right-hand side, the aggregate is shown with the ionic pairs in the center and non-polar chains moving outwards. The healing cycle is correlated to a heating/cooling cycle, as a crack occurs the heat increases and a new ordering of the aggregate occurs as the chains have a greater ability to move, eventually healing the crack as it cools downs, and the aggregates reassemble.

2.3.2. *Limitations and Analysis of Intrinsic Self-Healing Polymers*

Intrinsic polymers are conceptually promising as they can theoretically heal for an infinite amount of time. However, these materials need a stimulus to self-heal, for example, heat or radiation, and depend on good contact between the damaged surfaces to facilitate self-healing cycles. Such limitations are easy to overcome in a laboratory environment, however, they pose a major threat to the stated efficiencies if in a remote inaccessible area.

Moreover, the majority of intrinsic self-healing polymers from elastomers to supramolecular polymers are designed to self-heal yet not to be tough, while both characteristics are simultaneously desired.[128] Furthermore, the kinetics of the reversible reactions cause a slow healing rate.[88] Chain stiffness and crosslink functionality can lead to either brittle polymers with high chemical resistance or highly elastic polymers with low chemical resistance. The polymer architecture can present a possible solution where the architecture effects the chain stiffness and the crosslink functionality to attain a polymer with desired features.[94]

3. Modeling and Simulation of Self-Healable Polymers

Modeling and simulation are vital to understand the dynamic response to damage at the local interface of cracks, microcapsules, and vascular self-healing polymers to optimize the design and synthesis of self-healing polymers.[129–131] Yet simulation poses the challenge of capturing sufficient and accurate dynamic details while being computationally feasible, which is complicated by the multiphase (liquid and solid) and multicomponent (polymer and capsules/vessels) characteristics of self-healing polymers.[129]

Diffusion models and simulations are used to describe the release profile of a healing agent for microcapsules assuming

Fickian diffusion and Brownian motion.[132,133] Simulation using molecular dynamics (MD) was used to both confirm experimental results and study dynamic properties in experimental procedures. Hydrogen bonds, common in self-healing polymers and composites, are known to affect self-healing efficiency. Yet the type, strength, and exchange of hydrogen bonding are difficult to observe experimentally, and MD offers an excellent alternative. In separate studies on urea-formaldehyde polymers and polyurethane, an increase in temperature results in a decrease in O–O pairs attributed to hydrogen bonding and an increase in van der Waals forces, leading to lower self-healing efficiencies at higher temperatures.[134–136] The crosslinking between hydrogen bonds and van der Waal forces is the driving force behind the self-healing mechanisms yet MD also confirmed that an increase in cross-linking density results in a decrease of density in hydrogen bonding also leading to lower self-healing efficiencies.[135]

MD simulation was also used to simulate the healing ability of free ethylene dimethacrylate (EGDMA) molecules in a polyurethane network. Experiments and computational simulations were in good agreement and in fact, simulation results showed the healing ability is significantly dependent on the amount of EGDMA present in the network.[137] A dissipative particle dynamics (DPD) model examined dangling chains in a self-healing composite system. The simulations not only matched the experimental results but also provided the optimal conditions such as the thickness of films for the fastest self-healing recovery.[138]

Simulation of cracks, fractures, and the subsequent self-healing is most often achieved through the continuum damage mechanics (CDM).[133,139–141] Numerical analysis along with CDM, which cannot model stiffness of the healing agent, was used to find that the healing agent's stiffness in microcapsules plays a crucial role in self-healing efficiencies of self-healing polymers and composites.[142] More recently, a cohesive zone approach developed to model fracture was extended to self-healable polymers. The latter differs from CDM theory, as the cohesive zone approach views cracks as discrete events and can simulate multiple recoveries for repeated healing cycles.[133,143]

Computational simulations and models for self-healing polymers have not reached the same potential as their experimental counterparts, yet they provide a valuable resource for optimizing the material and reducing material cost. However, the accuracy of simulations is dependent on accurately modeling and articulating the evolution of damage and healing in self-healing polymers. To move forward, computational simulations must form a symbiotic relationship with their experimental counterparts, that is, both frameworks can be refined based on results from one another.[144]

4. Methods of Analysis and Characterization

The purpose of self-healing polymers is to extend the service life of a material while maintaining or enhancing functionality. However, inserting extrinsic (capsular and vascular self-healing mechanisms) into composite matrixes will surely alter its properties. Understanding such changes are vital to ensure the self-healing material performs equally or better than the virgin material. This section is an overview of the range of standard methods used for assessing the healability of polymers. We briefly explain the most common methods used in the literature as well as the common parameters tested to determine correlative relationships between the healability of the polymers to external environmental factors.

4.1. Defining Healing and Healing Efficiency

The healing of polymers has been defined and affirmed using several qualitative and quantitative procedures where the latter does not only verify the healing but also compares the properties of the healed specimen to that of the bulk. Healing is qualitatively confirmed by visual observation or pressure leakage tests, where a sustained pressure via a vacuum pump or nitrogen gas that shows no pressure leak or vacuum decay across a punctured site is considered a healed sample.[124,125,145] Quantitative procedures typically measure the increase or decrease of the functional properties of a healed sample using the healing efficiency obtained in the following Equations (1)–(3).[88]

$$\eta_{\text{eff}} = \frac{f^{\text{healed}} - f^{\text{damage}}}{f^{\text{virgin}} - f^{\text{damage}}} \times 100 \tag{1}$$

where f is the property of interest (e.g., tensile strength). Other variations of this definition have been used as shown in Equations (2) and (3).[13,104,146]

$$\eta_{\text{eff}} = \frac{f^{\text{virgin}} - f^{\text{healed}}}{f^{\text{virgin}}} \times 100 \tag{2}$$

$$\eta_{\text{eff}} = \frac{f^{\text{healed}}}{f^{\text{virgin}}} \times 100 \tag{3}$$

The use of different equations is specific to the damage and healing that is being evaluated. For repeating heating cycles on the same specimen Equation (3) is used, while Equations (1) and (2) are used to investigate the fatigue damage or single healing cycles.[13,104] In some cases, it is also challenging to measure the extent of damage on a property in Equation (1). The lack of standardization in defining damage and healing performances means studies in this field can have different healing measurements, which can cause discrepancies and inaccuracies within comparisons of different self-healing polymers.

4.2. . Qualitative Visualization

Optical microscopy (OM) uses a lens system coupled with light to magnify samples. OM can be used to qualitatively assess and obtain visual results of healing methods in self-healing polymers. OM is widely used to confirm the self-healability of ionic polymers, DA reaction-based polymers, hydrogels, and supramolecular networks.[147–150] OM can be used to observe the distribution of vessels or capsules, breakings of healing agent vessels, and the release of the healing agent, but cannot provide information on molecular healing mechanisms as they occur on lengths scales lower than that OM can attain.[151–153]

Scanning electron microscopy (SEM), allows the observation of microdefects not visible in OM .[154–156] Analysis of micro-

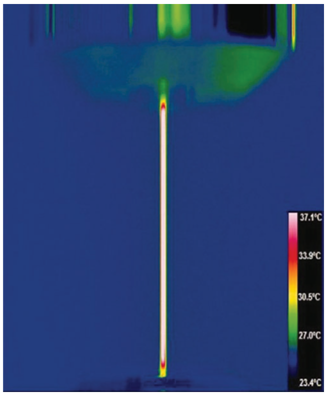

Figure 8. Camera captured an unexpected uniform increase in the specimen's temperature during tensile tests at a constant temperature. Reproduced with permission.[145] Copyright 2013, Wiley-VCH GmbH.

graphs from both OM and SEM does not follow a certain standard but the visual reference of successful or failed healing offers insight into mechanisms of healing that aid quantitative tests.

4.3. Mechanical Analysis

4.3.1. Static Recovery

Tensile testing applies a constant draw rate to a sample and measures the force until the breaking point.[157] A constant strain rate (exponential increase in draw rate) can also be used. Young's modulus, instantaneous Young's modulus (the derivative of the curve at strain = 0 or some arbitrary small strain respectively), yield strength, ultimate tensile strength, and percent elongation at break are some of the important parameters from this measurement.[150,158–] ASTM D638, ASTM D3039, and ISO 570 are typically used for polymers.[162–164]

Usually, tensile testing is employed to compare samples before and after the healing process or to compare healed samples with samples that have not yet been damaged. Through such a comparison, an analysis of the healing efficiency of the self-healing mechanism can be obtained. Also, tensile testing can also be used to measure the effect of adding a capsular-based or vascular self-healing system to a polymer versus the virgin material.

For example, an increase in curing temperature increases the elastic modulus and causes the healing efficiency to drop slightly in 1st generation epoxy-resins/ethylidene-norbornene/Hoveyda–Grubbs self-healing polymer.[159] For the intrinsic self-healable polymer, EMAA, tensile tests were performed at different temperatures and strain rates. At −40 °C the fracture behavior changes and causes a sudden break while at 60 °C, the opposite occurs, and whitening of the specimen appears due to strain-induced crystallization. As the temperature increases between −40 and 60 °C, the stiffness of the polymer decreases. Using an infrared camera while tensile testing the same EMAA specimens at a constant atmospheric temperature and different strain rates, the samples showed a uniform increase in temperature along its length as shown in **Figure 8**. For the fastest strain rate, the temperature difference between the sample and atmospheric temperature was as high as 9 °C. The unexpected increase in temperature confirmed that EMAA's self-healing mechanism, that was observed in projectile tests, is dependent on both a thermal response and a mechanical response.[145]

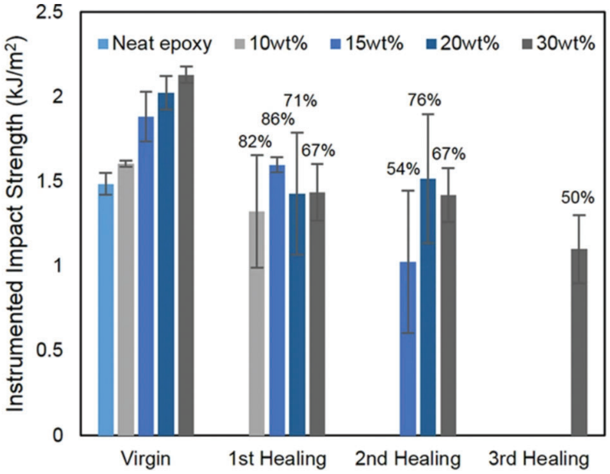

Figure 9. Healability of an epoxy matrix with embedded alginate microcapsules containing epoxy resin at different initial capsule loading (%). Reproduced under the terms of the Creative Commons CC-BY license.[167] Copyright 2016, The Authors, published by Springer Nature.

4.3.2. Impact Tests

Impact testing allows the study of the polymer's response to sudden deformation and high strain rates. The most common methods use Izod and Charpy pendulum impact tests or modified versions of these methods.[165–167] Both tests provide the energy absorbed by the specimen during fracture and typically these tests use a standard for the specimen which is either ASTM A370 or D256.[13,157]

The use of impact tests for self-healing polymers is crucial where damage occurs mostly during collision impact. Typically, specimens of self-healing polymers and polymer-based systems undergo impact tests, then the material is allowed to heal after which the sample undergoes the impact test again. A typical use of the Charpy impact test is seen in **Figure 9** which shows the healing efficiency of a microcapsuled epoxy resin self-healing polymer-based system at different initial capsule loading.[167] The impact strength increases gradually as capsule loading increases due to the toughening mechanisms such as crack pinning when capsules are introduced. Factors that should be taken into consideration when conducting impact testing are the temperature effect of material toughness and stress concentrators that could be formed by incorporating capsular and vascular healing into polymer-based systems.

