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A review on self-healing polymers for soft robotics

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The intrinsic compliance of soft robots provides safety, a natural adaptation to its environment, allows to absorb shocks, and protects them against mechanical impacts. However, a literature study shows that the soft polymers used for their construction are susceptible to various types of damage, including fatigue, overloads, interfacial debonding, and cuts, tears and perforations by sharp objects. An economic and ecological solution is to construct future soft robotic systems out of self-healing polymers, incorporating the ability to heal damage. This review paper proposes criteria to evaluate the potential of a self-healing polymer to be used in soft robotic applications. Based on these soft robotics requirements and on defined performance parameters of the materials, linked to the mechanical and healing properties, the different types of self-healing polymers already available in literature are critically assessed and compared. In addition to a description of the state of the art on self-healing soft robotics, the paper discusses the driving forces and limitations to spur the interdisciplinary combination between self-healing polymer science and soft robotics.

Introduction

The need for robots that can safely interact with humans has led to the emergence of the field of "soft robotics" [1,2]. This new class is recently gaining a tremendous interest in the robotics community, in academia [3] and in industry [4,5]. In soft robots, body parts, or in some cases the entire robot, consist of a continuously deformable structure, which is in many cases made out of elastomeric polymers [6,7] including silicones [8] and polyurethanes [9]. The soft body parts have a comparatively large number of degrees of freedom, leading to interesting large-scale deformation modes [10]. Most of these flexible devices are actuated through variable length tendons [11] which can be integrated tension cables or shape memory alloy cables [12] or through shape memory polymers [13–15] or they are pneumatically driven by placing their internal fluidic channels and chambers under pressure [16,17] or under vacuum [18]. Being made from flexible material, they have an intrinsic compliance that leads to interesting features, such as resilience to impacts and collisions due to shock absorbance [19,20] and safety [21,22]. Consequently, soft robots are suitable for applications in uncertain, dynamic task environments and for safe human-robot interac-

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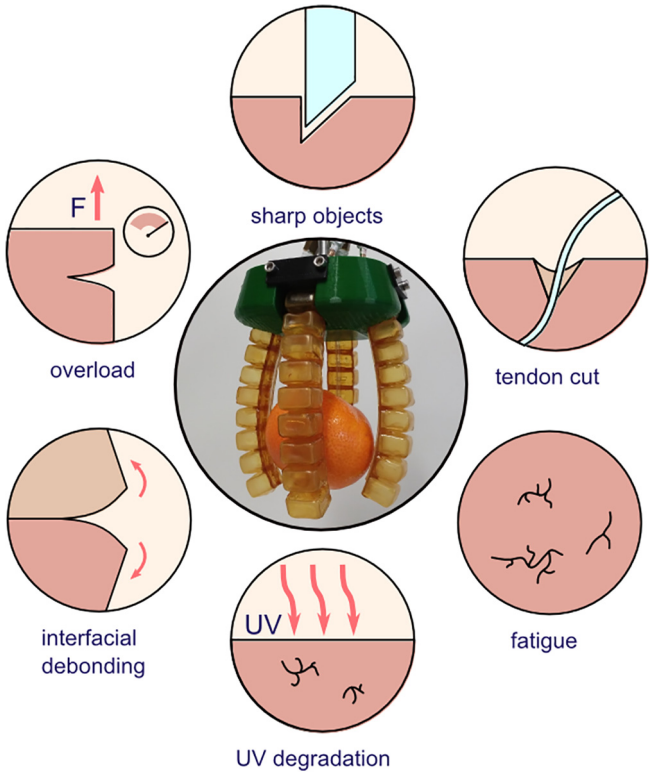

FIGURE 1

Damaging modes for soft robotics in unstructured and dynamic environments.

tions [23]. In addition, due to their high degree of compliance, soft actuators will adapt their shape when in contact with an object. This makes them good candidates for grippers and manipulators that handle soft and delicate objects [24,25] like fruits and vegetables that are susceptible to bruising [26] and even fragile corals [27]. They are already commercially available from companies like Softrobotics Inc. [4] and Empire Robotics [5,28] and will be increasingly operative in the food packaging industry [29,30] in agriculture, and in industrial pick and place of objects with irregular shapes [28,31]. Safe interaction with soft matter is also required in many biomedical applications. Soft robotics, consisting of synthetic materials with a compliance (elasticity modulus) comparable to the one found in soft tissue in the human body ($E = 10^3$–10^7 Pa) [32] are used in many biomedical applications [33,34] including minimal invasive surgery [35,36] prosthetics [37] and exoskeletons [38].

