Self-healing Elastomers

Zakariya Zubair, Ahmad Usman, and Asif Hafeez

Abstract The research in the field of self-healing elastomers (SHE) has resulted in different complex structures with various healing strategies (hydrogen bonds, covalent and non-covalent interactions and combinations of both). Elastomers with good mechanical performance and healing efficiency typically do not exist, as self-healing mechanism limits the mechanical properties. To get optimum mechanical and healing properties, using a combination of different mechanisms is emerging as a possible solution in SHEs. This chapter, mainly focused on SHEs, in which covalent bonds in combination with non-covalent interactions provide the best balance between repairability and mechanical performance. The applications of SHE include sensors, controlled drug release, coatings, actuators, railway components, hoses, seals, gaskets, and tires used in high-performance applications.

Keywords Self-healing · Elastomers · Hydrogen bonding · Thermoplastics · Covalent bonds · Self-sealing

1 Introduction

The last 100 years have witnessed amazing breakthroughs, resulting in the production of new materials with the desired characteristics [1]. Self-healing (SH) has been an inevitable trend among these properties over the past 20 years. Keeping in view the sustainability, the SH materials are the most desirable as it increases product life span, causing decrease in environmental waste. The circular economy presents challenges for some polymers, such as elastomers and thermosets, which are difficult to reprocess despite substantial efforts [2]. But due to their significant demand for industrial applications, it is crucial to make them appropriate for the circular economy paradigm and inducing SH characteristic is one approach to accomplish this [3].

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K. Shaker and A. Hafeez (eds.), *Advanced Functional Polymers*, Engineering Materials,
https://doi.org/10.1007/978-981-99-0787-8_6

1.1 Natural Self-healing Phenomenon

Human skin is by far the most known example of how tiny injuries to the skin heal completely but more severe injuries leave scars. Both situations almost completely restore the system's operational potential [4]. Other organisms' capacity for repair can be considerably more surprising; for instance, the Cnidarian hydra can reconstruct its entire body from its broken-up cells. The Lerna Hydra was viewed as the pinnacle of SH in Greek mythology [5].

Although the development of synthetic SH materials has long been a dream, there has been a notable rise in optimism in this area over the past 10 years. Polymers fall in two different types i.e. thermoplastics and thermosets, which are being used in several high-tech applications [6, 7]. To regain their mechanical properties, SH polymers need to be coupled across the interfaces created by rupture, breaking, or cracking. The crosslinks prevent polymer chains from creating entanglements, limiting the self healing in thermosets [8].

Reversible covalent and composite are the two main approaches that have emerged for SH in thermoset materials. When an external trigger like light or temperature is applied, covalent bonds are rearranged in the first method, which is frequently referred to as "self-mending": fractures in the material are fused by newly generated bonding, as in a reversible Diels–Alder reaction studied by Fred Wudl's research team (Fig. 1a). It is clear that this method has a lot of potential for reversible (but powerful) non-covalent bonds, and efforts to use hydrogen bonds for this purpose are being researched.

The second method, created by White, Sottos, and others, involves embedding monomers carrying microcapsules within the thermoset material. When a fracture appears in the capsules' skin, the capsules burst, and the catalyst is dispersed throughout the matrix, causing the unreacted monomer to discharge and harden (Fig. 1b). Since no external trigger is required to initiate healing, this sort of SH is referred to as "autonomous" [9]. Thermoplastics naturally have simpler SH than thermosets because heating induces chain mobility, which can result in the formation of entanglements across surfaces. Thermoplastic interfaces can be joined together without the need for an additional adhesive, unlike thermosets. Sometimes the material's impact, which can harm the substance, can supply the temperature needed to produce movement. This procedure is known as "ballistic impact self-repair" [10].

1.2 Self-healing Mechanism in Nature

A quick self-sealing (SS) leaves residual damage (fracture, cut, or crack) that has been repaired well to the point where it can continue to function as before (stiffness, self-cleaning), but the mechanical properties (rigidity, hardness) are not recovered [11]. The biological models of animals and plants have come to reflect hierarchically

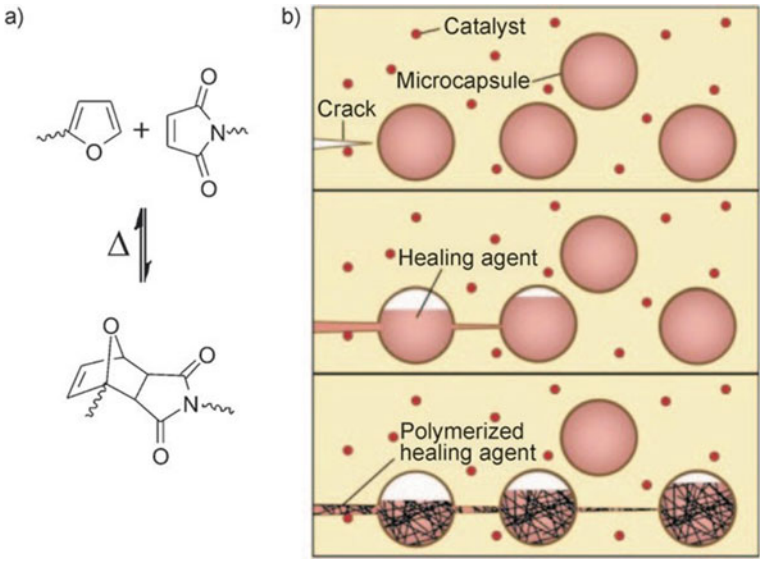


Fig. 1 Hitherto explored two different primary approaches; **a** reversible-covalent bonds and **b** thermoset matrix, embedded with microcapsules [10]

structured material systems. The number of hierarchical levels, their varying architectures and components, and the changes in functional requirements demonstrate how animals and plants developed a variety of SH strategies. All materials have a preliminary SS stage that quickly seals a wound or injury, which can be distinguished from a succeeding SH stage that leads to the most accurate possible recovery of the initial condition, despite different periods and procedures [12] (Fig. 2).

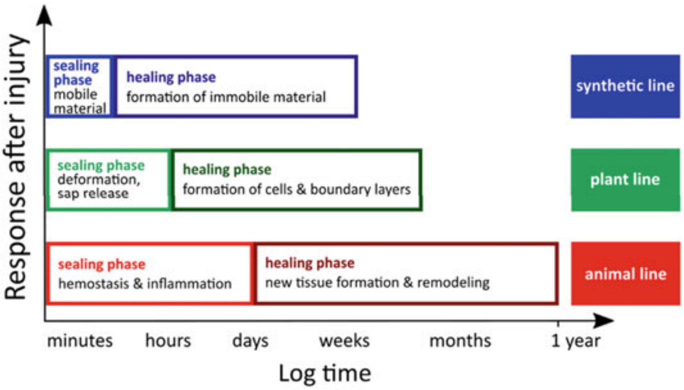


Fig. 2 Comparative analysis of self-repairing stages in technical materials, animals and plants [12]

1.3 Plants as Idea Generators or Inspiration Sources

With time, plants have developed several variations to dehydrated locations, such as water storage in the parenchyma of the succulent plant body and a reduction in branching, which causes moisture loss via quick sealing and bruising healing. Because quick and synchronized wound closure is essential for the development of the plant's water balance in conditions of water stress, the encapsulation mechanism is safe guarded several times by redundant mechanisms. The primary driving factors for the leaves of the SS in the Pink Carpet plant include hydraulic shrinkage and swelling as well as growth-induced mechanical prestresses [13].

1.3.1 Delosperma Cooperi Leaves-Inspired Self-healing Polymer

By forcing the five layers of tissue in a leaf to expand and contract simultaneously, a wound creates a mechanical imbalance that causes the leaf to change form until a new mechanical equilibrium is found. Based on a mechanically driven SS mechanism previously found in D. cooperi succulent leaves, Yang et al. developed a bioinspired SH polymer. They developed a commercial microphase detachable copolymer based on a biological function model composed of separate tissues with intrinsic strain and stress that has shape memory capabilities that enable the SH following mechanical injury [14].

1.3.2 Latex-Bearing Plants-Inspired Self-healing Elastomers

The weeping Fig. 3 (Ficus benjamina), the rubber tree (Hevea brasiliensis), and the various spurge species (Euphorbia spp.) were selected as the best case studies to address the technological challenge of limiting fracture propagation in self-repairing material systems. To examine how latex coagulation during fast fissure SH affected the recovery of tensile strength in F. benjamina bark samples, Bauer and Speck utilized mechanical experiments [15]. Figure 3 demonstrates that tensile strength substantially increases within 30 min of external injury, accounting for 55% of the value obtained for undamaged bark. If the latex is thrown away before the time limit runs out, there will be no SH [12].