Two types of specimens, the Charpy impact specimen and the tapered double cantilever beam (TDCB) specimen underwent the Charpy impact test to evaluate the effect of the damage caused on self-healing properties.[167] For the TDCB specimen, the epoxy film covered the fracture plane blocking the reserve of healing agents from the microcapsules and limiting the healing repeatability to only one cycle. Using the Charpy impact specimen, the specimen was able to reach up to three healing cycles in the Charpy test. These results indicate that the decision about what

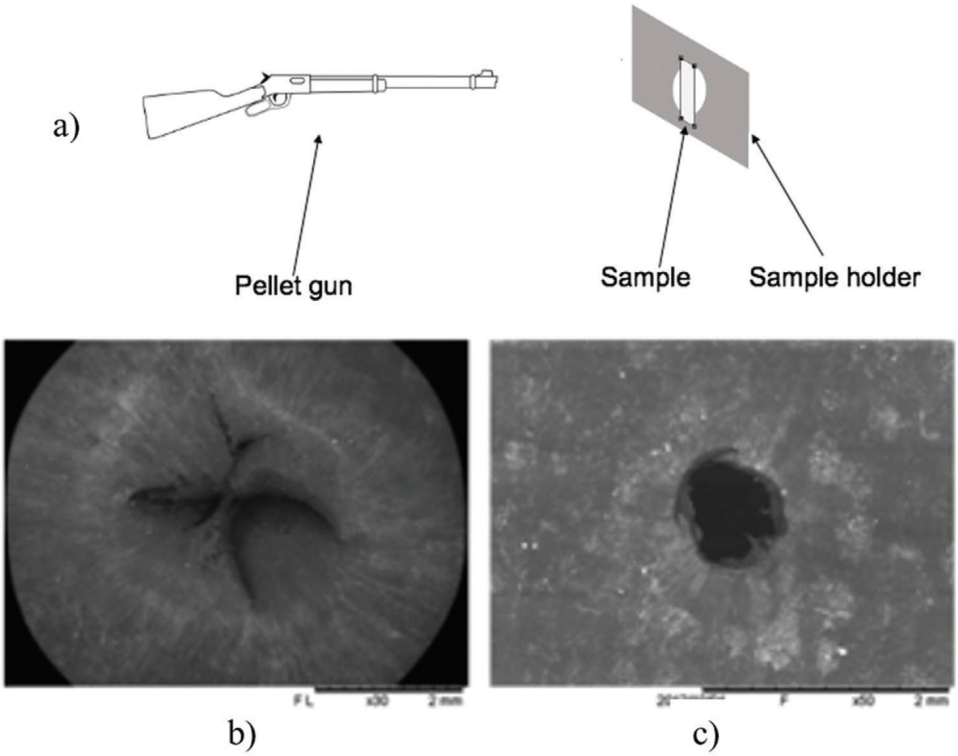

Figure 10. a) A schematic of projectile testing, b) SEM image of a healed damage site, and c) SEM image of unhealed damage site at low-velocity projectile. The petal formation is characteristic of impact/projectile testing. Reproduced with permission.[145] Copyright 2013, Wiley-VCH GmbH.

test to use should be based on the future use of the material, for example, material investigated for aerospace use will be subjected to impact damage more so than other forms of failure. This is a particular concern for composite materials that show sufficient resistance when load occurs in the fiber direction but display low resistance to impact loading in the transverse direction, which is why low-velocity weight impact tests are used.

Another impact testing method is the projectile test, shown in **Figure 10**a that is used to investigate ballistic or hypervelocity damage. Projectile testing, sometimes called ballistic testing, includes a gun, the self-healing specimen itself, and the specimen holder. To vary temperature, the specimen held within the specimen holder is placed in an oven.[124] There are no set standards for projectile testing although the bullet velocity, bullet diameter, gun model, sample polymer, and polymer thickness should be always stated.[124,145] After launching the projectile, various tests such as OM and qualitative tests are used to determine if the specimen healing by observing if the bullet hole has been fully closed.

The projectile test was used to successfully postulate a two-step healing process with the first step being an elastic response followed by a second viscous response for EMAA.[124,125] Over a range of temperatures, self-healing was confirmed from −10 to +60 °C. The study of EMAA under projectile testing was furthered by developing a ratio of film thickness to a bullet diameter, which acted as a cut-off ratio under which self-healing occurs. For low velocity and midrange velocity, the ratio was 0.2 and 0.33, respectively, while for hypervelocity a ratio was not determined due to limited diameter ranges.[145] Such results demonstrate that the size of the impact object in relation to the thickness of the self-healing sample is a vital parameter for successful healing results. In the same study, petal formation of healing was visible as shown in Figure 10b which confirmed the two-step process as the petals stretch on impact and their heated surfaces allow a viscous response that enables healing and the closing of the penetrated area.[145]

4.4. Electrical Healing Analysis

For electrical self-healing, the functional property under study is the conductivity of the polymer-based system. Similar to mechanical testing and evaluations of mechanical healing, electrical functionalities tested before and after damage for self-healing specimens do not have a standardized method of testing rather testing is study specific.

A self-healing electrode was developed using liquid crystal graphene oxide and silver nanowires printed on a poly(ethylene terephthalate) film.[168] The electrode was completely cut into two parts using a blade and then the two surfaces were brought together to heal. After healing, voltage-current curves were obtained with an 89% electrical healing in relation to the results obtained before the damage. In a similar manner, plots of the direct-current electrical resistance of a dielectric self-healing polymer were used to show the healing of dielectric degradation as manifested by repair of electrical treeing. A comparable value of resistance before treeing and after healing is a strong indication of successful healing.[169]

4.5. Thermal Characterization

Differential scanning calorimetry (DSC) is used to examine the thermal transitions of the polymer relevant for self-healing polymers, specifically the glass and melting temperatures.[170] DSC measures the amount of energy needed to change the temperature of a sample as a function of temperatures. For example, an endothermic peak will be shown if melting occurs because energy is required to melt a sample.

DSC is used to analyze self-healing polymers when the healing mechanism is linked to a temperature change that occurs within the polymer during or after the damage occurs.[171] Thermogravimetric analysis (TGA) can be done in conjunction with the DSC to measure mass changes as well. DSC tests, especially with thermogravimetric analysis (TGA), can show the thermal degradation of polymers which can stipulate the cycles of healing that can occur successfully for one polymer before reaching a failure to heal.

DSC was used to exhibit the repeatability of self-healing in EMAA by showing consistency of the melting point and the crystallization temperature after six cycles.[146] DSC tests showed that secondary crystallization was quenched after the first heating cycle reflecting a slow reformation of physical crosslinks compared to the rapid solidification.[146] For an intrinsic self-healing polymer, EMAA, that can theoretically heal for infinite cycles, the information from the DSC tests holds valuable information about the feasibility of self-healing polymers in real-life applications. In another study, the self-healing mechanisms of hydrogels of poly(2-hydroxyethyl methacrylate) were studied at different temperatures using multiple DSC analyses, which confirmed a minimum healing temperature of 48.5 °C due to chain slippage molecular diffusion.[172]

4.6. Spectroscopy

IR, near-infrared radiation (NIR), and NMR spectroscopy are used extensively for both extrinsic and intrinsic self-healing materials, yet they have an added value for intrinsic materials as the reversible nature of their bonds at the molecular level give the material its self-healing properties.[173]

4.6.1. Raman Spectroscopy, Fourier Transform, Infrared Radiation, and Near-Infrared Radiation

Both Raman and IR spectroscopy characterize the chemical and structural information as well as the chemical reactions in self-healing polymers in non-destructive manners without disturbing the healing process.[174] Raman spectroscopy records the emission intensity versus change in wavelength while IR measures light absorption by vibrating bonds as a function of wavelength. These techniques are especially useful in self-healing polymer-based systems where a reaction occurs because spectroscopy results quantitatively show the molecules that are present and analysis of such results and how much reactants have been converted can lead to presenting a degree of healing.

Using Raman spectroscopy over a period of time, an instantaneous record of the curing reaction of micro-capsuled epoxy and its hardener or in vascular based polymeric systems mercaptan can be obtained. For example, in one study 50% of the epoxide groups were consumed within 30 min showing that the majority of the self-healing mechanism occurs right after the damage occurs.[39] Similarly using IR spectroscopy, the progress of the self-healing mechanism was determined by following the disappearance of the epoxide group peak the curing of epoxy and boron trifluoride etherate loaded microcapsules.[175] IR spectroscopy has also been used to monitor the progress of self-healing mechanisms both in intrinsic and extrinsic materials.[156,166,167] Raman and IR spectroscopy coupled with DSC was used to show, for the first time, the dynamic character of the urea bonds in the solid-state of the intrinsic self-healing polyurea. IR spectroscopy at different temperatures proved the reversibility of the urea bonds in this polymer and correlated the opening of the bonds with the self-healing mechanism.[176]

Two-dimensional Fourier transform infrared radiation (FTIR) provides information beyond the traditional linear IR spectroscopy by providing a frequency correlation over two axes and information on a bands' relative intensity changes.[177,178] As shown in **Figure 11**, 2D FTIR results track the healing mechanism for a polyurethane where H-bonding urethane amide I, II, and III bands display positive peaks while free urethane amide I, II, and III display negative peaks. 2D FTIR showed that no covalent bond reformation and/or cleavage occurs after healing. However, when damage occurs reversible configuration changes from chain deformation do occur as bands associated with free urethane are larger than that of hydrogen bonding while bands associated with hydrogen bonding are larger during repair.[177] This result leads to postulate a two-step self-healing mechanism where in the first step a viscoplastic response is generated followed by a surface tension force that reduces surface areas by shallowing the crack until the crack heals.

4.6.2. Nuclear Magnetic Response Spectroscopy

While IR and Raman spectroscopy are used to identify the functional group and chemical reactions of healing agents, solid-state NMR allows the examination of chemical structures. These techniques are often used in a complementary manner to validate the findings in each technique.[179] NMR aligns the magnetic nuclear spins of the specimen and after reaching equilibrium disrupts the alignment with a weak radiofrequency pulse. The disruption causes the nuclei to return their excess energy and return to low energy levels, the detection of the resulting electromagnetic waves emitted, and their analysis constitute the results obtained from NMR.[180]

NMR is used to identify the formation of the expected healed structure such as cross-linked polymers, to demonstrate polymerization of a released healing agent, and to display the molecular changes that are occurring in intrinsic self-healing polymers. Using NMR and solid-state NMR, a UV curable poly(methacrylate) contain DA crosslinks were characterized and indicated that unwanted irreversible reactions where prevented through the DA adduct.[181] NMR was used to monitor DA conversion as a method to monitor the healing process. Furthermore, multiple NMRs including concentration-dependent ^{1}H NMR and diffusion-ordered ^{1}H NMR spectroscopy were used to assign and correlate protons on the metallacycle as they present a method

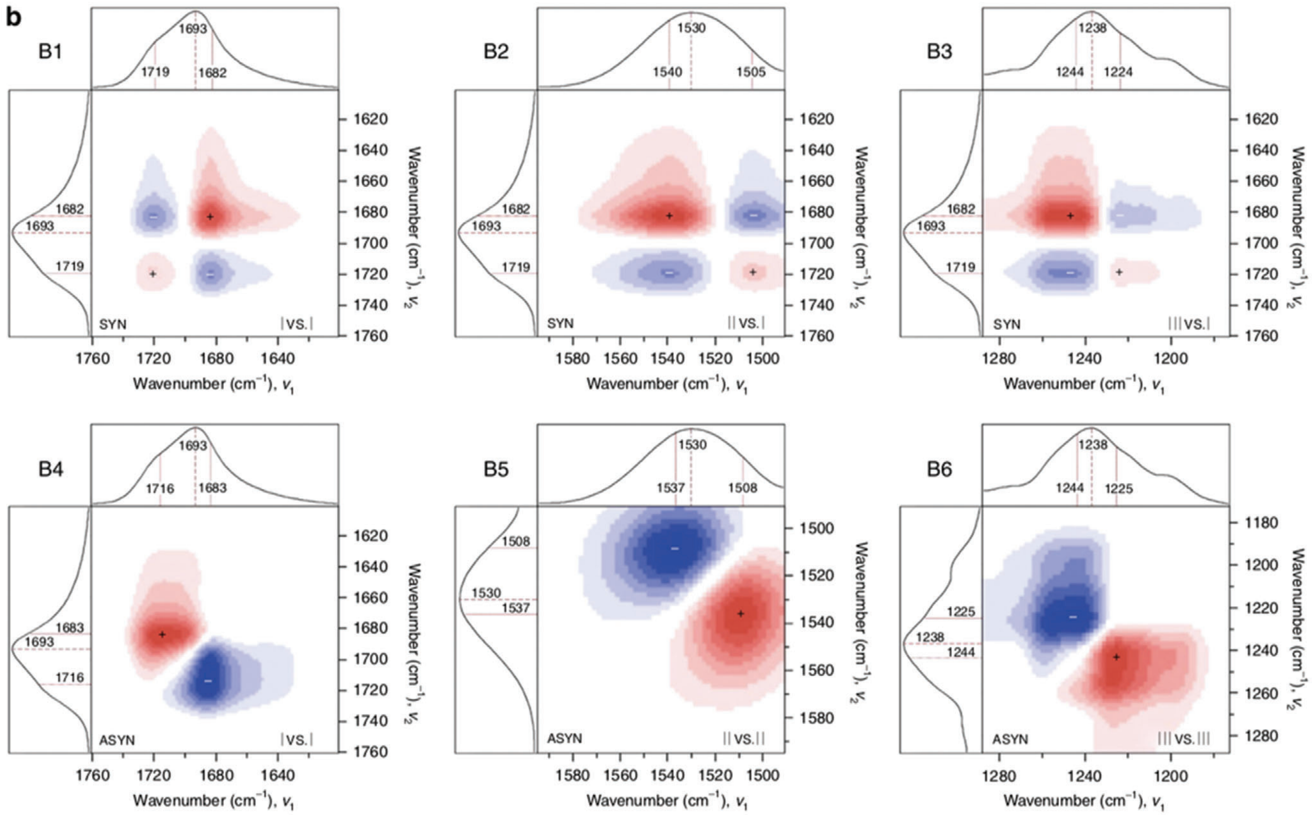

Figure 11. FTIR of damaged to a healed state, red are positive peaks and blue are negative peaks. Reproduced under the terms of the Creative Commons CC-BY license.[177] Copyright 2020, the Authors, published by Springer Nature.