Despite the many advantages of soft materials, their usage in robotics does present challenges in terms of damage resistance. Due to the flexibility of the synthetic materials, soft robots are prone to a number of damaging modes (Fig. 1). First, the soft parts are highly susceptible to cuts, tears and perforations caused by **sharp objects** present in the uncontrolled and unpredictable environments, in which these robots operate. This highly limits their lifespan. In case of the commercial jamming gripper Versaball of Empire Robotics, its lifetime is reduced from 50,000 to 5000 grips in situations where sharp objects can be present [28]. When actuating soft robotics using tendon mechanisms, the hard tendons, which are in many cases polyamine or Kevlar wires, can cut through the soft parts [39]. This **tendon cut** can occur gradually, due to abrasive damage resulting from repetitive friction between the tendon and the soft materials [40] or upon overloading the actuators, when the tendon slices through the soft material.

As typically a large part of the soft robot's body undergoes cyclic deformation upon operation, these parts are susceptible to **fatigue**, the formation of microdamages due to cyclic loading, which gradually propagate into larger macroscopic damages and eventually failure of the components [41]. In soft pneumatic actuators, fatigue results in leaks and therefore a decreased efficiency, a change in actuator dynamics and eventually failure, as described for the soft muscles in [42] and [43]. Fatigue occurs more quickly and more pronounced at the location of the highest local stress. As such, the fatigue life can be improved by design principles that reduce stress–strain concentrations [44]. However, this principle limits the design freedom for future soft robotics.

When **overloading** a soft robotic component, the induced stresses can exceed the mechanical strength of the elastomer, which can lead to rupture of the flexible body of the robot. These ruptures can occur when a too high force or power output is requested, due to external impact or collision, or when the parts unintentionally snag on an object or surface. In pneumatic actuators the air chambers or channels can burst upon excessive pressurizing.

Many soft robots are produced through moulding or casting techniques [7]. Often multi-step casting or moulding is required, in particular for manufacturing fluidic actuators [17] where hollow structures need to be produced, and in case of multi-material designs. During a moulding or casting step, the prepolymer cross-links and solidifies in a mould. Parts made in different moulding steps are joined by an adhesive or some uncured prepolymer. However, this multi-step manufacturing technique introduces weak (multi-) material interfaces in the soft robots that rely almost fully on secondary (physical) interactions rather than covalent bonds. Upon extensive loading or multiple actua-

TABLE 1

Traditional classification of SH mechanisms in polymers.

Non-autonomous	Autonomous	
Thermoreversible covalent bonds	Hydrogen bonds	Healing agents encapsulated in:
Photoreversible covalent bonds	π- π stacking	Capsules
Exchange reaction covalent bonds	Metal-ligand (coordination) complexes	Tubes
Ionic (coordination) complexes	Mechanochemical covalent bonds	Vascular systems
High-temperature transition phase		
Intrinsic		**Extrinsic**

tion cycles, these weak interfaces fail and **interfacial debonding** occurs. Researchers often refer to this phenomena as delamination, [26,45,46]. Delamination is problematic in fluidic actuators, as it leads to leaks and a reduced performance. In some additive manufacturing techniques for soft robots, like fused filament fabrication, weak interfaces are created between the print layers. Consequently, delamination at the print layer interface can cause failure as well [47,48]. Finally, being constructed out of organic materials, soft robots will suffer from photodegradation when exposed to UV radiation. Although not reported in robotics papers, **UV degradation** of silicones [49] or polyurethanes [50] will affect the properties of soft robots over time.