It is widely known that H. brasiliensis coagulates plant latex. Microtubes are made of latex emulsions containing membrane vesicles (laticifers). Within the laticifers, there is an overpressure of up to 1.5 megapascals. After an injury, the emulsion's pressure decreases, causing protein-containing membranous vesicles to rupture and release the hevein proteins they had been holding in. protein-binding sites which are located on the surface of the rubber particles, and when the hevein protein forms dimers with these protein-binding sites (beginning with Ca^{2+} ions), latex particle coagulation results [16]. Innovative bioinspired SHEs with expressive mechanical

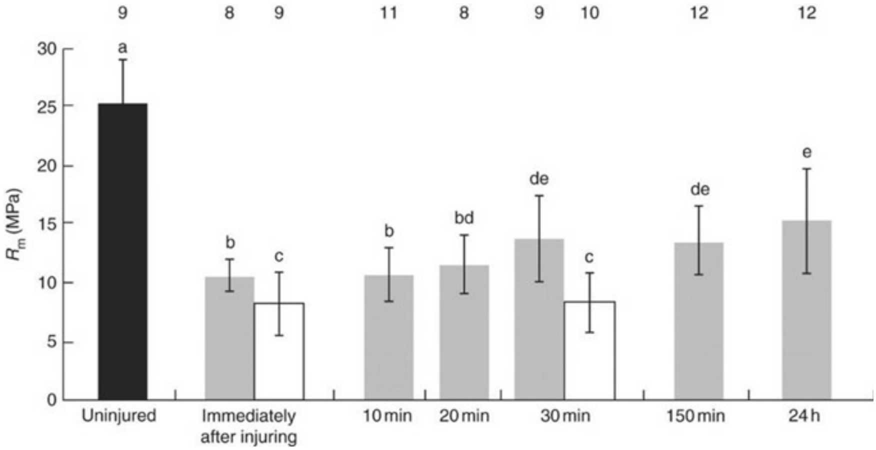


Fig. 3 SH and SS phenomenon in the barks of Ficus benjamina tree. Rm (tensile strength) of unmarked bark (the black columns), and at different times after mark (gray columns). The white columns show bark specimens from which the latex was immediately wiped after mark. Results marked with same letter don't differ significantly [12]

restoration following a macroscopic incision were created using two ways. These SHEs were dependent on the SH mechanism.

First, SH ionomeric elastomers with self-repair capabilities during the nonvulcanized stage but not after full vulcanization were created based on the function of Ca^{2+} ions. Chemically mimicked microcapsules containing SH agents without a hull were created using microphase detached NBR (nitrile butadiene rubber) or hyperbranched PEI (polyethyleneimine) blends in a second method [17].

1.3.3 Nacre-Inspired Self-healing Composites

Because it creates an exceptional mechanical characteristic in combination with strength, toughness, and stiffness, the brick and howitzer edifice of a rigid inorganic portion (95 volume percent interlocking aragonite platelets) and a comfortable biological matrix (5 volume percent protein-polysaccharide) in nacre have attracted a lot of attention in recent years. According to fracture morphologies, Feng et al. found that the three main toughening mechanisms operating on nacre are crack deflection, fiber pullout, and organic-matrix bridging [18]. The remarkable properties of the nacre, a substance made by some mollusks, have inspired many scientific organizations to create synthetic materials with properties similar to the nacre. These attributes include the combination of toughness and stiffness that leads to long-lasting structural ceramics. By combining dynamic polymers with low glass transition temperatures, four hydrogen-bonding motifs, and high aspect-ratio synthetic nano-clays, Zhu et al. were able to produce films that resembled nacre. Because of their exceptional dynamics, all so-called EG-UPy-()-polymers self-heal swiftly and independently following a rupture or cut, and when combined into nanocomposites inspired by nacre, they at least provide the healing of nanoscopic and nanovoid fractures [19].

1.3.4 Hemostasis-Inspired Self-healing Composites

Typically challenging to diagnose, structural issues like delamination, debonding, or matrix cracking finally result in catastrophic failure scenarios. Among other measures, SH systems can stop these problems. In response to these technological difficulties, SH methods for the lightweight materials listed below have been created [20]. Pang and Bond created "bleeding composites," which are SH and are meant to resemble the natural mending process in living things. The release of a healing agent that penetrates the damaged area and can significantly subsidize the restoration of mechanical properties as well as the clemency of a fluorescent tint that contributes to the ocular improvement of the bruise section are two functional principles of the bleeding behavior of liquid-filled cavern fibers. In this instance, hollow glass tubes that function as plies in the composite are packed with healing components (resin with hardener) and fluorescent dye. Based on the healing analysis and healing therapy, these composite systems show point-bending flexural testing [21].

1.4 Self-healing Mechanism in Polymers

When SH occurs in polymers that mechanical characteristic must be recovered by fixing across interfaces created by cutting, breaking, or cracking. It is particularly difficult to repair in thermosets because crosslinks prevent polymer chains from tying surfaces together by creating entanglements over the boundary.

1.4.1 In Thermoplastic

Thermoplastic elastomers are an effective and valuable family of thermoplastics with flexible (rubber-like) properties and essentially no viscous flow at operating temperatures because the chains form physical crosslinks in glassy or crystalline zones with restricted mobility. SH requires a high degree of chain motility without the aid of cures or external stimuli, which seems to conflict with the fixing needed by thermoplastic elastomers to form a lasting network. This remarkable fusion of elastic and SH properties was discovered earlier this year [22]. Leibler and colleagues discovered the complete and spontaneous restoration of mechanical properties in a thermoplastic elastomer by only bringing broken surfaces together.

The system is distinguished by endlessly repeated healing at a low cost and with simple processing, suggesting that it is likely to be applied in industry, as well as thermoplastic melt behavior and consequently less toxicity. This uncommon confluence

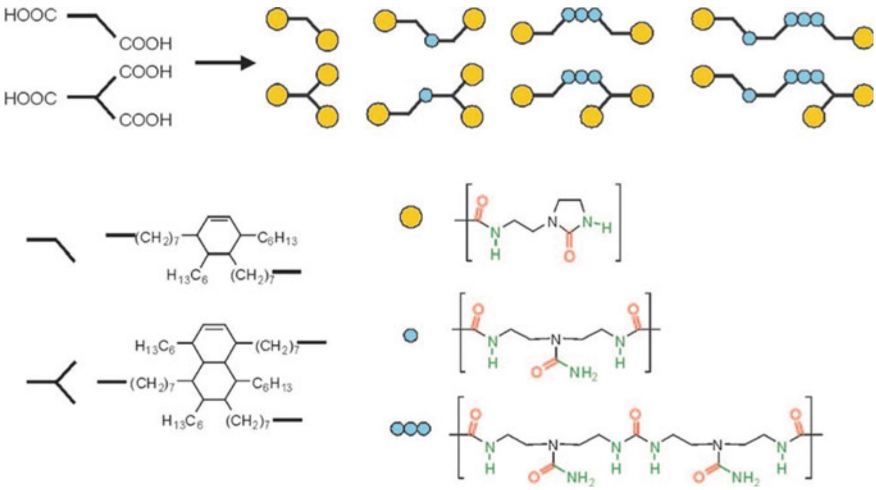


Fig. 4 Schematic diagram of Leibler's SH rubber [10]

of characteristics marks a turning point in the understanding of the SH mechanism and explains why this discovery has attracted the interest of the scientific community, popular science media, and the international press. Leibler's method consists of a few straightforward stages. Diethylenetriamine and later urea are used to treat dimer and trimer fatty acids that are derived from renewable herbal oils (Fig. 4).

The result is a transparent vitreous solid with a 288 °C Tg (glass transition temperature). Multiple di- and trifunctional structural building blocks are combined with various urea and amide compounds that have strong hydrogen bonds to form a supramolecular connection. Because there is a wide variety of species, crystallization is prevented, resulting in higher degrees of stretchability. High temperatures result in a significant reduction in viscosity due to the temperature-dependent strength of hydrogen-bonding units, which makes it possible to quickly melt-process the material into any desired shape [23]. The glass transition temperature (Tg) was decreased, converting the substance into a thermoplastic elastomer by using dodecane (11% by weight) as a plasticizer. Tensile tests revealed elongations at break of more than 500%, which is typical of soft rubber.

Rheological measurements in the shear mode, which showed normal lifetimes for the network of many weeks, revealed the truth of rubbery behavior. This is essential for the material to have low creep: the sample (material) had low and no creep when it was subjected to initial strains of 144 and 32%, respectively, over a long period under continuous loads. Additionally, it was shown that creep is almost entirely recoverable, which means that the sample gradually takes on its former shape. This essential requirement for a functional rubbery material is adequately met by Leibler's substance. The low but significant creep reported here is not conclusive, although the majority of conventional rubbers have no creep at all; the material is likely to work satisfactorily if the right operating circumstances are met. The most surprising quality of this material is its capacity for self-healing [24].