Table 1. Current tests being used to study and characterize self-healing polymers.

Test	Result
Optical microscopy	Visual characterization of damage and healing
Tensile test	Measure the mechanical properties of the samples before and after healing
Impact test	Characterize the behavior of polymers subjected to impact loading before and after healing
Resistance analysis, conductivity analysis, current analysis	Measure the electrical conductivity of the systems before and after healing
Differential scanning calorimetry	Measure the thermal behavior of the samples and their glass transition temperature and melting point
Infrared radiation Fourier transform Raman spectroscopy	Characterize chemical reactions in the self-healing mechanisms, monitor the progress of self-healing mechanisms
Nuclear magnetic response spectroscopy	Examine chemical structures during the self-healing mechanism, monitor the progress of the self-healing process

for the building of new bicyclic heterometallic cross-linked self-healing supramolecular polymers.[182]

4.7. Analysis and Summary of Tests

Various analytical methods can be used for the characterization of self-healing polymers. Some of the most important test methods along with their possible results are summarized in **Table 1**.

While the capabilities of self-healing polymers have advanced greatly, the methods of analysis have yet to be standardized. Standardization will allow comparative analysis which will further the end goal of self-healing polymers entering the market. Such a step can facilitate not only the promise of self-healing polymers as a solution for current economic and environmental issues but allow the fabrication and implementation of self-healing polymers on a much larger scale.

5. Applications

Self-healing polymers are attractive candidates to be used in several applications with a high risk of material damage, especially under extreme working conditions, to prolong the service life of the material without human intervention. Using self-healing materials can postpone the recycling, re-manufacturing, and reinstalling of parts. Therefore, the aerospace industry was an early proponent and supporter of self-healing polymer research.[91,183–185] The advancement in the field of self-healable polymers has expanded to structural materials,[186,187] biomedical engineering,[188,189] coatings,[190] automotive systems,[191] and military infrastructure.[192] As shown in **Figure 12**, three different applications: coatings, self-healing electronics, and self-healing insulation and building material, demonstrate the far reach of self-healing polymers in multiple fields. The current self-healable polymers available on the market are primarily used as coatings as shown in **Table 2**.

5.1. Self-Healing Composites

Self-healing polymer composites have been extensively explored for aerospace and underwater applications; materials used in these applications are not easily accessible for repairs. Researchers at NASA published separate work in 2003 on the self-healing properties of EMAA polymers specifically for impact damage caused by ballistic or penetrative forces as they are analogous to the collision nature of small space debris on the surface of shuttles, satellites, and orbiting technologies as shown in Figure 12b.[183,199]

FRPs have been investigated in several different applications due to their orientation which can provide an increase in strength and resistance to structural deformation. Thus the orientation depends on the context in which it is used to provide the right balance of strength and elasticity. Building on their wide use in industry, self-healing carbon FRPs are currently being researched through the introduction of both microcapsule and vascular self-healing methodologies.[91,200–202] FRP composites are also used in research for potential use in offshore applications due to their low density, standard processability, and resistance to high salt environments.[88] A self-healing FRP system with glass FRP composite and self-healing alternating layers of glass FRP and PNC film was proposed specifically for offshore structures that could be integrated with sensing and operated remotely.[106] Marine and offshore applications have been adapted from earlier self-healing polymer composites made for aerial vehicles as self-healing polymers research tends to be application-specific.[203] While the self-healing glass FRP and PNC composite are appropriate for offshore spoolable pipes and pressure vessels, other self-healing composites were developed for marine vehicles such as boats and kayaks that simultaneously retain shape memory.[78,204]

Besides structural applications, self-healing polymer composites have been used in the biomedical field, where repeated external intervention is costly and can put the patient at risk. Self-healing dental composites are one example and aim to improve the service life of resin-based dental restoration that are applicable in onlays, cements for tooth prostheses, orthodontic devices, inlays, cores, and root canal posts.[205] Its commercial use depends on its success in clinical testing, bio-applicable materials, and the availability of appropriate materials. Using different materials yet for the same purpose of achieving self-healing dental composites, Huyang et al. developed while Yahyazadehfar et al. tested the durability of a composite that combines clinically acceptable glass ionomer cement with two self-healing materials; strontium fluoroaluminosilicate particles and microencapsulated solutions of PAAs.[206,207]

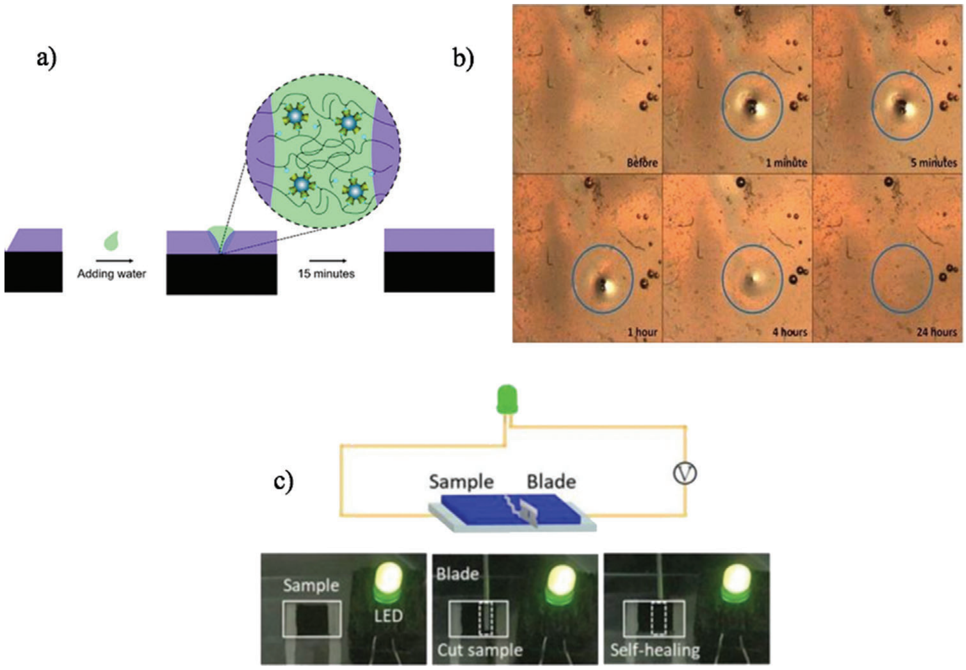

Figure 12. a) A self-healing coating with hydrophobicity and UV-shielding. Reproduced under the terms of the Creative Commons CC-BY license.[193] Copyright 2020, the Authors, published by MDPI. b) Self-healing low melt polyamide from the Kennedy Space Station to be used in wire insulation, inflatable structure inner linings, and spacesuits. Reproduced (Adapted) with permission.[194] Copyright 2020, NASA. c) Demonstration of a cutting and healing process for a composite film connected in a circuit with a LED lamp operated with a constant voltage of 3 V. Reproduced with permission.[195] Copyright 2019, Wiley-VCH GmbH.

Table 2. Current self-healing polymers and manufacturers.

Use	Mechanism	Manufacturer	Tradename	Reference
Coating	Intrinsic thermoplastic dispersion in thermoset	NEI Corporations	Nanomyte Mend 1000 Nanomyte Mend 2000Nanomyte Mend 3000	[196]
Coating with UV protection	Intrinsic thermoplastic dispersion in thermoset		Nanomyte Mend 1000 UVP Nanomyte Mend 2000 UVPNanomyte Mend 3000 UVP	[196]
Coating	Dual capsule self-healing polymer	Autonomic Materials	AmpArmor 1000 series	[64]
	Single capsule self-healing polymer		AmpArmor 2000 series	[63]
	Single capsule self-healing polymer		AmpArmor 3000 series	[62]
Adhesives, coatings, and elastomeric materials	Supramolecular self-healing polymer	SupraPolix	SupraB	[114, 198]
Coating		Nippon Paint Automotive System	CyGLAZ	[198]

5.2. Self-Healing Coatings

Organic and inorganic coatings are used to enhance performance and create a barrier in addition to their cosmetic function.[208] The most studied performance parameters of coatings are corrosion and wear resistance, however recent studies have expanded the functionality of coating to study bio-inhibition, thermal resistance, and radar absorption.[209] Coats are applied in thin layers to increase service life and decrease the risk of failure. The global cost of coating is valued at more than \$2.5 trillion per year. Self-healing coatings have been subject to international interest due to their added benefits.[210] Currently, self-healing coatings can be compartmentalized into two primary groups, one whose healing function is to heal themselves and the other is to protect the structure they are coating. In the latter, self-healing coatings were developed to respond directly to corrosion by containing triggered species generated by corrosion while the former focuses on increasing the service life of the coating itself which will increase the overall performance of the coated product.[211,212]

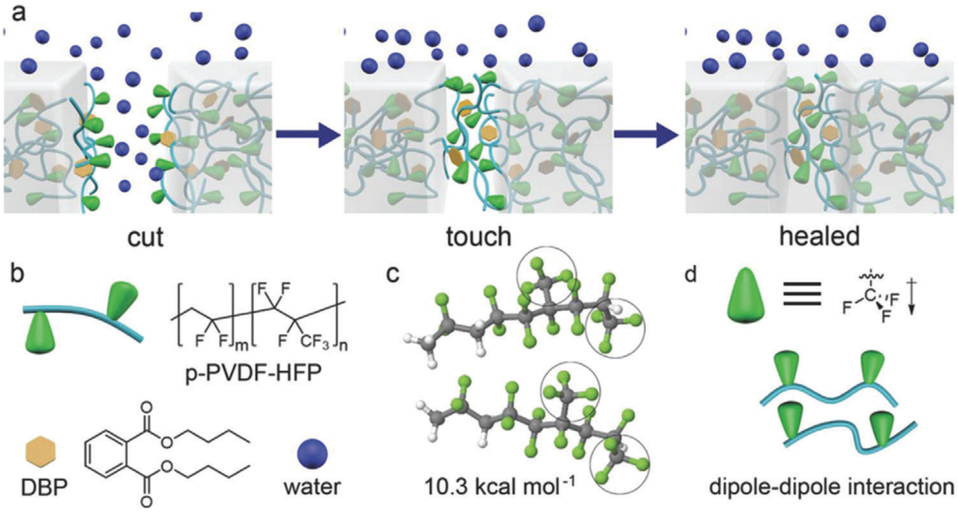

Figure 13. a) Water molecules are rejected due to the hydrophobic C–F and healing occurs by dipole–dipole interaction. b) Chemical structure of polymer and plasticizer. c) Interactions between two monomers through dipole–dipole forces and van der Waals d) dipole–dipole interaction. Reproduced with permission.[213] Copyright 2021, Wiley-VCH GmbH.