Aside from the above-mentioned classification of the origin of damages, damages can be classified into *damages that lead to a loss in performance and efficiency* and *damages that lead to a complete loss of functionality and failure of the component*. Currently damage in soft robotics systems is solved by simply replacing the damaged component. Although being manufactured out of relatively inexpensive materials, the cost of replacing a failed component can be high. The robotic systems can be complex, consisting out of many components, which can complicate repair, leading to long offline times. One way to deal with this is to construct the soft robotic systems out of modules [51,52] that facilitate replacing damaged parts. When a soft robot that is performing a task in the open field fails, a spare part must be brought to the location of failure or the robot must be transported to a maintenance point. This transport can add to both the offline time and the maintenance cost. In addition, replacing damaged components is not the most ecological solution since it leads to waste components, made from synthetic polymers that are in most cases not recyclable.

Looking at biology, there is another approach for dealing with damaging conditions. A large part of the human body consists of soft tissue that gets easily injured. To compensate for this weakness, our body possesses a healing ability that allows healing small wounds, like scratches or cuts in our skin, and even larger injuries, like torn muscles or broken bones. Developing soft robotic components out of synthetic materials possessing a biomimetic healing ability would permit the healing of microscopic and macroscopic damages. This would provide a more economical and ecological solution to the fragility of soft robots. Over the last 20 years, chemists inspired by the powerful biological healing function have managed to incorporate similar functions into synthetic materials to create **self-healing (SH) polymers** [53–55]. Since the pioneering works by C. Dry in 1994 [56] and later by White et al. [57] a wide range of SH polymers and SH mechanisms has been developed, based on a variety of chemical principles [54,58–61].

In this review, the potential of diverse SH polymers to construct soft robotics components with an incorporated healing ability is investigated. To introduce the SH technology, the paper starts with a general classification of SH mechanisms. To evaluate and compare the SH mechanisms, five criteria were defined based on the requirements for future self-healing soft robotic systems. Next, the most promising SH polymers described in literature are listed and compared based on their mechanical properties, healing stimulus or the lack of it, and healing efficiency. Based on this, limitations, general trends and trade-offs in material properties are identified. Finally, the few self-healing soft robotic systems already found in literature and their respective SH mechanisms are critically reviewed.

Classification of self-healing polymers

While healing mechanisms have been incorporated in ceramics [62,63] and metals [64–66] most progress has been made in SH polymers [54,58–60,67] due to their higher molecular mobility, which enhances healing and can provide the flexible characteristic required for soft robotics [68]. The healing mechanisms in polymers [61,69–73] can be classified as illustrated in Table 1. Based on the need for an external trigger to start the healing action, healing mechanisms can be defined as autonomous or non-autonomous. In **Autonomous** systems the healing mechanism is triggered by the damaging itself. Many of them closely resemble biological systems, which deliver healing agents to compromised regions as soon as damage is initiated. **Non-autonomous** systems require an external stimulus to activate the healing mechanism. This stimulus can be in the form of heat, light, mechanical force or a chemical change. Note that in some conditions, the healing action may not happen autonomously in SH polymers classified as autonomous, *e.g.*, at very low temperatures. Conversely, materials from the non-autonomous class can heal autonomously in certain environmental conditions, *e.g.*, when exposed to heat during normal application cycles or to irradiation from direct sunlight.

Alternatively, SH mechanisms can be classified as extrinsic or intrinsic (Table 1). **Extrinsic** SH materials have a healing ability incorporated into the material system that is not original to the material, such as healing agents that are encapsulated in microcapsules [74] or in vascular systems [75]. These extrinsic SH materials are often autonomous, as the trigger used to activate the healing action is the damaging force that leads to the rupture of the encapsulation and the release of the healing agent. **Intrinsic** SH materials on the other hand, rely for their healing capacity on chemical groups and properties inherent to the material, *e.g.* reversible chemical bonds [76].