When a sample is divided into two halves by cutting or shredding it, the halves can be brought together and squeezed together to restore the sample's original strength. While bonding takes time to begin and only takes 3 h to attain its maximum strength, adhesion almost immediately takes hold and is strong enough for elements to support their weight. How do Leibler and his friends prevent too much creep from endangering SH? Understanding SH in this material necessitates having a grasp of the kinetics and concentration of highly coupled hydrogen-bonding groups. The hydrogen bonds, not the covalent bonds, are destroyed when the elastomer ruptures, leaving a substantial layer of unconnected groups at the contact. Non-connected hydrogen bonds persist for a while, looking for a friend when they come into contact with another freshly cut surface. The free hydrogen-bonding units on the first surface will automatically look for alternate companions within the same piece if the second surface is not available. The healing process was significantly slower and required longer healing durations when shattered portions were separated for 6 or 18 h before being pressed together. The relatively quick group rearrangements at the boundary produce a special mending process that joins chains that are even a part of the networks on both sides of the boundary rather than relying on the creeping motion of entire polymer chains to restore mechanical properties. In this way, the procedure is practically comparable to Wudl's "reversible-covalent" method [10].

1.4.2 In Elastomers

SH is a valuable characteristic of living tissues that enables them to appropriately mend themselves after suffering mechanical harm. This SH feature, which was inspired by nature, increases the stability and durability of artificial materials, reduces maintenance expenses, and opens up new applications. As a result, SH materials have drawn a lot of attention and have demonstrated great promise in many industries, including flexible robotics, electronic enclosures, and automotive coatings. The first SH compounds in this field 20 years ago were based on extrinsic mending reagents. Their ability to heal is constrained due to a lack of healing agents. Because of this, current research is concentrating on naturally healing substances that rely on non-covalent interactions or reversible-covalent bonds. Inputs of external energy, such as heat and light, are typically needed for the SH process. The development of materials that can self-heal at 25 °C is particularly beneficial because many materials deteriorate in real life when there are no external stimuli present [25].

A typical method for creating materials that heal at room temperature involves taking into account non-covalent interactions such as metal–ligand coordination, hydrogen bonds, host–guest interactions, ionic interactions, and physical forces. A limited number of non-covalent contacts may enhance SH. The materials that are created are, however, typically somewhat fragile. However, a high number of non-covalent connections may compromise the material's SH, flexibility, and stiffness while enhancing mechanical properties. Due to their linear molecular structures, these materials may also exhibit low resistance and probable creep. Many scientists have used dynamic covalent contacts including urea bonds, boron–oxygen bonds, and ionic bonding to generate crosslinked structures to produce reasonably robust healable materials. Conversely, crosslinked networks hinder chain movement and reduce healing capacity. Usually, a material's ability to self-heal and its mechanical properties are interdependently special. Due to their occasionally contradictory demands on molecular structures, it is currently challenging to simultaneously achieve high mechanical robustness and healing efficiency, especially in ambient conditions [26].

Successfully developed SHEs have excellent mechanical qualities and potential functionality. However, although this additional function can significantly expand their uses, adhesion force has gotten relatively little research in these SHEs. SHEs with good stickiness are crucial in applications including artificial skins, wearable electronics, and sealants where direct contact of the functional moieties with elastic substrates is required throughout the lifespan of the product. For instance, the wearable strain sensors described by Zeng et al. depend on close, sustainable contact with human skin to accurately detect human activity, and a break from the skin could impair functioning. In addition, the SH capability extends the lifespan of the device by automatically healing any fractures that may develop over time. Several elastomers simultaneously exhibit SH and sticky properties. However, the bulk of them has significant flaws, such as weak mechanical performance, restricted adhesion strength, or strong adhesion only to specific substrates [27].

2 Evolution of Self-healing Polymers

The progression of SH polymers has occurred in multiple SH strategies that have yielded complex structures competent for supporting numerous cycles, among other properties. This advancement enables us to offer the exertion of a timetable that segregates generations of SH polymers based on the healing mechanism and associated with historical development.

2.1 Key Concepts in Self-healing

Influenced by natural phenomena, SH substances possess the potential to self-heal or self-repair harmful imitating mechanisms originating in living things, like humans and plants. Three ideas have been developed to assure the success of SH: (1) localization; (2) temporality; (3) mobility, as well as a fourth crucial idea; and (4) a classification system (shown in Fig. 5) for different groups of SH materials. The term "localization" is related to the location or magnitude of injury in a product. It might exist on the surface, like scratch marks, (micro) fractures, or cuts, or it might be inside the product, such as the extension of fiber bonding, surface damage, or delamination, leading to serious breakdown or molecular scale damage, such as material network rupture. When examining the material's SH potential, the location and magnitude of these damages are important. The goal is to develop a single technique that ensures healing on all scales. The second component, for the time being, is determined by the difference between the time of occurrence of the injury and its correction. Self-healing is a slow process, not immediate, even in nature. The goal is to decrease the time it takes to heal the body. The third important principle, giving mobility to the material, is one approach to shortening such time. Mobility helps in the delivery of the healers to the damaged region and reestablishment of broken bonds. This concept is important for helping others; for example, if the agent's mobility is insufficient, it will not flow toward the injury or will flow slowly [28].

The mechanism is the final crucial concept in SH. This concept can be used to differentiate between extrinsic and intrinsic SH materials. Extrinsic SH materials depend on an external agent to initiate the healing process, typically in the form of capsules or circulatory networks. Such agents are launched to repair the damage but have no interaction with the matrix. Intrinsically SH materials, on the other hand, are those in which the material's reversible bonds may be reestablished following a damaging event. Extrinsic systems are utilized in thermosets, primarily epoxy-resins, but intrinsic systems are heavily studied in elastomers including silicones, polyurethanes, and GP rubbers [29]. On the basis of SH phenomena and evolution, the SH substances are classified into four generations (Fig. 6).

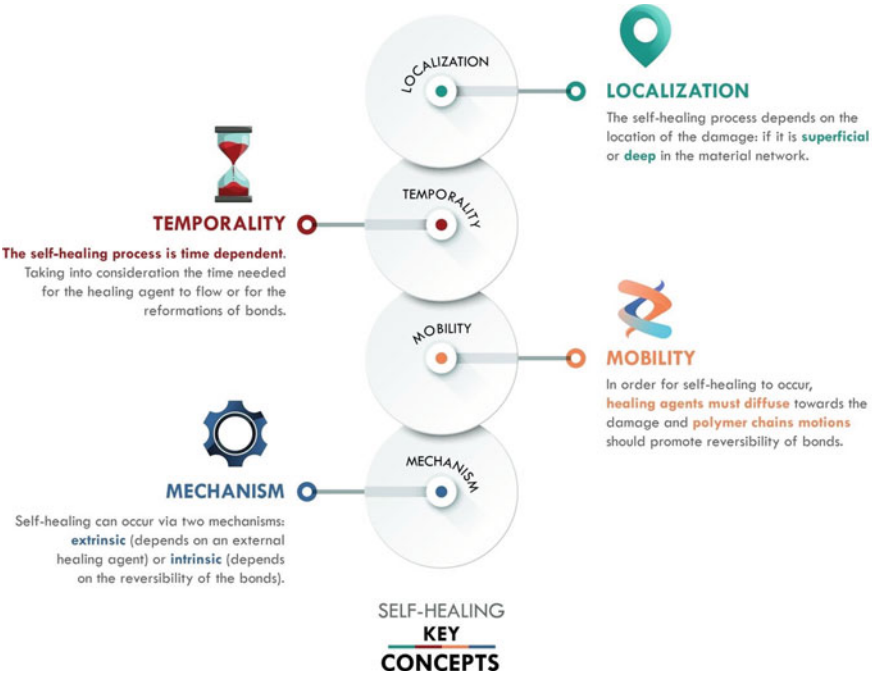


Fig. 5 Key concepts in SH [28]