5.3. Self-Healable Wires and Electronics

Self-healable electronics are classified into two categories: insulators and conductors. Polymers tend to be insulators due to the covalent bonds between polymer chains and self-healable polymers have been incorporated as protective wire encapsulations and shown great promise as dielectric layers. Remarkably, a poly(vinylidene fluoride-co-hexafluo-ropropylene) polymer (PVDF-HFP) with varying plasticizers achieved the ability to self-heal while submerged underwater.[213] PVDF-HFP itself cannot heal as it requires a lower glass temperature to allow chain entanglement and diffusion. Self-healing was achieved through the dipole–dipole interaction between carbon and fluorine as shown in **Figure 13** through the introduction of the plasticizer dibutyl phthalate (DBP). This advancement showed great potential in prolonging the life of sea cables.

The conductivity of self-healing materials is another focus for creating successful electronics. Based on self-sorting chemistry, a supramolecular polymer, poly(dimethylsiloxane) oligomers linked by 4,4′-methylenebis(phenyl urea), and isophorone bisurea units, was synthesized to create a wafer-scale fabrication of an elastic self-healable e-skin acting as dielectric layers that can be incorporated into soft robotics and prosthetics.[214] The progress in self-healable conductive polymers has led to their integration in sensors, e-skins, solar energy, transistors, and electronics devices.[215–217] In 2016, traditional perovskite solar cell architecture was advanced by manufacturing a novel approach that is polymer-based perovskite solar cells (PPSC) that is both self-healing and water-resistant if in contact with water. Using polyethylene gel as the long-chained insulating polymer, PPSC showed that it can heal itself and almost regain its original open voltage value in 45 s.[218] Applications generating interest are wearable healable devices such as self-healable wearable real-time sweat sensors as a biomonitoring device.[219] The conductive polymer polyethylenedioxythiophene doped with polystyrene sulfonate (PEDOT:PSS) has been explored for its ability to immediately heal in 150 ms when thin films were damaged with a blade yet not completely separated. The healing process of PEDOT:PSS requires the wetting of the area which heals both its mechanical and electrical properties, finding new use in implanted electronics and e-skin.[220] From the mentioned applications, the definition of successful healing is based on the intended use of the polymer-based systems. While this definition can cause discrepancies in the standardizing healing efficiencies, the flexibility of the definition itself allows self-healing polymers to be advanced and accommodate the shortcomings of polymers in different fields.

6. Recent Advances in the Field

6.1. Recent Advances in Capsular-Based Self-Healing Polymers

A single healing cycle has been the main limitation and concern for capsular-based self-healing polymers, especially as the healed area is often the weakest part of the polymer. A novel alginate multicore capsule was developed capable of repeated local healing up to 3 times leading to progress and a wider scope of applications by integrating it into self-healing epoxy composite, fiber composite, coating, and cement.[167] The multicore microcapsules are able to control the release of the healing agents at the local damage site, leading to repeated cycles of healing. Repeated cycling was explained by cohesive failure of the capsules, and the next damage broke the capsules further and released more healing agents as shown in **Figure 14**. Another approach for efficient release of capsular-based self-healing polymers is a novel polyelectrolyte multilayered microcapsule, with a double-stimuli response as an anti-corrosion coating.[221] A layer by layer technique as shown in **Figure 15** is used incorporating the healing agent linseed oil and dodecylamine as a corrosion inhibitor making the capsule both a preventative and also a healing treatment for corrosion. While the second layer does not heal the coating, it does increase its service life and the novel multilayered technique can be enhanced further to provide multiple healing cycles for local damage.

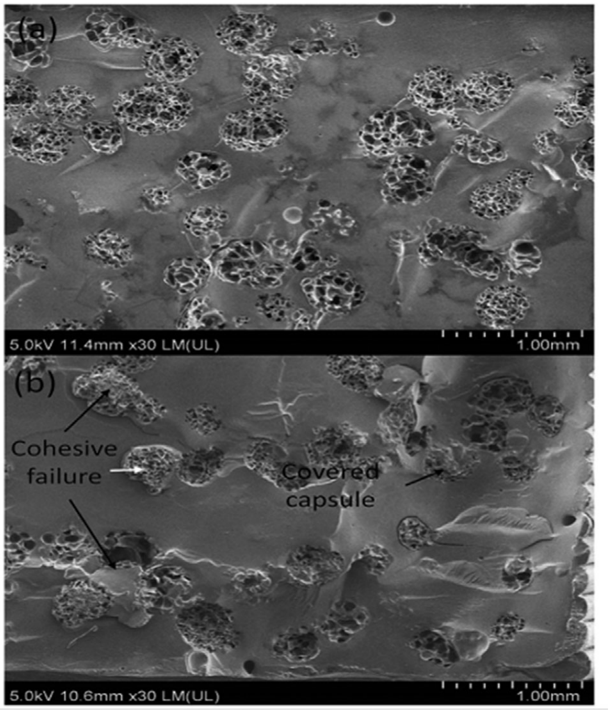

Figure 14. A fracture surface study of the dual capsule self-healing composite. FESEM images of a) the fracture surface of the specimen fractured for the first time and b) the fracture surface of the self-healed specimen fractured a second time after the first healing cycle. Reproduced under the terms of the Creative Commons CC-BY license.[167] Copyright 2016, The Authors, published by Springer Nature.

Predominantly popular as coatings and for mechanical healing, research on capsular-based self-healing polymers have recently branched out to other uses. Microencapsulated polymer-based systems have been used to decrease electrical degradation in dielectric polymers under high electric stress in power systems.[169] The electrical treeing that occurs in dielectric polymers is considered a warning to discard and replace the polymer. However, remarkably the electroluminescence caused by electrical treeing was incorporated into the self-healing mechanism of encapsulated photoresponsive bisphenol A epoxy acrylate.[169] Electroluminescence acts as stimuli for cross-linking to occur in the healing agent, allowing a self-healing mechanism to occur under ambient conditions. Such an advancement proposes a rethinking of external stimulus by either incorporating them as an occurrence triggered by the damage itself or by ensuring they can be provided in the operating conditions of future applications.[222] The cause of damage becoming the trigger for the self-healing mechanism is seen in UV curable microencapsulated epoxy resin, where UV light damages the self-healing coating and is also a key component in the curing mechanism of the healing agent. Two different studies detailed the development of a UV curable microencapsulated epoxy resins showing up to a 65% increase in protection against corrosion.[223,224]

6.2. Recent Advances in Vascular-Based Self-Healing Polymers

After fabricating vascular networks in a composite matrix, filling the network with a healing agent presents major challenges. The thickness of the vessels, unexpected blockage, and the viscosity of the healing agent all play a major role in determining whether the specimen will be successfully filled. To mitigate this issue 3D printing technique was used to create a vascular self-healing polymer in a one-step process.[225] The 3D printing technique can fabricate the sample layer by layer, where some resin is trapped uncured in the structure which can act as a self-healing agent.[225] Another challenge is the design of the network itself. Recently the network of a vascular self-healing system was optimized using a genetic algorithm that leads the polymer composite to have a minimal void fraction volume, which lowers the risk of changing the polymer composite and resulting in a weaker yet self-healable specimen. Due to high-density vascular systems in polymers most often weakening the mechanical properties of the non-healing polymer, there is a steady pace in investigating vascular self-healing systems whose properties are not drastically affected by the introduction of vascular systems as is in polymers.[226,227]

6.3. Recent Advances in Intrinsic Self-Healing Polymers

Within intrinsic self-healing polymers, the production and synthetization of polymers, in particular polyurethanes, incorporating the retro-Diels-Alder (rDA) reaction are of interest to incorporate self-healing polymers into the market.[228–235]

Recently a one-component polyurethane was successfully synthesized beginning with 2,2-bis(hydroxymethyl)propionic acid and thermo-responsive monoalcohol (with furfuryl or maleimide functions) that are found commercially. Maleimide and furfuryl were mixed with polypropylene glycol. With the addition of hexamethylene diisocyanate (HMDI) into the solution, the diol monomers were incorporated into the polyurethane, which was then obtained as the solvent was removed in a vacuum oven as shown in **Figure 16**.[235]

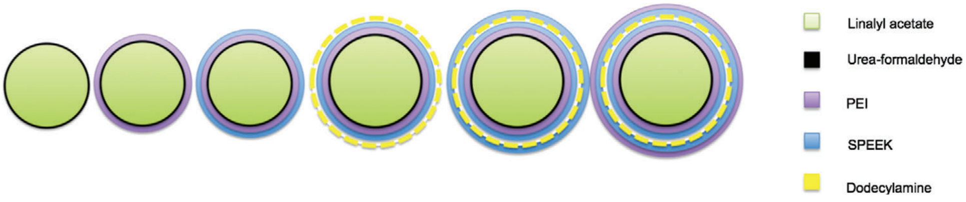

Figure 15. Schematic representation of the structure of as-synthesized layered microcapsules in polyelectrolyte materials polyethylenimine (PEI) and sulfonated polyether ether ketone (SPEEK).

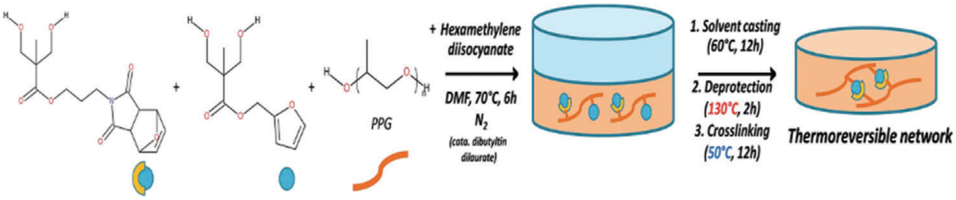

Figure 16. A scheme showing the synthetize of a thermo-healable system based on polyurethane. Reproduced under the terms of the Creative Commons CC-BY license.[235] Copyright 2017, The Authors, published by the Royal Society of Chemistry.

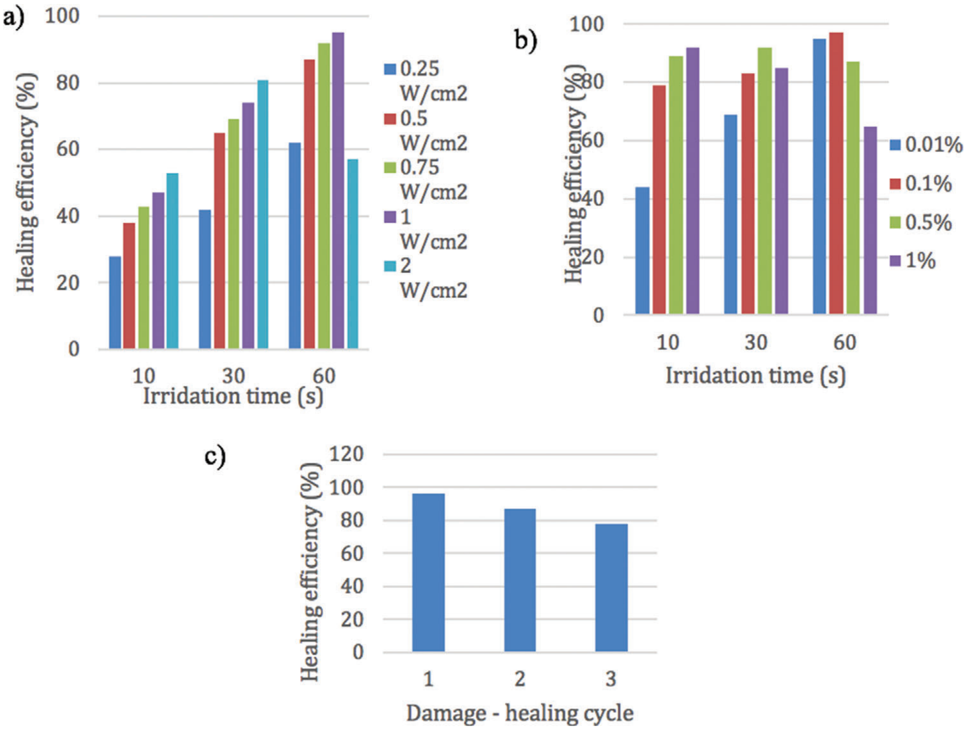

Figure 17. a) Effect of the NIR output power on the self-healing efficiency of DAPU–PDAP-0.01, with an 81% healing efficiency at 30 s. b) Effect of the PDAP content on the self-healing efficiency of DAPU–PDAP composites under 0.75 W cm^{-2} NIR irradiation, c) self-healing efficiency of DAPU–PDAP-0.01 after multiple "damage–healing" cycles (NIR output power: 1 W cm^{-2}, irradiation time: 60 s). Reproduced with permission.[236] Copyright 2018, the Royal Society of Chemistry

A poly(urethane-urea) was developed using inexpensive, off-the-shelf products that are capable of a catalyst-free self-healing making this material a very desirable development in intrinsic self-healing polymers that can be adapted into the market.[232] Zakharova et al. developed the widely adopted intrinsic self-healing polymer based on the DA reaction by using industrially produced inexpensive amines and furfural as starting material.[231] All of these developments are part of the growing research narrowing the gap between research and the implementation of self-healing polymers in the industry.

An ultra-fast self-healing response was developed by introducing polydopamine particles (PDAPs) into polyurethane-containing DA bonds, progressing the extensive work on DA self-healing polymers.[236] The mechanical properties of the polyurethane composites are significantly enhanced with the addition of PDAPs due to the strong interfacial interaction between PDAPs and polyurethane segments. Owing to the outstanding photothermal effect of PDAPs and excellent dynamic properties of DA bonds, the composites possess rapid light-responsive shape memory and self-healing properties as shown in **Figure 17** with up to 81% healing efficiency at only 30 s exposure to NIR.

Besides advancement in self-healing polymer-based systems incorporating reversible DA-reactions, dual functionality is another frontier that is becoming heavily explored in intrinsically self-healing polymers. Combining high thermal conductivity with self-healing properties led to the production of a liquid crystal epoxy film which can maintain 90.6% of its tensile strength after one healing cycle and 60.3% of its tensile strength after four healing cycles while showing high thermal conductivity.[237] Similarly to epoxy self-healing polymers but using supramolecular self-healing mechanisms, Wang et al. presented a solid-state self-healing polymer electrolyte that both satisfied the discharge rate and remarkably fully recovered both the mechanical and conductivity up to 100 cycles.[238] The authors of both studies suggested that these materials can be used in flexible electronic devices and intelligent systems. While self-healing polymers are still limited at healing large cracks, the development of dual functioning self-healing polymers can lead to a new multidisciplinary approach by incorporating self-healing polymers into soft robotics and flexible electronics at a smaller scale.

Some researchers have tried to address the major limitation for intrinsic self-healing polymers, namely these polymers should be both tough and self-healable, Wan et al. enhanced self-healing polyurethane through the synthetization and insertion of crystallization nanostructures.[239] These structures consisted of poly(L-lactic acid) crystalline domains, a reversible H-bond region, and a poly(tetrahydrofuran) soft chain placed in self-healing polymers. These changes greatly improving the tensile stress from 1.1 to 18.7 MPa.[239] Similarly, cellulose nanorods were placed in self-healing hydrogels to achieve greater stiffness while maintaining the healing efficiency.[240]

Ionomeric self-healing polymers have been increasingly incorporated with non-healing polymers to create novel self-healing polymer blends. EMAA was introduced into poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate) (PETG) to create EMAA/PETG blends that exhibited the ability to self-repair in response to Vickers microhardness indentations. Blends of 50/50 wt% exhibited a remarkable recovery of 100% healing efficiency after only 60 s. PETG is commonly used in 3D printing and this presents a promising direction for self-healing 3D products.[241] Polydimethylsiloxane (PDMS) based polyurethane ionomer blends were also produced and the self-healing dependency on temperature and humidity were investigated. Specimens were completely separated into two parts during an initial tensile test and reconnected between glass slides. After 14 days and at room temperature and low humidity, the PDMS polyurethane ionomer blend recovered up to 47% of its tensile strength while a 100% healing efficiency was achieved for the samples by moderate heating at 50 °C for only 1 h.[242]

The limit of self-healing polymers at healing large cracks was tackled by presenting a self-healable shape memory polymer (SMP) that responds to stimuli.[243] Using polyurethane-containing crosslinked elastomeric styrene–butadiene–styrene block copolymer spheres, the polymer preserved its shape through retraction by thermal stimuli while the thermally reversible bonds provided its self-healing ability. The design of a polymer that has the ability to both heal and preserve its shape under the same thermal stimulus presents a new possibility of coupling a polymer's characteristics to create a multi-step healing process. A novel framework to overcome the shortcomings of intrinsic self-healing polymer-based systems is to create polymers with several reversible healing processes. This was achieved in butyl methacrylate-based polymers that incorporate urea group-containing spherosilicates where self-healing occurs through both hydrogen bonds and DA reactions.[244]

7. Conclusion Remarks and Future Perspectives

In all three classifications: capsular-based, vascular, and intrinsic self-healing polymers, novel work has been achieved to develop new self-healing polymer-based systems, increase healing efficiencies, extend use into multiple fields of study, and to enable successful healing with minimum stimuli or human intervention. The increasing ability of self-healing polymers to overcome material limitations and ensure repeatable healing demonstrates that the most recent generation of self-healing polymers exhibit higher performance, longer service life, and have a lower environmental impact. These improvements were achieved through progress and novel approaches in designing, fabricating, and characterizing the polymers. Such advances have allowed self-healing material to be used in several new applications including in coatings, the automotive, aerospace, electronics, and the biomedical.

Capsular-based self-healing polymers have been developed into multiple classes of single capsule systems, dual capsule systems, multilayered capsules, and liquid–liquid self-healing mechanisms. Currently, capsular-based self-healing polymers are already produced and mass-manufactured, predominantly in the coating industry. The limitation of a single healing cycle has been circumvented with multicore and multilayered capsules, yet the healing repetition is still limited to 3 successful healing cycles. Vascular-based self-healing systems do not have this limitation and can be refilled and novel methods of creating complex 3D vascular structures within polymer-based systems have been achieved through the use of 3D robotics and novel scaffolding techniques. However, their fabrication poses complexity of scale, efficiency, and production that have yet to be extensively tackled. A thorough coupling of the experimental and modeling is necessary to overcome the aforementioned limitations and generate a greater understanding of the physical and chemical exchange that occurs during self-healing mechanisms. This effort requires further modeling and simulation to study dynamic mechanisms and to define the lifespan of self-healing polymers and entails a more rigorous study of fatigue failure and self-healing under constant load. Intrinsic self-healing polymers have notably advanced in the past decade and novel polymers exhibit high healing efficiencies in less than a minute. Researchers were also able to achieve dual-functional intrinsic self-healing polymers that recover mechanical and thermal properties or mechanical and electrical properties simultaneously. While a few notable studies presented intrinsic self-healing polymers that were tough and self-healable, most intrinsic self-healing polymers still suffer from being too soft for structural applications due to their low glass transition temperature.

The type of methods and characterization tests used to determine the healability of polymers depends on the functional properties being examined within the polymer. For mechanical properties, tensile and impact testing are predominantly used, while thermal and electrical conductivity or insulation are measured in various ways for thermal and electrical healing polymer-based systems. Qualitative characterization tests such as OM, SEM, and pressure tests confirm healed specimens however they do not measure the extent of healability provided in characterization tests from which healing efficiencies can be obtained. Testing of self-healing polymers should abide by a general standard as well as specific tests that are determined by their projected use in applications. Standardization will allow the lifespan of self-healing polymers to be compared against each other while also relating their lifespan to their functionality in different applications.

A major issue is the lack of appropriately tested application models. To have self-healing material's value change from promissory value to commodity value, large-scale fabrication is vital. The repeatability of self-healing mechanisms should be advanced so as to not require human intervention. The immediate future of self-healing materials lies in applications where the material is employed in restricted access areas such as underwater/underground piping and outer space where inspection, intervention, and maintenance are not an option.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

applications, characterization tests, classification, coatings, limitations, mechanical properties, modeling, recent advances, self-healing polymers