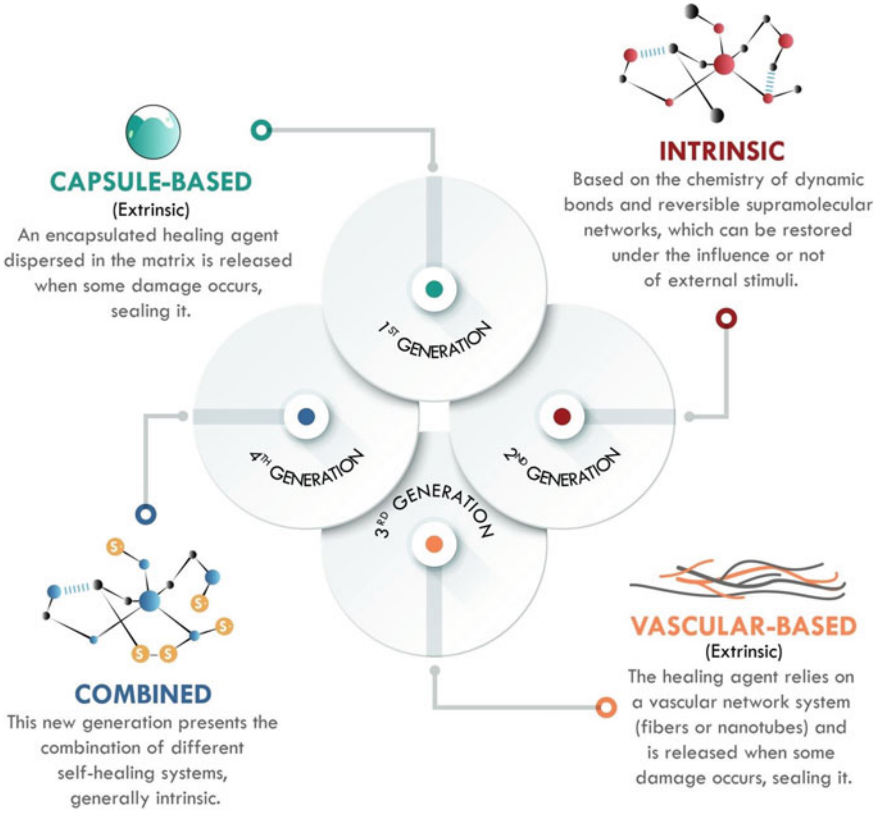


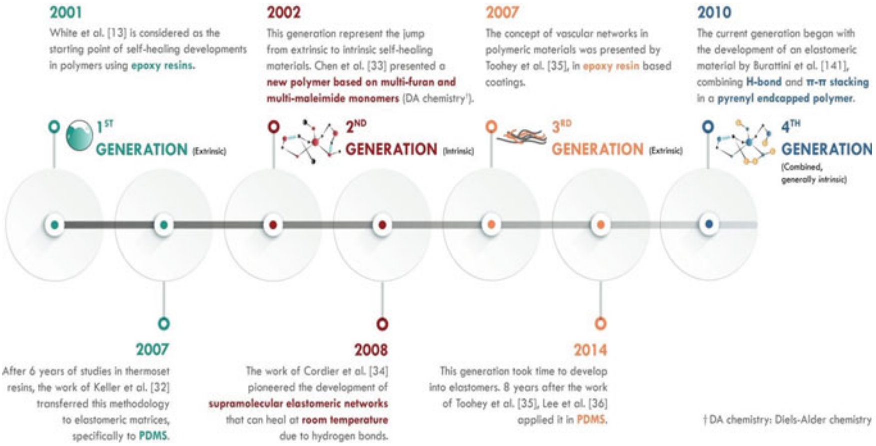
Fig. 6 The SH mechanism involved the different generations of SH materials [28]

Extrinsic processes were used in the first generation of SH substances, which used encapsulated external healing substances. This generation has the limitation of being able to support a single SH cycle only. To address this limitation, the second generation of SH polymer-based substances was developed, based on intrinsic processes and reversible bonds. The material's SH ability and strength, on the other hand, were incompatible: enhancing one meant reducing the other. The intrinsic concept has been investigated in a wide range of polymers, with a focus on elastomers. Furthermore, extrinsic mechanisms were further developed by enclosing healing in vascular networks, opening the pathway for the third generation of SH polymer-based substances. The third generation of SH polymers was inspired by nature. Finally, the fourth generation is rapidly developing, intending to overcome the flaws of the prior generations. As a result, the goal is to combine several healing processes to create a polymer having outstanding mechanical characteristics, good healing efficiency, and resilience to numerous injury loops [30].

2.2 Timeline of Self-healing Polymers

Malinskii et al. published some of the early studies on polymeric SH, notably in PVA (poly-vinyl acetate), in the 1970s, according to the literature (PVAc). Jud et al. and Wool et al. later conducted an extensive study on self-healing in polystyrene (PS), poly-methacrylate (PMA), and hydroxy-terminated polybutadiene (PB). However, all of these investigations, as well as those conducted in the years that followed, were built on chain crosslinking, a well-known polymer concept that requires just a temperature marginally greater than the substance's glass transition (Tg) to occur. According to White et al., the SH was achieved by mixing a healing agent dicyclopentadiene contained in microcapsules with a Grubb's catalyst (platinum catalyst) spread in resin (epoxy). The dicyclopentadiene polymerizes and plugs the fracture when the agent is released and gets into touch with the catalyst. This technique, in its early phases, may recover the maximum weight in a toughness test at up to 75% effectiveness. Keller et al. used a chemical based on the two kinds of microcapsules to implement this method in elastomers, namely, poly (dimethylsiloxane) (PDMS). They entrapped a copolymer (PDMS) and an initiator with an active site that serves to associate the vinyl groups of the bifunctional resin through platinum catalyst accomplishment in one. This chemical process, which also depends on the polymerization of other chemicals, allowed for tears strength of up to 120 percent efficient recovery [31]. The healing agents and catalysts in this initial generation have been categorized in many ways based on their arrangement. The most frequent categories are single capsule, disperse catalyst/capsule, process capsules/droplet, and double capsules, so all capsules (Fig. 7).

In the second generation, dynamic bonding chemistry is applied. Dynamic bonds and contacts are those that are changeable under equilibria and might be covalent or non-covalent. Although reverse chemistry-based polymers have previously been



2001: White et al. [13] is considered as the starting point of self-healing developments in polymers using **epoxy resins.**

2002: This generation represent the jump from extrinsic to intrinsic self-healing materials. Chen et al. [33] presented a **new polymer based on multi-furan and multi-maleimide monomers** (DA chemistry†).

2007: The concept of vascular networks in polymeric materials was presented by Toohey et al. [35], in **epoxy resin** based coatings.

2010: The current generation began with the development of an elastomeric material by Burattini et al. [141], combining **H-bond** and **π-π stacking** in a **pyrenyl endcapped polymer.**

2007: After 6 years of studies in thermoset resins, the work of Keller et al. [32] transferred this methodology to elastomeric matrices, specifically to **PDMS.**

2008: The work of Cordier et al. [34] pioneered the development of **supramolecular elastomeric networks** that can heal at **room temperature** due to hydrogen bonds.

2014: This generation took time to develop into elastomers. 8 years after the work of Toohey et al. [35], Lee et al. [36] applied it in **PDMS.**

† DA chemistry: Diels-Alder chemistry

Fig. 7 Different generations of SH polymers [28] established, Chen et al. created the first SH polymers employing multi-maleimide and multi-furan monomer (Diels–Alder chemistry). Years ago, Cordier et al. discovered and manufactured molecules capable of generating chains and linkers by hydrogen bonding (HB), for the first time incorporating the inherent SH process into an elastomer. As a consequence, they built a supramolecular association capable of self-restoration at ambient temperature [32].

Toohey and colleagues created the third phase of SH polymers. The ultimate stimulation for this generation took a long time to design due to the complexity of combining vascular systems into a polymer matrix. Third generation is categorized based on the properties of the vascular network and the technology used to prepare it. A fourth generation is evolving in this sector. This new phenomenon does not, however, imply that previous approaches are no longer being researched.

2.3 Fourth Generation of Self-healing Elastomers

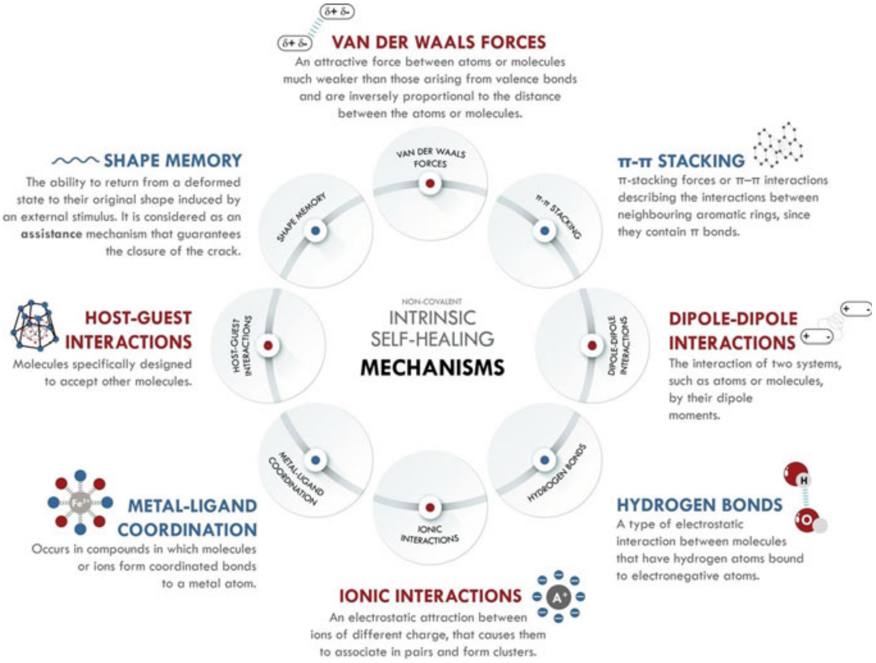
Because of the research of Burattini et al., the scholarly works on merged SH processes have been growing steadily and it has centered on SH intrinsically methodologies, every time searching for an optimum solution pairing of bonds dynamically, whether covalent (the ones that require stimulation for reversibility) or non-covalent (those that do not require a stimulus for reversibility) (due to their ability those are reversible intrinsically) [32].