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[1] R. Scalenghe, *Heliyon* **2018**, *4*, e00941.
[2] X. Li, H. A. Hristov, A. F. Yee, D. W. Gidley, *Polymer* **1995**, *36*, 759.
[3] G. Scott, *Polymers and the Environment*, The Royal Society Of Chemistry, London **1999**.
[4] J. P. Reis, M. de-Moura, S. Samborski, *Materials* **2013**, *13*, 5832.
[5] A. K. Mohanty, M. Misra, L. T. Drzal, *Natural Fibers, Biopolymers, and Biocomposites*, Taylor & Francis, Boca Raton, FL **2005**.
[6] M. Jamshidian, E. A. Tehrany, M. Imran, M. Jacquot, S. Desobry, *Compr. Rev. Food Sci. Food Saf.* **2010**, *9*, 552.
[7] Z. Yang, J. Hollar, X. He, X. Shi, Cem. Concr. Compos. **2011**, *33*, 506.
[8] M. Graziani, P. Fornasiero, *Renewable Resources and Renewable Energy: A Global Challenge*, 2nd ed., CRC Press, Boca Raton **2012**. https://doi.org/10.1201/b16003.
[9] A. C. Jackson, J. A. Bartelt, K. Marczewski, N. R. Sottos, P. V. Braun, *Macromol. Rapid Commun.* **2011**, *32*, 82.
[10] G. Pećanac, S. Foghmoes, M. Lipińska-Chwałek, S. Baumann, T. Beck, J. Malzbender, *J. Eur. Ceram. Soc.* **2013**,*33*, 2689.
[11] M. Enomoto, in *Materials Science Forum*, Trans Tech Publications Ltd, Aedermannsdorf, Switzerland **2014**, pp. 273–277.
[12] P. C. Chou, R. Croman, in *Composite Materials: Testing and Design (Fifth Conference)* (Ed: S. W. Tsai), ASTM International, West Conshohocken, PA **1979**, pp. 431–454.
[13] W. Hayes, B. W. Greenland, Hayes W., Greenland B. W., Healable Polymeric Materials. *Healable Polymer Systems*, vol. *5*, The Royal Society of Chemistry **2013**, pp. 6–15.
[14] M. M. Shokrieh, R. Rafiee, in Fatigue life prediction of wind turbine rotor blades manufactured from composites. *Fatigue Life Prediction of Composites and Composite Structures* (Ed: A. P. Vassilopoulos), Woodhead Publishing, Cambridge **2010**, pp. 505–537.
[15] Y. Wei, Y. Li, L. Zhu, Y. Liu, X. Lei, G. Wang, Y. Wu, Z. Mi, J. Liu, H. Wang, H. Gao, *Nat. Commun.* **2014**, *5*, 1.
[16] R. S. Trask, H. R. Williams, I. P. Bond, *Bioinspiration Biomimetics* **2007**, *2*, P1.
[17] O. Speck, T. Speck, *Biomimetics* **2019**, *4*, 26.
[18] C. M. Dry, N. R. Sottos, Proc. SPIE ,Passive smart self-repair in polymer matrix composite materials,Proc. SPIE 1916, Smart Structures and Materials 1993: Smart Materials, (23 July 1993); https://doi.org/10.1117/12.148501.
[19] C. Dry, *Compos. Struct.* **1996**, *35*, 263.
[20] C. M. Dry, W. McMillan, Crack and damage assessment in concrete and polymer matrices using liquids released internally from hollow optical fibers, Proc. SPIE 2718, Smart Structures and Materials 1996: Smart Sensing, Processing, and Instrumentation, (30 May 1996); https://doi.org/10.1117/12.240898.
[21] C. Dry, W. Mcmillan, *Smart Mater. Struct.* **1996**, *5*, 297.
[22] S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, E. N. Brown, S. Viswanathan, *Nature* **2001**, *409*, 794.
[23] https://www.scopus.com/ data search results. (accessed: March 2022).
[24] R. S. Trask, I. P. Bond, *Smart Mater. Struct.* **2006**, *15*, 704.
[25] G. Williams, R. Trask, I. Bond, *Composites, Part A* **2007**, *38*, 1525.
[26] J. C. Cremaldi, B. Bhushan, *Beilstein J. Nanotechnol.* **2018**, *9*, 907.
[27] S. Meure, D. Y. Wu, *Prog. Polym. Sci.* **2008**, *33*, 479.
[28] H. H. Zamal, D. Barba, B. Aïssa, E. Haddad, F. Rosei, *Sci. Rep.* **2020**, *10*, 2973.
[29] K. Wang, Z. Zhou, J. Zhang, J. Tang, P. Wu, Y. Wang, Y. Zhao, Y. Leng, *Nanomaterials* **2020**, *10*, 753.
[30] L. Zhao, X. Shi, Y. Yin, B. Jiang, Y. Huang, *Compos. Sci. Technol.* **2020**, *186*, 107919.
[31] Y. J. Jeong, J. Jung, E. H. Suh, D.-J. Yun, J. G. Oh, J. Jang, *Adv. Funct. Mater.* **2020**, *30*, 1905809.
[32] R. Purohit, N. K. Gupta, M. R. Purohit, A. Patil, R. K. Bharilya, S. K. Singh, *Mater. Today: Proc.* **2015**, *2*, 3371.
[33] Z. Karami, M. Zolghadr, M. J. Zohuriaan-Mehr, *Self-Healing Polymer-Based Systems*, Elsevier, Amsterdam **2020**, pp. 209–233.
[34] B. J. Blaiszik, S. L. B. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos, S. R. White, *Annu. Rev. Mater. Res.* **2010**, *40*, 179.
[35] I. L. Hia, V. Vahedi, P. Pasbakhsh, *Polym. Rev.* **2016**, *56*, 225.
[36] D. Y. Zhu, M. Z. Rong, M. Q. Zhang, *Prog. Polym. Sci.* **2015**, *49–50*, 175.
[37] S. A. Mcdonald, S. B. Coban, N. R. Sottos, P. J. Withers, *Sci. Rep.* **2019**, *9*, 17773.
[38] M. W. Lee, *Polymers* **2020**, *12*, 379.
[39] Y. C. Yuan, M. Z. Rong, M. Q. Zhang, J. Chen, G. C. Yang, X. M. Li, *Macromolecules* **2008**, *41*, 5197.
[40] S. D. Mookhoek, S. C. Mayo, A. E. Hughes, S. A. Furman, H. R. Fischer, S. Van Der Zwaag, *Adv. Eng. Mater.* **2010**,*12*, 228.
[41] L. Yuan, G. Liang, J. Xie, L. Li, J. Guo, *Polymer* **2006**, *47*, 5338 .
[42] C. Zhang, H. Wang, Q. Zhou, *Prog. Org. Coat.* **2018**, *125*, 403.
[43] Y. C. Yuan, M. Z. Rong, M. Q. Zhang, *Polymer* **2008**, *49*, 2531.
[44] M. Hu, S. Peil, Y. Xing, D. Döhler, L. Caire Da Silva, W. H. Binder, M. Kappl, M. B. Bannwarth, *Mater. Horiz.* **2018**, *5*, 51.
[45] Y. C. Yuan, Y. Ye, M. Z. Rong, H. Chen, J. Wu, M. Q. Zhang, S. X. Qin, G. C. Yang, *Smart Mater. Struct.* **2011**, *20*, 015024.
[46] Q. Li, Siddaramaiah, N. H. Kim, D. Hui, J. H. Lee, *Composites, Part B* **2013**, *55*, 015024.
[47] Y. an. Ma, Y. ing. Zhang, J. ia. Liu, M. eng. Li, Y. a. Xu, *Key Eng. Mater.* **2019**, *821*, 313.
[48] M. M. Caruso, B. J. Blaiszik, H. Jin, S. R. Schelkopf, D. S. Stradley, N. R. Sottos, S. R. White, J. S. Moore, *ACS Appl. Mater. Interfaces* **2010**, *2*, 1195.
[49] E. Mostavi, S. Asadi, M. M. Hassan, M. Alansari, *J. Mater. Civ. Eng.* **2015**, *27*, 04015035.
[50] M. Kosarli, D. G. Bekas, K. Tsirka, D. Baltzis, D. T. Vaimakis-Tsogkas, S. Orfanidis, G. Papavassiliou, A. S. Paipetis, *Composites, Part B* **2019**, *171*, 78.
[51] B. F. Gibbs, S. Kermasha, I. Alli, C. N. Mulligan, *Int. J. Food Sci. Nutr.* **1999**, *50*, 213.
[52] A. Madene, M. Jacquot, J. Scher, S. Desobry, *Int. J. Food Sci. Technol.* **2006**, *41*, 1.
[53] M. A. Augustin, Y. Hemar, *Chem. Soc. Rev.* **2009**,*38*, 902.
[54] O. G. Schramm, M. A. R. Meier, R. Hoogenboom, H. P. Van Erp, J.-F. Gohy, U. S. Schubert, *Soft Matter* **2009**, *5*, 1662.
[55] E. Perrier, J. Hart, *Delivery System Handbook for Personal Care and Cosmetic Products: Technology, Applications and Formulations*, Elsevier Inc, Amsterdam **2005**, pp. 797–816.

[56] C. Perignon, G. Ongmayeb, R. Neufeld, Y. Frere, D. Poncelet, G. le Ongmayeb, R. Neufeld, Y. Frere, D. Poncelet, C. Perignon, G. Ongmayeb, R. Neufeld, Y. Frere, D. Poncelet, *J. Microencapsulation* **2015**, *32*, 1.
[57] H. Yi, Y. Yang, X. Gu, J. Huang, C. Wang, *J. Mater. Chem. A* **2015**,*3*, 13749.
[58] A. M. B. Rodriguez, B. P. Binks, *Curr. Opin. Colloid Interface Sci.* **2019**, *44*, 107.
[59] G. Nelson, *Advances in the Dyeing and Finishing of Technical Textiles*, Elsevier Inc, Amsterdam **2013**, pp. 78–104.
[60] R. al Shannaq, M. M. Farid, *Advances in Thermal Energy Storage Systems: Methods and Applications*, Elsevier Inc, Amsterdam **2015**, pp. 247–284.
[61] N. Gendelberg, D. Bird, N. M. Ravindra, *Polymer-Based Multifunctional Nanocomposites and Their Applications*, Elsevier, Amsterdam **2018**, pp. 175–199.
[62] "AmpArmor 3000,", https://www.autonomicmaterials.com/our-products/AMPARMOR-3000 (accessed August 2020) (n.d.).
[63] "AmpArmor 2000,", https://www.autonomicmaterials.com/our-products/AMPARMOR-2000 (accessed August 2020) (n.d.).
[64] "AmpArmor 1000,", https://www.autonomicmaterials.com/our-products/AMPARMOR-1000 (accessed August 2020) (n.d.).
[65] H. Ullah, K. A. M. Azizli, Z. B. Man, M. B. C. Ismail, M. I. Khan, *Polym. Rev.* **2016**, *56*, 429.
[66] S. J. García, H. R. Fischer, S. Van Der Zwaag, *Prog. Org. Coat.* **2011**, *72*, 211.
[67] T. Szmechtyk, N. Sienkiewicz, K. Strzelec, *Polym. Bull.* **2018**, *75*, 149.
[68] N. M. Hettiarachchi, R. T. De Silva, M. M. M. G. P. G. Mantilaka, P. Pasbakhsh, K. M. N. De Silva, G. A. J. Amaratunga, *RSC Adv.* **2019**, *9*, 23666.
[69] Z. Li, L. R. de Souza, C. Litina, A. E. Markaki, A. Al-Tabbaa, *Mater. Des.* **2020**, *190*, 108572.
[70] Y. C. Yuan, T. Yin, M. Z. Rong, M. Q. Zhang, *eXPRESS Polym. Lett.* **2008**, *2*, 238.
[71] K. Van Tittelboom, N. De Belie, *Materials* **2013**, *6*, 2182.
[72] A. Kousourakis, A. P. Mouritz, *Smart Mater. Struct.* **2010**, *19*, 085021.
[73] K.-M. Wang, S. Lorente, A. Bejan, *J. Phys. D: Appl. Phys.* **2006**, *39*, 3086.
[74] S. Lorente, A. Bejan, *J. Porous Media* **2009**, *12*, 1.
[75] S. Kim, S. Lorente, A. Bejan, *J. Appl. Phys.* **2006**,*100*, 063525.
[76] H. Zhang, S. Lorente, A. Bejan, *J. Appl. Phys.* **2007**, *101*, 094904.
[77] M. S. Razavi, E. Shirani, M. R. Salimpour, G. S. Kassab, *PLoS One* **2014**, *9*, e116260.
[78] H. R. Williams, R. S. Trask, I. P. Bond, *Smart Mater. Struct.* **2007**, *16*, 1198.
[79] H. R. Williams, R. S. Trask, I. P. Bond, *Compos. Sci. Technol.* **2008**, *68*, 3171.
[80] G. Postiglione, M. Alberini, S. Leigh, M. Levi, S. Turri, *ACS Appl. Mater. Interfaces* **2017**, *9*, 14371.
[81] J. F. Patrick, K. R. Hart, B. P. Krull, C. E. Diesendruck, J. S. Moore, S. R. White, N. R. Sottos, *Adv. Mater.* **2014**, *26*, 4302.
[82] D. Therriault, S. R. White, J. A. Lewis, *Nat. Mater.* **2003**, *2*, 265.
[83] L. Liu, M. R. Zachariah, S. I. Stoliarov, J. Li, *RSC Adv.* **2015**, *5*, 101745.
[84] J. F. Patrick, B. P. Krull, M. Garg, C. L. Mangun, J. S. Moore, N. R. Sottos, S. R. White, *Composites, Part A* **2017**, *100*, 361.
[85] L. M. Bellan, M. Pearsall, D. M. Cropek, R. Langer, *Adv. Mater.* **2012**, *24*, 5187.
[86] L. M. Bellan, S. P. Singh, P. W. Henderson, T. J. Porri, H. G. Craighead, J. A. Spector, *Soft Matter* **2009**, *5*, 1354.
[87] C. Gualandi, A. Zucchelli, M. Fernández Osorio, J. Belcari, M. L. Focarete, *Nano Lett.* **2013**, *13*, 5385.
[88] J. K. Banshiwal, D. N. Tripathi, *Functional Materials* (Ed. D. Sahu), IntechOpen, London **2019**. https://www.intechopen.com/chapters/64985.
[89] I. P. S. Qamar, N. R. Sottos, R. S. Trask, *Multifunct. Mater.* **2020**, *3*, 013001.
[90] H. R. Williams, R. S. Trask, A. C. Knights, E. R. Williams, I. P. Bond, *J. R. Soc., Interface* **2008**, *5*, 735.
[91] R. Das, C. Melchior, K. M. Karumbaiah, *Advanced Composite Materials for Aerospace Engineering* (Eds: S. Rana, R. Fangueiro), Woodhead Publishing, Cambridge **2016**. https://doi.org/10.1016/B978-0-08-100037-3.00011-0
[92] B. Jony, M. Thapa, S. B. Mulani, S. Roy, *Smart Mater. Struct.* **2019**, *28*, 025037.
[93] S. J. Garcia, H. R. Fischer, *Smart Polymers and Their Applications* (Eds: M. Aguilar, J. San Román), Woodhead Publishing, Cambridge **2014**. https://doi.org/10.1533/9780857097026.1.271.
[94] S. J. Garcia, *Eur. Polym. J.* **2014**, *53*, 118.
[95] X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science* **2002**, *295*, 1698.
[96] Z. Li, R. Yu, B. Guo, *ACS Appl. Bio Mater.* **2021**, *4*, 5926.
[97] M. M. Perera, N. Ayres, *Polym. Chem.* **2020**, *11*, 1410.
[98] N. Zheng, Y. Xu, Q. Zhao, T. Xie, *Chem. Rev.* **2021**, *121*, 1716.
[99] S. Zechel, R. Geitner, M. Abend, M. Siegmann, M. Enke, N. Kuhl, M. Klein, J. Vitz, S. Gräfe, B. Dietzek, M. Schmitt, J. Popp, U. S. Schubert, M. D. Hager, *NPG Asia Mater.* **2017**, *9*, e420.
[100] J. S. Park, T. Darlington, A. F. Starr, K. Takahashi, J. Riendeau, H. T. Hahn, *Compos. Sci. Technol.* **2010**, *70*, 2154.
[101] G. Postiglione, S. Turri, M. Levi, *Prog. Org. Coat.* **2015**, *78*, 526.
[102] J. Kötteritzsch, S. Stumpf, S. Hoeppener, J. Vitz, M. D. Hager, U. S. Schubert, *Macromol. Chem. Phys.* **2013**, *214*, 1636.
[103] W. Zhang, J. Duchet, J. F. Gérard, *J. Colloid Interface Sci.* **2014**, *430*, 61.
[104] X. Lu, G. Fei, H. Xia, Y. Zhao, *J. Mater. Chem. A* **2014**, *2*, 16051.
[105] S. A. Hayes, F. R. Jones, K. Marshiya, W. Zhang, *Composites, Part A* **2007**, *38*, 1116.
[106] R. Gupta, D. Huo, M. White, V. Jha, G. B. G. Stenning, K. Pancholi, *Compos. Commun.* **2019**, *16*, 67.
[107] J. Nji, G. Li, *Polymer* **2010**, *51*, 6021.
[108] L. Huang, N. Yi, Y. Wu, Y. Zhang, Q. Zhang, Y. Huang, Y. Ma, Y. Chen, *Adv. Mater.* **2013**, *25*, 2224.
[109] Y. Fan, H. Yang, M. Li, G. Zou, *Mater. Chem. Phys.* **2009**, *115*, 696.
[110] J. Liang, Y. Xu, Y. Huang, L. Zhang, Y. Wang, Y. Ma, F. Li, T. Guo, Y. Chen, *J. Phys. Chem. C* **2009**, *113*, 9921.
[111] X. Sun, Z. Liu, K. Welsher, J. T. Robinson, A. Goodwin, S. Zaric, H. Dai, *Nano Res.* **2008**, *1*, 203.
[112] T. F. A. de Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687.
[113] L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071.
[114] A. W. Bosman, R. P. Sijbesma, E. W. Meijer, *Mater. Today* **2004**, *7*, 34.
[115] Y. Wang, D. T. Pham, C. Ji, *Cogent Eng.* **2015**, *2*, 1075686.
[116] F. Herbst, W. H. Binder, *Polym. Chem.* **2013**, *4*, 3602.
[117] Y. Huang, M. Zhong, Y. Huang, M. Zhu, Z. Pei, Z. Wang, Q. Xue, X. Xie, C. Zhi, *Nat. Commun.* **2015**, *6*, 10310.
[118] M. Yamaguchi, S. Ono, K. Okamoto, *Mater. Sci. Eng., B* **2009**, *162*, 189.
[119] S. Prager, M. Tirrell, *J. Chem. Phys.* **1981**, *75*, 5194.
[120] M. Yamaguchi, S. Ono, M. Terano, *Mater. Lett.* **2007**, *61*, 1396.
[121] L. McKeen, *Polyolefins, Polyvinyls, and Acrylics Permeability Properties of Plastics and Elastomers* (Ed: L. McKeen), William Andrew Publishing; **2012**. https://doi.org/10.1016/B978-1-4377-3469-0.10009-8.
[122] A. Eisenberg, *Macromolecules* **1970**, *3*, 147.
[123] A. Eisenberg, B. Hird, R. B. Moore, *Macromolecules* **1990**, *23*, 4098.
[124] S. J. Kalista, T. C. Ward, Z. Oyetunji, *Mech. Adv. Mater. Struct.* **2007**, *14*, 391.
[125] S. J. Kalista, T. C. Ward, *J. R. Soc. Interface* **2007**, *4*, 405.