2.3.1 Combined Non-covalent Systems

In intrinsic SH processes of non-covalent nature, all poor interactions which can occur among various families of atoms, like van der Waals forces, ionic interactions, HB, stacking, metal–ligand cooperation, dipole–dipole interrelations, and presenter interactions, are included. According to some researchers, the presence of the effect of shape memory is responsible for SH abilities (SM). It’s controversial if SM may be considered a process of SH in itself. All non-covalent interactions are summarized in Fig. 8 along with their fundamental description [33].

Although the bonding energy of non-covalent systems is lower than that of pure covalent systems, this system offers better efficiencies of healing because they make it easier to restore broken connections even though kept at room temperature. HB is the most common interaction of non-covalent in elastomers, which has been paired with several other interactions of non-covalent to generate materials for SH with a range of characteristics. Burattini et al. presented a combination of healing components (π-π-stacking and h bonding) in an elastomer network based upon polyimide and PU (polyurethane) including pyrenyl end groups.

The stacking of π-π was because of the diamide groups’ π-electron deficiency and the pyrenyl units’ π-electron abundance. Meanwhile, hydrogen bonds are formed between the pyrenyl groups’ terminal residues in polyurethane at the intermolecular



An attractive force between atoms or molecules much weaker than those arising from valence bonds and are inversely proportional to the distance between the atoms or molecules.

π-stacking forces or π–π interactions describing the interactions between neighbouring aromatic rings, since they contain π bonds.

The ability to return from a deformed state to their original shape induced by an external stimulus. It is considered as an **assistance** mechanism that guarantees the closure of the crack.

Molecules specifically designed to accept other molecules.

The interaction of two systems, such as atoms or molecules, by their dipole moments.

Occurs in compounds in which molecules or ions form coordinated bonds to a metal atom.

A type of electrostatic interaction between molecules that have hydrogen atoms bound to electronegative atoms.

An electrostatic attraction between ions of different charge, that causes them to associate in pairs and form clusters.

Fig. 8 Intrinsic non-covalent SH mechanisms [28]

level. 0.2 MPa was the tensile strength of this material with the efficiency of healing at 80% or more for tensile strength. Ionic interactions are the second most frequent non-covalent mechanism. Xu et al. successfully coupled chitosan nanoparticles with HB to carboxyl styrene-butadiene rubber (XSBR) stacked with them. The synthesis of ionic clusters at room temperature resulted in the network formation of crosslinked supramolecular with reversible links and healing efficiency of up to 92 percent and 1.3 MPa tensile strength. For the first time, Sattar et al. utilized the same combination to make silica-loaded (SiO_2) natural rubber (NR) composites. In their process, ionization of the elastomer's inherent proteins and lipids was employed to form ionic crosslinks [33]. The dynamical supramolecular network was established by the addition of magnesium sulfate ($MgSO_4$), which formed Mg^{2+} ions that produced electrostatic interactions with the negatively charged lipids as a result of acidic ionization. At 50 °C, this procedure yielded healing efficiency of 79% and 18.5 MPa of tensile strength. Fourier-transform infrared spectroscopy (FTIR) compared with hydrolyzed NR indicated the creation of the ionic network, which had a healing efficiency of just 52%.

Polyurethane (PU) was also shown to have these two mechanisms. Because PU and its alternatives are the materials that were studied the most in terms of the mechanism of the intrinsic process, it's not astonishing that they were the first to report a network comprised of three kinds of dynamic bonds: one covalent and two non-covalent, the closing of which is in charge for SH at ambient temperature. Zhang et al. developed a polyurethane elastomer based on a Cu (II)-dimethylglyoxime-urethane complex (Cu-DOU-CPU). Copper ions provided coordination in metal–ligand and formed hydrogen bonds between groups of amino and ester’s main chain. Researchers achieved 14.8 MPa tensile strength and 92 percent efficiency, which could be used in wires [34].

2.3.2 Combined Covalent Systems

Intrinsic covalent processes include any chemical bonds that form between other atoms and can be active in reaction to an external incitement. A schematic representation of several of these bonds as well as their fundamental description is shown in Fig. 9. Disulfides, which can experience catalyzed processes, and Diels–Alder chemistry, in which retro-Diels–Alder and Diels–Alder interactions occur at various temperatures, are other notable examples. Since these bonds have higher energy over non-covalent interactions, their participation is significantly connected to the mechanical performance of the material. Further, it is an important aspect of obtaining high healing efficiency [35].

In opposition to aliphatic disulfides, which require external stimuli, Lee et al. used aromatic disulfides, which may undergo metathesis at room temperature [36]. They developed a PDMS that could be repaired in 4 h, but its mechanical properties

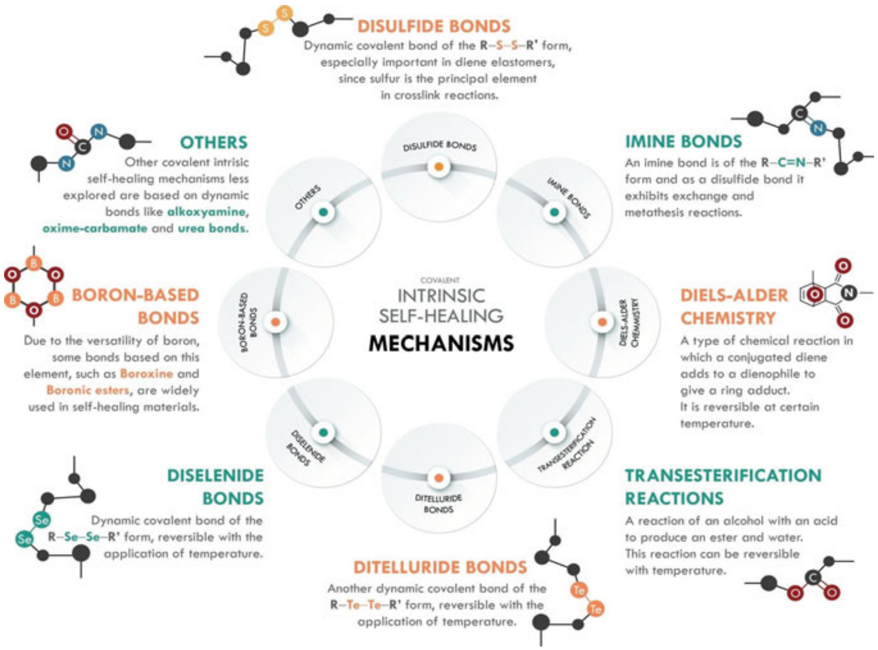


Fig. 9 Intrinsic covalent SH mechanisms [28]

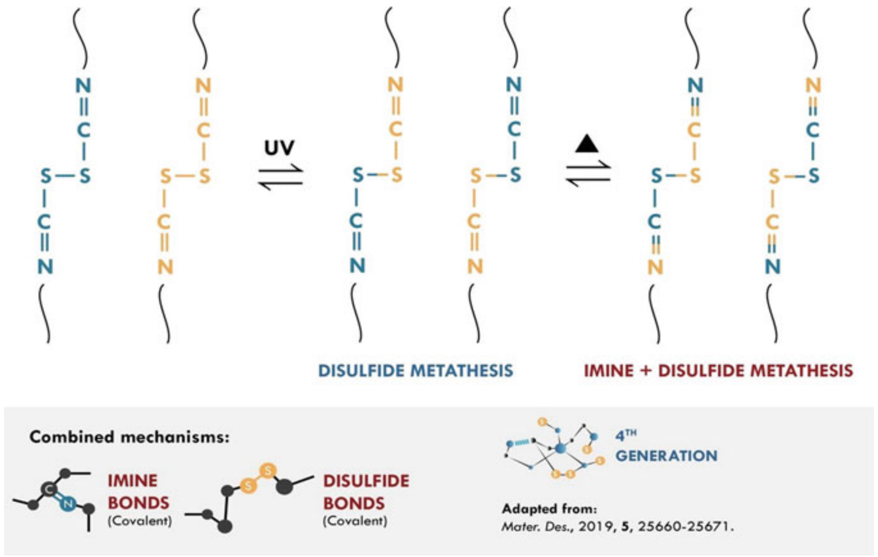


Fig. 10 Disulfide and imine metathesis in PU [28]