[126] K. K. Ajekwene, J. E. Johny, T. Kurian, *Prog. Electromagn. Res. C* **2018**, *88*, 207.
[127] R. Dolog, R. A. Weiss, *Macromolecules* **2013**, *46*, 7845.
[128] B. Aïssa, D. Therriault, E. Haddad, W. Jamroz, *Adv. Mater. Sci. Eng.* **2012**, *2012*, 1.
[129] A. C. Balazs, *Mater. Today* **2007**, *10*, 18.
[130] N. de Alwis Watuthanthrige, B. Ahammed, M. T. Dolan, Q. Fang, J. Wu, J. L. Sparks, M. B. Zanjani, D. Konkolewicz, Z. Ye, *Mater. Horiz.* **2020**, *7*, 1581.
[131] S. F. Duki, G. V. Kolmakov, V. V. Yashin, T. Kowalewski, K. Matyjaszewski, A. C. Balazs, *J. Chem. Phys.* **2011**, *134*, 084901.
[132] M. Andersson Trojer, L. Nordstierna, M. Nordin, M. Nydén, K. Holmberg, *Phys. Chem. Chem. Phys.* **2013**, *15*, 17727.
[133] S. Wang, M. W. Urban, *Nat. Rev. Mater.* **2020**, *5*, 562.
[134] Y. Luo, X. Chen, J. Chen, Z. Wu, H. Ma, X. Liu, B. Xiang, X. Ma, Z. Luo, *Soft Matter* **2021**, *17*, 2191.
[135] B. Arab, A. Shokuhfar, *J. Mol. Model.* **2013**, *19*, 5053.
[136] J. Chen, F. Li, Y. Luo, Y. Shi, X. Ma, M. Zhang, D. W. Boukhvalov, Z. Luo, *J. Mater. Chem. A* **2019**, *7*, 15207.
[137] X. Zheng, H. Yang, Y. Sun, Y. Zhang, Y. Guo, *Smart Mater. Struct.* **2018**, *27*, 105013.
[138] K. Lyakhova, A. C. C. Esteves, M. W. P. van de Put, L. G. J. van der Ven, R. A. T. M. van Benthem, G. de With, *Adv. Mater. Interfaces* **2014**, *1*, 1400053.
[139] G. Z. Voyiadjis, A. Shojaei, G. Li, P. I. Kattan, *Proc. R. Soc. A* **2012**, *468*, 163.
[140] J. Bluhm, S. Specht, J. Schröder, *Arch. Appl. Mech.* **2015**, *85*, 1469.
[141] J. Mergheim, P. Steinmann, *Comput. Mech.* **2013**, *52*, 681.
[142] S. Zhou, H. Zhu, J. W. Ju, Z. Yan, Q. Chen, *Int. J. Damage Mech.* **2017**, *26*, 340.
[143] S. A. Ponnusami, J. Krishnasamy, S. Turteltaub, S. van der Zwaag, *Int. J. Solids Struct.* **2018**, *134*, 249.
[144] E. Javierre, *Coatings* **2019**, *9*, 122.
[145] A. M. Grande, L. Castelnovo, L. D. Landro, C. Giacomuzzo, A. Francesconi, M. A. Rahman, *J. Appl. Polym. Sci.* **2013**, *130*, 1949.
[146] R. J. Varley, S. van der Zwaag, *Acta Mater.* **2008**,*56*, 5737.
[147] M. Khamrai, S. L. Banerjee, S. Paul, S. Samanta, P. P. Kundu, *Int. J. Biol. Macromol.* **2019**, *122*, 940.
[148] B. Zhou, Y.e H. Jo, R. Wang, D. He, X. Zhou, X. Xie, Z. Xue, *J. Mater. Chem. A* **2019**, *7*, 10354.
[149] Y. S. Ryu, K. W. Oh, S. H. Kim, *Text. Res. J.* **2019**, *89*, 814.
[150] J. Cui, Z. Ma, L. Pan, C.-H. An, J. Liu, Y.-F. Zhou, Y.-S. Li, *Mater. Chem. Front.* **2019**, *3*, 464.
[151] D. A. Mcilroy, B. J. Blaiszik, M. M. Caruso, S. R. White, J. S. Moore, N. R. Sottos, *Macromolecules* **2010**, *43*, 1855.
[152] S. Billiet, X. K. D. Hillewaere, R. F. A. Teixeira, F. E. du Prez, *Macromol. Rapid Commun.* **2013**, *34*, 290.
[153] J. Yang, M. W. Keller, J. S. Moore, S. R. White, N. R. Sottos, *Macromolecules* **2008**, *41*, 9650.
[154] D. Sun, M. O. R. Siddiqui, K. Iqbal, *Smart Textile Coatings and Laminates*, Elsevier, Amsterdam **2018**, pp. 99–116.
[155] J. Fickert, M. Makowski, M. Kappl, K. Landfester, D. Crespy, *Macromolecules* **2012**, *45*, 6324.
[156] T. C. S. R. Reddy, A. R. Theja, C. Sashidhar, *Civ. Eng. J.* **2018**, *4*, 971.
[157] N. Saba, M. Jawaid, M. T. H. Sultan, *Mechanical and Physical Testing of Biocomposites, Fibre-Reinforced Composites and Hybrid Composites*, Elsevier, Amsterdam **2018**, pp. 1–12.
[158] L. Guadagno, M. Raimondo, C. Naddeo, P. Longo, A. Mariconda, W. H. Binder, *Smart Mater. Struct.* **2014**, *23*, 045001.
[159] L. Guadagno, M. Raimondo, U. Vietri, C. Naddeo, A. Stojanovic, A. Sorrentino, W. H. Binder, *Int. J. Aerosp. Eng.* **2016**, https://doi.org/10.1155/2016/7817962.
[160] X. Xing, L. Li, T. Wang, Y. Ding, G. Liu, G. Zhang, *J. Mater. Chem. A* **2014**, *2*, 11049.
[161] J. R. Davis, *Tensile Test*, 2nd ed, ASM International, Materials Park, Ohio **2004**, https://doi.org/10.1361/ttse2004p001.
[162] J. J. Laureto, J. M. Pearce, *Polym. Test.* **2018**, *68*, 294.
[163] A. Miller, C. Brown, G. Warner, *Smart Sustainable Manuf. Syst.* **2019**, *3*, https://10.1520/ssms20190051.
[164] ASTM-D638-14 ASTM International. ASTM. 2014. Standard Test Method for Tensile Properties of Plastics. ASTM. D638-14. 2014; ASTM International: West Conshohocken, PA, USA. pp. 1–2.
[165] T. Szmechtyk, N. Sienkiewicz, K. Strzelec, *eXPRESS Polym. Lett.* **2018**, *12*, 640.
[166] X. Yuan, Q. Su, L. Han, Q. Zhang, Y. Chen, Y. Liu, T. Liu, L. Gao, *Key Eng. Mater.* **2014**.
[167] I. L. Hia, P. Pasbakhsh, E. Chan, S. Chai, *Sci. Rep.* **2016**, *6*, https://doi.org/10.1038/srep34674.
[168] H. J. Sim, H. Kim, Y. Jang, G. M. Spinks, S. Gambhir, D. L. Officer, G. G. Wallace, S. J. Kim, *ACS Appl. Mater. Interfaces* **2019**, *11*, 46026.
[169] L. Gao, Y. Yang, J. Xie, S. Zhang, J. Hu, R. Zeng, J. He, Q. Li, Q. Wang, *Matter* **2020**, *2*, 451.
[170] B. T. Tomoda, P. H. Yassue-Cordeiro, J. V. Ernesto, P. S. Lopes, L. O. Péres, C. F. da Silva, M. A. de Moraes, *Biopolymer Membranes and Films*, Elsevier, Amsterdam **2020**, pp. 67–95.
[171] S. Bode, M. Enke, M. Hernandez, R. K. Bose, A. M. Grande, S. van der Zwaag, U. S. Schubert, S. J. Garcia, M. D. Hager, *Self-Healing Materials* (Eds: M.D. Hager, S. van der Zwaag, U.S. Schubert), Springer International Publishing, Cham **2016**, pp. 133–134.
[172] N. A. S. M. S. Md Jamil, A. M. Lazim, *AIP Conf. Proc.*, American Institute Of Physics Inc, New York **2014**, pp. 469–475.
[173] R. A. Chowdhury, M. V. Hosur, M. Nuruddin, A. Tcherbi-Narteh, A. Kumar, V. Boddu, S. Jeelani, *J. Mater. Res. Technol.* **2015**, *4*, 33.
[174] L. Zedler, M. D. Hager, U. S. Schubert, M. J. Harrington, M. Schmitt, J. Popp, B. Dietzek, *Mater. Today* **2014**, *17*, 57.
[175] D. S. Xiao, Y. C. Yuan, M. Z. Rong, M. Q. Zhang, *Polymer* **2009**, *50*, 2967.
[176] S. Zechel, R. Geitner, M. Abend, M. Siegmann, M. Enke, N. Kuhl, M. Klein, J. Vitz, S. Gräfe, B. Dietzek, M. Schmitt, J. Popp, U. S. Schubert, M. D. Hager, *NPG Asia Mater.* **2017**, *9*, e420.
[177] C. C. Hornat, M. W. Urban, *Nat. Commun.* **2020**, *11*, 1028.
[178] Y. Yang, D. Davydovich, C. C. Hornat, X. Liu, M. W. Urban, *Chem* **2018**, *4*, 1928.
[179] Y.-G. Luan, X.-A. Zhang, S.-L. Jiang, J.-H. Chen, Y.-F. Lyu, *Chin. J. Polym. Sci.* **2018**, *36*, 584.
[180] J. Janovick, A. Spyros, P. Dais, E. Hatzakis, *Chemical Analysis of Food*, Elsevier, Amsterdam **2020**, pp. 135–175.
[181] D. Ehrhardt, K. van Durme, J. F. G. A. Jansen, B. van Mele, N. van den Brande, *Polymer* **2020**, *203*, 122762.
[182] Q. Zhang, D. Tang, J. Zhang, R. Ni, L. Xu, T. He, X. Lin, X. Li, H. Qiu, S. Yin, P. J. Stang, *J. Am. Chem. Soc.* **2019**, *141*, 17909.
[183] G. Janszen, G. Capezzera, A. Grande, L. di Landro, *Aerospace* **2019**, *6*, 14.
[184] G. Williams, R. Trask, I. Bond, *Composites, Part A* **2007**, *38*, 1525.
[185] L. Guadagno, M. Raimondo, C. Naddeo, P. Longo, *Self-Healing Polymers*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany **2013**, pp. 401–412.
[186] L. Guadagno, M. Raimondo, C. Naddeo, P. Longo, A. Mariconda, *Polym. Eng. Sci.* **2014**, *54*, 777.
[187] M. Scheiner, T. J. Dickens, O. Okoli, *Polymer* **2016**,*83*, 260.
[188] S. J. Benight, C. Wang, J. B. H. Tok, Z. Bao, *Prog. Polym. Sci.* **2013**, *38*, 1961.
[189] J. Chen, Y. Huang, X. Ma, Y. Lei, *Adv. Compos. Hybrid Mater.* **2018**, *1*, 94.
[190] J. Cui, X. Li, Z. Pei, Y. Pei, *Chem. Eng. J.* **2019**, *358*, 379.