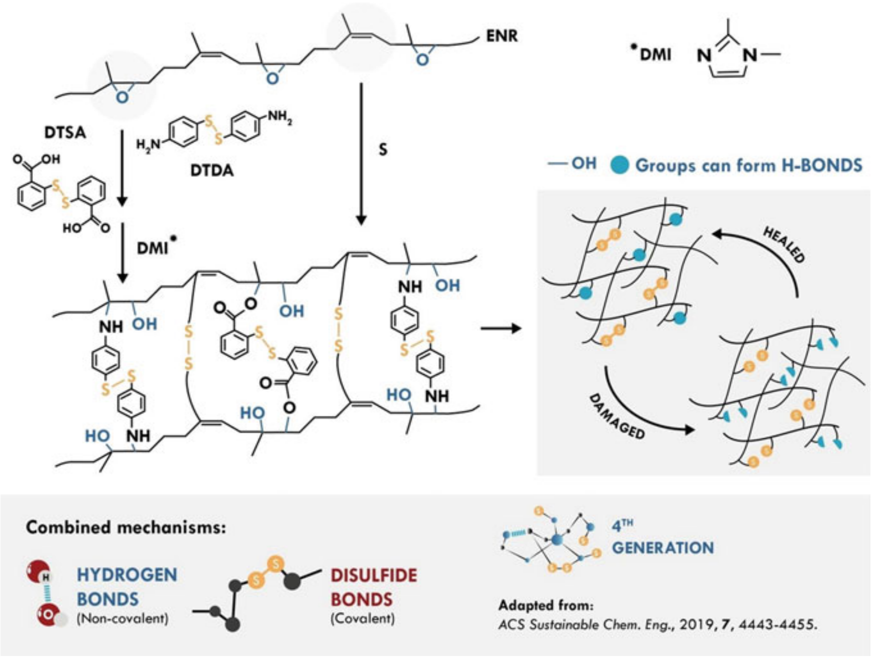
were only 0.15 MPa, which is typical of siloxane-based systems. The disulfide bond, which acts as a sacrificial bonding, is primarily responsible for SH, while the imine bond serves as a crosslink of the semi-permanent site for flexibility and keeping the actual form. Despite its low mechanical strength, this research provides a prototype for some applications (such as adhesives) where good mechanical performances are not necessary. Lee et al. studied the metathesis of both dynamic bonds in PU using the same technique as shown in Fig. 10. The elastomer was formed in two stages. They began by creating a Schiff base using biomaterials such as vanillin and cystine, which is important for disulfide and imine connections [35, 37]. Before adding the PU intermediates (IPDI, isophorone diisocyanate, and poly (propylene glycol)-based thiol), the base was blended with 1,4-butanediol to confirm miscibility. Optical microscopy is used by them to track the healing process and found that using UV radiation and heat (65 ºC), fractures healed completely in 120 min. In addition, the material is 97% recyclable [38].

2.3.3 Combined Covalent and Non-covalent Systems

Among the fourth generation, one of the most traverse systems is the covalent and non-covalent combination, having good efficiency of healing and mechanical properties. As a delegated combination, the generality of PU as material and disulfide bonds/hydrogen bonds can be observed as dual systems. This strategy was first applied by Rekondo et al. using the metathesis of aromatic sulfide to design PUU networking of SH. Thanks to aromatic sulfide, which at room temperature is a constant exchange, and the urea group which can form quadruple hydrogen bonds, they reached 97% healing efficiency [39]. But for high-performance applications the mechanical properties were limited. This limitation was solved by Xu et al. who developed an interesting healing system where it was assisted through sunlight, having a high tensile strength in the production of photosensitive materials with potential applications. Even though to generate disulfide oxide a pure UV was known, if the UV content is low (between 3 and 5%) in sunlight the same effect will be generated [40]. By light chromatography (HPLC) and mass spectroscopy, it's demonstrated that in small molecules the reaction of disulfides was capable of being generated by the component of UV sunlight. This exchange was assisted in this case by the creation of HB between amino groups close to disulfide main chains. With 9.5 MPa tensile strength, they found the efficiency of healing up to 96%. The production of PU with sufficient mechanical toughness has proceeded. All of these advancements in PU permitted employment in the novel application, like 3D printing for other elastomeric materials, which were previously unthinkable. Li et al. announced the creation of the first SH PUs works' digital light 3D printing (DLP), with possible applications in the production of flexible electronics and sensors. Liu et al. have expanded their research on PU below this mixture of processes of healing. Poly (vinyl alcohol)-graft-(-caprolactone) (PVA-PCL) was introduced into isocyanate terminating PU with disulfide bonding. PVA-PCL inclusion increased the production of bonds of hydrogen, which served as crosslink sites physically [41, 42]. They observed a 20 MPa increase in tensile strength and a beneficial impact of the disulfide bonds and hydrogen on the efficiency of healing, which at 90 °C reached 94%. All of the PU work demonstrates a great balance that may be achieved between healing capabilities and good performance mechanically. A general-purpose elastomer has been the second most studied system, particularly epoxidized natural rubber (ENR). Cheng et al. looked into two well-known fundamentals: the vulcanization of the main chains double bonds of cis-1,4 poly(isoprene) as well as the epoxy ring reaction. They used the standard procedure of vulcanization to build numerous sulfur linkages in the main chain, as well as disulfides of aromatic to couple the radical created during the reaction of ring-opening (Fig. 11). At the same time, the event of ring-opening produced a large number of hydroxyl groups, which formed hydrogen bindings that aided the process of SH [43]. At 120 °C this combination produced 9.30 MPa tensile and 98% healing efficiency, as compared to just 22% in an equal sample of free disulfide.

2.3.4 Hydrogen Bonds

Although the specific moment in history when humans discovered HB is still debated, it is believed that humans developed HB more than a century ago. HB is a sort of intermolecular bonding that is available in nature and is vital in activities such as the replication of DNA, protein, molecule recognition, and so on. In recent years, HB has also been used to create novel materials such as elastomers, supramolecules, and SH materials. Figure 3a shows the HB among two water molecules. The fundamental



Adapted from: ACS Sustainable Chem. Eng., 2019, 7, 4443-4455.

Fig. 11 Relation between hydrogen bonds and disulfide in ENR [28]

structure of HB is X–H. Y is made up of two main parts: the acceptor of a proton (with lone pair electrons in Y atom, A for short) and the proton donor (XH, D in short) [44]. A single hydrogen bond has low bond energy below 40 kJ/mol, which equates to one-tenth of binding energy for covalent (400 kJ/mol of CC bonding). As a result, we may be able to use dynamic HB to construct polymers having high SH but weak mechanical properties and tensile modulus. Even though HB can result in potent polymers with good mechanical properties comparable to hydrogen bonds, covalent polymers in such polymers are reliable, necessitating the extra energy required to fracture the prior strong interaction and afterward reconstruct an innovative HB system. Large polymers can be formed by powerful connection bonding, but their ability to self-heal is impaired. Multifunctional hydrogen with high accredited and the directed link receives a lot of attention for balancing bond strength and SH capacity [45].

Quadruple hydrogen bonds have a complicated system that must be created by two distinct molecules or by the oligomerization of a single molecule. The triple hydrogen-bonding relationship is quite strong. As shown in Fig. 12, we want to include two self-complementary triple hydrogen-bonding configurations: ADAD-DADA and AADD-DDAA [46].

The type of ADAD dimerization of the molecule results in six mutually exclusive secondary interactions resulting in the weak strength combination of the hydrogen bonds ADAD-DADA quadruple, whereas the dimer of DDAA-type molecules

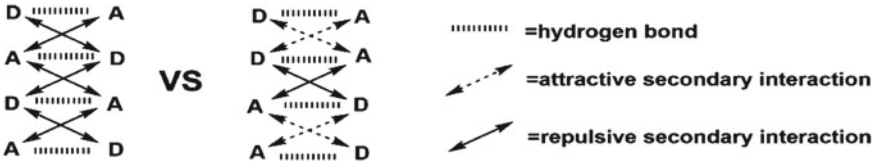


Fig. 12 Interactions and chemicals structures of DDAA and DADA dimers [46]

only has two mutually unique secondary interactions as well as four mutually hyper-attractive secondary interactions [46, 47]. As a result, the hydrogen-bonding quadruple has stronger connection in the DDAA-AADD dimer than in the dimer of ADAD-DADA.

2.3.5 Positions of H-Bonding Units in Elastomers

As previously noted, the several hydrogen-bonding dimer units can influence the characteristics of elastomers that as SH, like increased in strength mechanically, extensibility, expandability, and toughness in the resulting polymers. The density of crosslinked H-bond is determined by the location of numerous hydrogen-bonding units, which affects the properties of the ultimate material. The mechanical characteristics of various hydrogen-bonding polymers are mostly determined by the number of dissimilar hydrogen-bonding molecules and by crosslinking density [47].

2.3.6 H-Bonding Units as Chain Terminals

Because of significant constants of the heterodimer, UPy units near terminals of the chain (or ends) might be thought to increase the lengths of the main chain of the polymer, hence promoting characteristics thermally and mechanically. Furthermore, the UPy unit at the ends of the chain can provide the exceptional SH capabilities of polymers. Guan group created the first block copolymer of SH in solid form utilizing a new multiphase and biomolecule copolymer structure (poly1,2,3, Fig. 13a).

These microphase-separated molecule copolymers integrate the rigidity and toughness of thermoplastics with the dynamic and healing abilities of biomolecule materials, resulting in fast structural rigidity and elasticity recovery. Pyun et al. synthesized perfluoropolyether's (UPyPFPEs, Fig. 13b) UPy-capped that recovered the modulus of storage to its original value at 130 °C in 2 min due to the creation of crystalline structure phase separation based on UPy domains between the softer polymer matrices and the hydrogen-bonding molecules [48]. The PFPE surface modification with alkylated UPy groups, on the other hand, showed an increased time to regain the compressibility of 18 min at 110 °C, suggesting hindered crystallization.

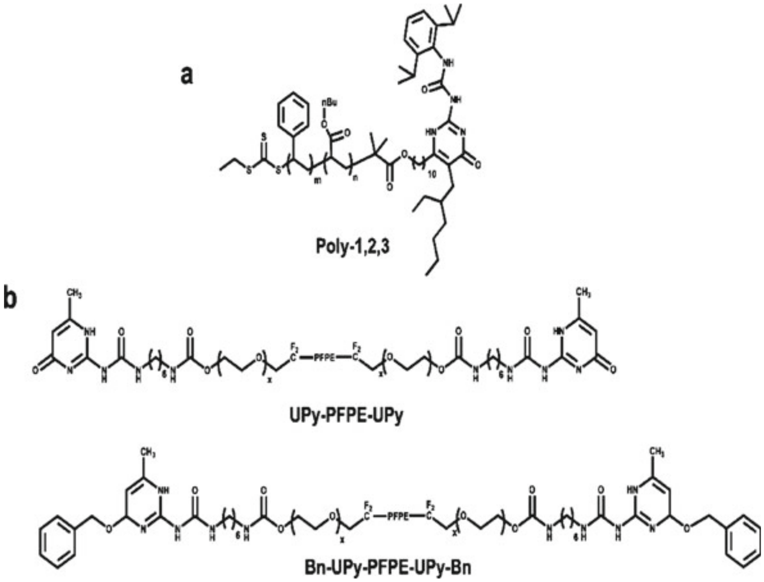


Fig. 13 Self-healing elastomers with H-bonding units as chain terminates [46]

2.3.7 Hydrogen-Bonding Units in the Main Chain

The creation of solid-like hydrogels was induced by the separation of phase domains of hydrophobic hydrogen bonding formed by UPy molecules with a PEG backbone network inside the main chain of bifunctional PEG to UPy (Fig. 14a). When the solid-like hydrogels were heated at 50 °C, they discovered SH activity. Bao and colleagues have synthesized polymeric supramolecular materials (SPMs) containing units of UPy in different concentrations (from 0 to 30 mol percent) in the main chain. Figure 14b illustrates the chemical compositions of the SPMs. The Fu group devised a unique technique based on numerous active HB to provide quick and efficient SH under room temperature or in difficult settings. Thiourea molecules were integrated into the separated microphase network of polyurea at the same time to generate multi-strength H-bonds (Fig. 14d), and hard domain crystallization was introduced with the dynamic H-bonds reversibly both in segments of soft and hard. Another elastomer based on UPy was constructed with spacers units packed loosely in a supramolecular elastomer, illustrated as shown in Fig. 14e, to resolve the mismatch of SH and strong strength at room temperature inherently. Aida report indicates strong mechanical SH materials with thiourea create an unusual zig-zag hydrogen-bonded structure (Fig. 14f).

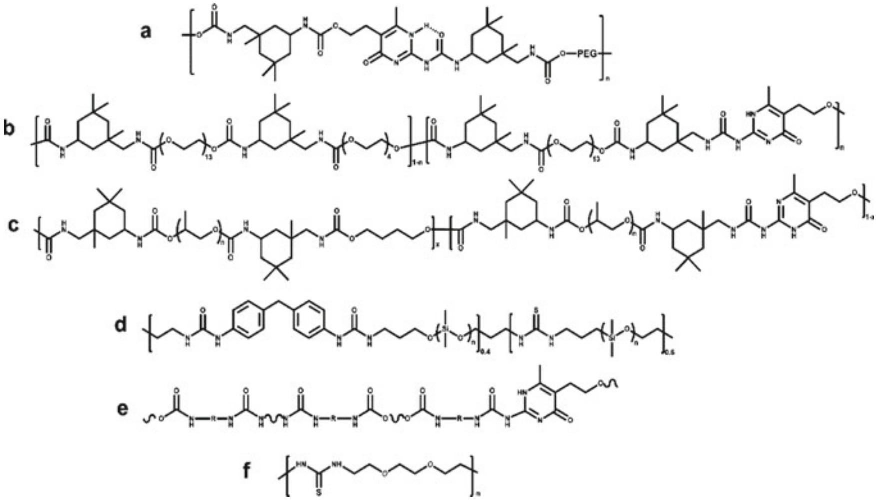


Fig. 14 SHEs with hydrogen-bonding units in the main chain (**a**–**f**) [46]

2.3.8 Hydrogen-Bonding Units in the Side Chain

By adding units of UPy into the side chain, Zhu et al. generated PU. They created a copolymer with a side chain of carboxyl\and then combined it with glycidol to create PU via UPy with NCO molecules. When heated, the as-synthesized PU displayed SH properties for thermal reversibility of UPy units. Lei and colleagues developed a biomass-derived elastomer for SH by combining multiple hydrogen bond formations (UPy) in the side chain with crosslinked covalent. The elastomer's dynamic nature and soft features resulted in greater extensibility and SH capacity, where the crosslink of covalent can help in the re-assembly of disrupted H-bonds (Fig. 15). As a result, the coarse elastomer had a 2600 percent break elongation and 42.76 MJ m^{-3} toughness. Furthermore, after 24 h of healing at 60 °C, the elastomer showed excellent SH ability with full scratch healing and outstanding mechanical recovery at 1900% extension and 24.1 MJ m^{-3} toughness [49].

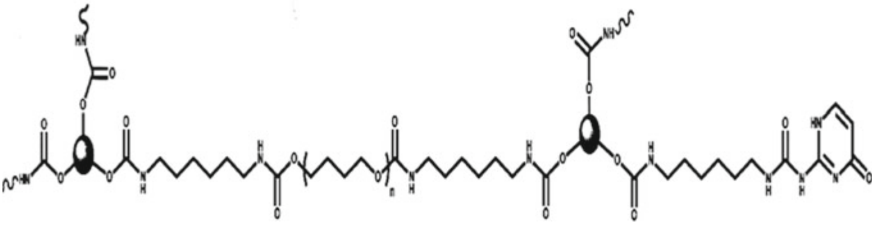


Fig. 15 Chemical structures of SHEs with H-bonding unit in the side chain [46]