[191] L. Guadagno, C. Naddeo, L. Vertuccio, E. Calabrese, G. Barra, M. Raimondo, *Revolutionizing Aircraft Materials and Processes*, Springer International Publishing, Berlin **2020**, pp. 277–302.
[192] G. Li, P. Xiao, S. Hou, Y. Huang, *Carbon* **2019**, *147*, 398.
[193] L. Peng, M. Lin, S. Zhang, L. Li, Q. Fu, J. Hou, *Coatings* **2019**, *9*, 421.
[194] *Self-Healing Low-Melt Polyimides NASA Kennedy Space Center Seeks Partners Interested in The*, **n.d.**
[195] S. Kee, M. A. Haque, D. Corzo, H. N. Alshareef, D. Baran, *Adv. Funct. Mater.* **2019**, *29*, 1905426.
[196] "NEI Coating Technical Data Sheets | NEI Corporation," https://www.neicorporation.com/media/tds/ (accessed: August 2020).
[197] "Polymers – SupraPolix," http://www.suprapolix.com/pages/polymers (accessed: August 2020).
[198] "Technology – Nippon Paint Singapore Nippon Paint Singapore, " https://www.nipponpaint.com.sg/automotive/technology/ (accessed: August 2020).
[199] K. L. Gordon, E. J. Siochi, W. T. Yost, P. B. Bogert, P. A. Howell, K. E. Cramer, E. R. Burke, *Ballistic Puncture Self-Healing Polymeric Materials*, **2017**, (accessed: August 2020).
[200] M. R. Kessler, N. R. Sottos, S. R. White, *Composites, Part A* **2003**, *34*, 743.
[201] C. J. Norris, I. P. Bond, R. S. Trask, *Compos. Sci. Technol.* **2011**, *71*, 847.
[202] C. J. Norris, I. P. Bond, R. S. Trask, *Composites, Part A* **2011**, *42*, 639.
[203] E. P. Meents, T. J. Barnell, K. M. Cable, T. W. Margraf, E. Havens, *Int. SAMPE Symp. Exhib. (Proc.)* **2009**.
[204] L. Santo,F. Quadrini, Shape memory composite sandwich with self-healing properties for marine applications; Proceedings of the ICCM International Conferences on Composite Materials, ICCM 2015; Copenhagen, Denmark. 19–24 July 2015; p. 138792.
[205] J. L. Ferracane, *Dent. Mater.* **2013**, *29*, 51.
[206] G. Huyang, A. E. Debertin, J. Sun, *Mater. Des.* **2016**, *94*, 295.
[207] M. Yahyazadehfar, G. Huyang, X. Wang, Y. Fan, D. Arola, J. Sun, *Mater. Sci. Eng., C* **2018**, *93*, 1020.
[208] R. A. T. M. van Benthem, W. (Marshall) Ming, G. (Bert) de With, *Springer Series in Materials Science*, Springer Verlag, Berlin **2007**, pp. 139–159.
[209] G. Li, H. Meng, *Recent Advances in Smart Self-Healing Polymers and Composites* **2015**.
[210] G. Koch, in Cost of corrosion. El-Sherik A.M., *Trends in Oil and Gas Corrosion Research and Technologies* (Ed: A. El-Sherik), Woodhead Publishing, Boston **2017**, pp. 3–30. https://doi.org/10.1016/B978-0-08-101105-8.00001-2
[211] M. L. Zheludkevich, J. Tedim, M. G. S. Ferreira, *Electrochim. Acta* **2012**, *82*, 314.
[212] D. O. Grigoriev, K. Köhler, E. Skorb, D. G. Shchukin, H. Möhwald, *Soft Matter* **2009**, *5*, 1426.
[213] Y. Cao, H. Wu, S. I. Allec, B. M. Wong, D.-S. Nguyen, C. Wang, *Adv. Mater.* **2018**, *30*, 1804602.
[214] J. Kang, D. Son, G.-J. N. Wang, Y. Liu, J. Lopez, Y. Kim, J. Y. Oh, T. Katsumata, J. Mun, Y. Lee, L. Jin, J. B.-H. Tok, Z. Bao, *Adv. Mater.* **2018**, *30*, 1706846.
[215] Y. J. Tan, J. Wu, H. Li, B. C. K. Tee, *ACS Appl. Mater. Interfaces* **2018**, *10*, 15331.
[216] C. S. Luo, P. Wan, H. Yang, S. A. A. Shah, X. Chen, *Adv. Funct. Mater.* **2017**, *27*, 1606339.
[217] M. Shi, H. Wu, *Flexible and Stretchable Triboelectric Nanogenerator Devices*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany **2019**, pp. 281–303.
[218] Y. Zhao, J. Wei, H. Li, Y. Yan, W. Zhou, D. Yu, Q. Zhao, *Nat. Commun.* **2016**, *7*, 10228.
[219] J. o. Yoon, S.-M. Kim, Y. Eom, J. un. Koo, H.-W. Cho, T. ae. Lee, K. G. Lee, H. ong. Park, Y. eong. Kim, H.-J. Yoo, S. ung. Hwang, J. Park, B. ong. Choi, *ACS Appl. Mater. Interfaces* **2019**, *11*, 46165.
[220] S. Zhang, F. Cicoira, *Adv. Mater.* **2017**, *29*, 1703098.
[221] A. Khan, F. Ubaid, E. M. Fayyad, Z. Ahmad, R. A. Shakoor, M. F. Montemor, R. Kahraman, S. Mansour, M. K. Hassan, A. Hasan, A. M. Abdullah, *J. Mater. Sci.* **2019**, *54*, 12079.
[222] Y.-T. Zhang, H.-C. Yu, M.-C. Shen, Y.-T. Chern, C.-C. Li, *Mater. Chem. Phys.* **2020**, *240*, 122161.
[223] M. Odarczenko, D. Thakare, W. Li, S. P. Venkateswaran, N. R. Sottos, S. R. White, *Adv. Eng. Mater.* **2020**, *22*, 1901223.
[224] P. Li, W. Guo, Z. Lu, J. Tian, X. Li, H. Wang, *Prog. Org. Coat.* **2021**, *151*, 106046.
[225] K. Davami, M. Mohsenizadeh, M. Mitcham, P. Damasus, Q. Williams, M. Munther, *Sci. Rep.* **2019**, *9*, 7474.
[226] T. Selvarajoo, R. E. Davies, D. R. Gardner, B. L. Freeman, A. D. Jefferson, *Constr. Build. Mater.* **2020**, *245*, 118332.
[227] T. Selvarajoo, R. E. Davies, B. L. Freeman, A. D. Jefferson, *Constr. Build. Mater.* **2020**, *254*, 119245.
[228] A. Lapprand, F. Méchin, J.-P. Pascault, *J. Appl. Polym. Sci.* **2007**, *105*, 99.
[229] L. Gu, Q.-Y. Wu, *J. Appl. Polym. Sci.* **2018**, *135*, 46272.
[230] C. Zeng, H. Seino, J. Ren, K. Hatanaka, N. Yoshie, *Macromolecules* **2013**, *46*, 1794.
[231] D. V. Zakharova, A. A. Pavlov, in *IOP Conf, Ser.: Mater. Sci. Eng*, Institute Of Physics Publishing, Bristol, UK **2019**, p. 012002.
[232] H. Ying, Y. Zhang, J. Cheng, *Nat. Commun.* **2014**, *5*, 3218.
[233] P. Du, X. Liu, Z. Zheng, X. Wang, T. Joncheray, Y. Zhang, *RSC Adv.* **2013**, *3*, 15475.
[234] Q. Huang, F. Yang, X. Cao, Z. Hu, C. Cheng, *Macromol. Res.* **2019**, *27*, 895.
[235] B. Willocq, F. Khelifa, J. Brancart, G. Van Assche, P. Dubois, J.-M. Raquez, *RSC Adv.* **2017**, *7*, 48047.
[236] L. Yang, X. Lu, Z. Wang, H. Xia, *Polym. Chem.* **2018**, *9*, 2166.
[237] X. Yang, X. Zhong, J. Zhang, J. Gu, *J. Mater. Sci. Technol.* **2021**, *68*, 209.
[238] C. Wang, R. Li, P. Chen, Y. Fu, X. Ma, T. Shen, B. Zhou, K. Chen, J. Fu, X. Bao, W. Yan, Y. Yang, *J. Mater. Chem. A* **2021**, *9*, 4758.
[239] D. Wan, Q. Jiang, Y. Song, J. Pan, T. Qi, G. L. Li, *ACS Appl. Polym. Mater.* **2020**, *2*, 879.
[240] J. R. Mckee, E. A. Appel, J. Seitsonen, E. Kontturi, O. A. Scherman, O. Ikkala, *Adv. Funct. Mater.* **2014**, *24*, 2706.
[241] P. A. P. Silva, A. B. Silva, J. P. F. Santos, R. L. Oréfice, *J. Appl. Polym. Sci.* **2021**, *138*, 50148.
[242] F. Da Via, R. Suriano, O. Boumezgane, A. M. Grande, C. Tonelli, S. Turri, *Polym. Adv. Technol.* **2022**, *33*, 556.
[243] L. F. Fan, M. Z. Rong, M. Q. Zhang, X. D. Chen, *ACS Appl. Mater. Interfaces* **2018**, *10*, 38538.
[244] S. Schäfer, G. Kickelbick, *Macromolecules* **2018**, *51*, 6099.

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