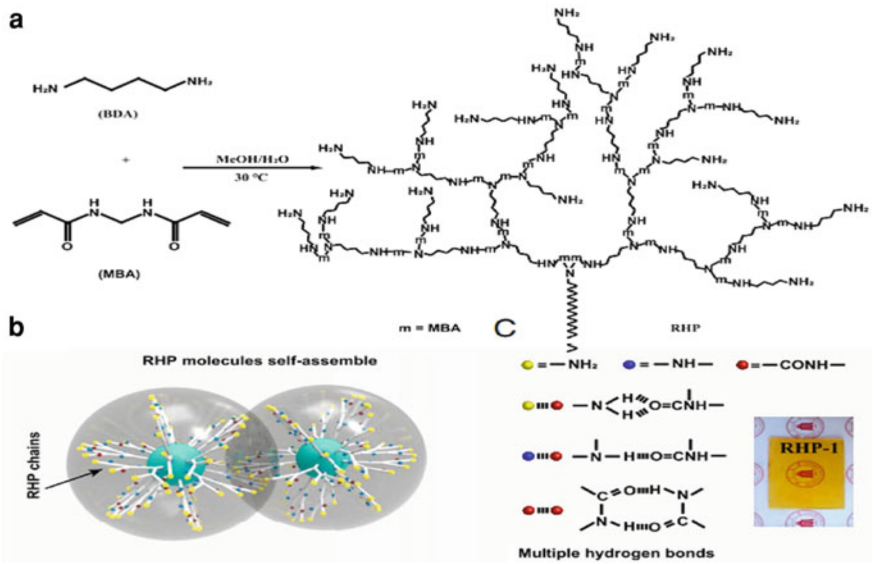


Fig. 16 Synthesis of RHPs: **a** Synthesis of the RHP, **b** Interactions between the two RHP molecules. **c** Multiple H-bonds of RHP. (Inserted) An image of (RHP-1) [46]

2.3.9 Hydrogen-Bonding Units in Branched Polymers

The Wu group created a series of random hyperbranched polymers (RHPs) with a higher density of bonds of hydrogen enabling the mechanism of SH at room temperature, as illustrated in Fig. 16. Internal molecular fragments are severely limited and have little molecular mobility in glassy hyperbranched polymers, but exterior units of branching have significant mobility in end groups [50]. As a result, the authors proposed many hydrogen-bonding groups of complimentary achieve SH by adjusting the polymer's exterior group of terminal and side chain. These polymers include many amino, amide, or other groups and are capable of forming high-density hydrogen bonds. At room temperature, 5.5 MPa tensile strength may be recovered after contact with the substance for 1 min.

2.4 Different Categories of Self-healing Elastomers

2.4.1 Self-healing PDMS

The well-known elastomer is PDMS composed of Si–O–Si molecules. Because of its exclusive structure, poly-siloxane provides compensations such as low and extreme temperature resistance, resistance to weather, ozone resistance, electrical insulation, gas permeability, hydrophobicity, bio-inertness, and non-toxicity. It's extensively used in electronics, universal health care, aircraft, textile, and other fields. Normal poly-siloxane, on the other side, does not have the same mechanical strength as polyurethane. Because poly-siloxane products are usually affected by external forces throughout the molding and usage process, scientists are striving to develop poly-siloxane elastomers having SH characteristics [51]. In the following sections, we shall explore various forms of PDMS SHEs due to several dynamic bonding mechanisms.

2.4.2 Diels–Alder Bonds

Even though a variety of SH polymeric materials based on DA connections have been developed, the large bulk of the system is PUs. SH poly-siloxane elastomers based on DA interactions are seldom described, likely due to the difficulty in identifying a suitable precursor for the production of SH PDMS. To create a successful SH PDMS, the stability of the two major pioneers, the reactivity of DA bond components (maleimide or furan) inside the predecessor, and the network of crosslinking variables such as molecular chain motility and degree of crosslinking must all be taken into account. Zhao et al. developed thermal-treatable PDMS elastomers for the first time by employing the DA reaction to crosslink polydimethylsiloxane with maleimide pendants with furan-end bifunctional siloxane [51, 52]. DA bonds could be ruptured at 140 °C and reconstructed at 80 °C. As a consequence, the healing therapy is divided into two phases: heat at 140 °C for 3 h and at 80 °C for 24 h, with a SH competence of 95%. They developed another thermally treatable poly(siloxane-urethane) elastomer (PDMS–DA–PU and PDMS/ PCL–DA–PU) to DA bonds distributed throughout the polymer chain among crosslinked locations to use self-made soft sections, isocyanate discharged polydimethylsiloxane (NCO–PDMS–NCO), or a combination of NCO–PDMS–NCO as well as polycaprolactone diol.

2.4.3 Disulfide Bonds and Hydrogen Bonds

Using a urea-containing chain-extended PDMS and multi-amino terminated hyperbranched poly-siloxane, Zhang et al. developed an innovative type of keep-going trying to expand PDMS rubber (LP2-SS-HP) with dynamic changing crosslinks due to hydrogen bonds and also chemical crosslinking induced by controlled interchangeable aliphatic disulfide. Tg, tensile strength, elastic modulus, and hardness of customization are as strong as 96 °C, 8.6, 188.5 MPa, and 16.3 MJ m^3, correspondingly. Depending on tensile, elongation at break, or toughness, the cut-off films had a healing efficiency of greater than 90%. These materials have a significant advantage in that they have a high modulus and strength without compromising ductility, and they can also be mended fast following mechanical failure [53].

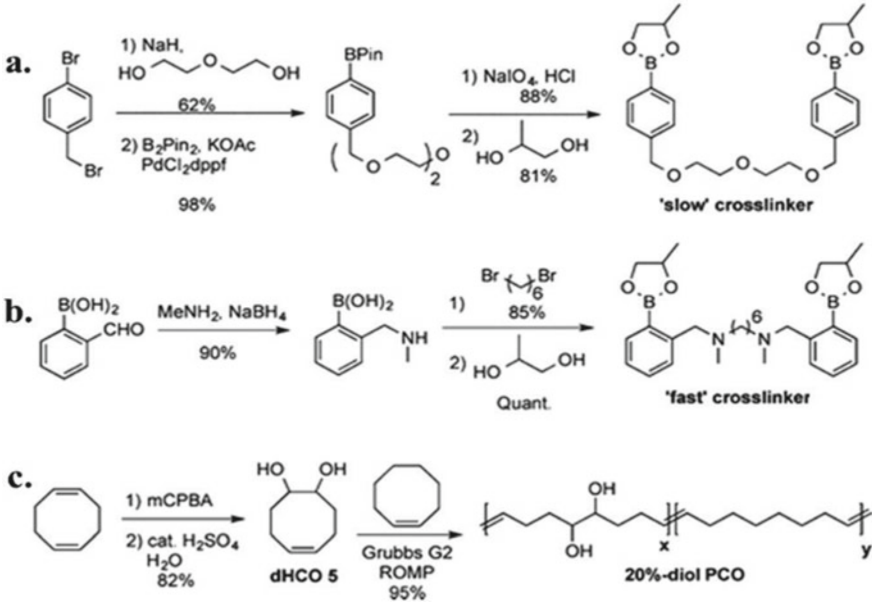


Fig. 17 Synthesis of **a** slow diphenyl-boronic ester crosslinker 3, **b** fast-di(o-amino-phenyl-boronic) ester crosslinker 4, **c** 1,2-diol-containing polycyclooctene (20% diol-PCO) [20]

2.4.4 Boronic Ester Bonds

Sumerlin et al. presented an elastomer based on thiolene reaction with outstanding SH expected to attain a dynamical boronic ester link. In their investigation, they synthesized and integrated a boronic ester diene into supporting a radically based thiolene technique. This elastomeric can be repaired at room temperature and has an efficiency of SH of 90%. However, water or a high moisture environment must be present to encourage SH action [54]. Guan et al. demonstrated how to use varying degrees of boronic ester esterification reaction to adjust the mutability and SH effectiveness of bulk polyolefin materials. They used a "slow" di phenylboronic esters crosslinker and a “fast” di (o-amino phenylboronic) ester crosslinker to crosslink 1,2-diol-containing polycyclooctene (Fig. 17a–c).

3 Applications

Contrary to conventional inorganic non-metallic and metallic materials, polymer materials own a more friendly preparation technology. Because of their functionality, multiple forms, and lightweight properties, resulting in irreversible roles in our routine life and industrial applications. Among the other polymer-based materials, SHEs can not only increase the stability and safety of procedures. They also stimulate industrial development, prolong the service life, and have colossal commercial value. Other than this, SHEs also play an important part in expediting the effective usage of properties and the viable development of mortal society. The proclaimed SH elastomeric materials with a specific function have provoked great interest, implying the vision of effective growth.

4 Conclusions

The biological evolution, healing, and sealing wounds have been a fundamental function of the living environment, operating freely and at varied times in animals, plants, and all other living groups of things. Engineers and biologists have developed an increasing interest in these SH mechanisms as they represent a rich resource. The most common and well-known methods to gradually translate biological perceptions into technical objectives are biologically stimulated design and biomimetic access. However, just a handful of SH materials systems based on biological techniques have been developed in recent years. In contrast to the undamaged sample, these procedures can restore structural integrity and mechanical qualities as well as heal or (partially) repair damage. Most solutions presented are schematic conceptions created on a laboratory scale, but only a small number of situations can typically be realized as market items.

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