Requirements of SH polymers for soft robotics

The integration of a healing ability will significantly reduce maintenance costs of the robotic system, only if the recovery of functionality is performed completely autonomously, *i.e.* without human intervention. Considering this, autonomously healing polymers are interesting, because their healing mechanism does not have to be triggered externally. However, for soft robotics applications, non-autonomous healing mechanisms should not be excluded. The demand for an external stimulus is not necessarily a big obstacle, as in most soft robotic systems, a power source, *e.g.*, a battery or connection to the grid, and a control system are present. A stimulus providing system can be added to the soft robotic device. For example, a heating system can be integrated on the material level by incorporating conductive or magnetic fillers in the self-healing matrix for ohmic or inductive heating [77] by incorporating conductive fibres [78] or on the actuator level by adding flexible heaters, similar to what is done in [79,80] for temperature controlled actuation. Another approach for untethered robotic systems is to use a

"healing station". Because of the finite battery capacity of robotic systems, they need to regularly go to a recharge point. This recharge point can be expanded with a system that provides the stimulus required for the healing process. In addition, the need for a stimulus can be an advantage in robotic systems, because it enhances the control over the healing action, which can be performed at any desired time. This is particularly interesting when damage does not lead to complete failure and the system can temporarily continue its functionality with reduced performance. Healing in soft robots made of autonomous SH polymers should be performed instantaneously after damage, possibly requiring an immediate halting of all operations to ensure correct healing.

To determine the potential of the various SH mechanisms (Table 1), five criteria (C) were defined that ensure a successful incorporation of a relevant healing ability in soft robotics.

C1: Macroscopic damage can be healed completely. A first criterion for evaluating SH materials for soft robotics is that both microscopic and macroscopic damages of adequate sizes for the intended application need to be healed completely. Relevant damage sizes could for example depend, depend on the expected size of sharp objects encountered in the robot's environment. Fatigue damage in soft robotics is in general difficult to measure at an early, microscopic stage. Remaining unnoticed, the microcracks propagate during cyclic loading into larger, macroscopic cracks [44,48,81,82] that may become more difficult to heal. Hence healing them at an early stage in their development would be advantageous.

C2: The healing can take place multiple times at the same location. Soft robots will meet various dangerous situations while exposed to an unstructured and dynamic environment and can be damaged multiple times. Similar to the human body, specific locations will be more likely to be exposed to damage events, *e.g.*, the contact surfaces of soft grippers, external surfaces, surfaces touching tendons, or locations having higher stress concentrations during actuation, which are more prone fatigue and delamination. Damage is likely to, occur multiple times in such location. Therefore, the healing mechanism should allow multiple damage-healing cycles at a single location.

C3: The initial properties are completely recovered after healing. The control of soft robotic components depends on accurate knowledge of the structure and mechanical properties of the components. In order to maintain full performance and to retain control capabilities, the material properties should be completely preserved. Although not preferred, to some extent, an incomplete recovery could be compensated by a recalibration. In view of criterium C2, also the healing properties should be recovered completely.

C4: It is possible to obtain an elastomeric behaviour. The healing ability will be introduced into soft materials to construct flexible structural components. Although SH glassy thermosets [83] can be used to make healable stiff components for (soft) robotics, the focus of this review is on elastomers. Therefore, the SH mechanisms should function in polymers with an elastomeric behaviour and the resulting elastomers need to meet the requirements for soft robotic materials [8,68]. The viscous contribution in their viscoelastic behaviour should be limited, to avoid undesired phenomena like stress–strain hysteresis and creep [68] which have a negative effect on the energy efficiency and the dynamics of the soft robotic components. Hence, the elastic recovery should be fast and complete. Preferably, the mechanical properties of the elastomers can be tuned over a broad range, to match their intended application, and high mechanical strengths can be achieved. A low mechanical strength will limit the force output that can be generated by actuators constructed out of these SH elastomers. The implementation of a SH mechanism must not lead to a high increase in surface adhesion, leading to tacky or sticky materials that might be detrimental to soft robotics operation.

C5: The SH polymer can be reprocessed and/or recycled. In general, the components in soft robotics are of a medium to high degree of complexity. Therefore, manufacturing techniques like injection moulding, compression moulding, and additive manufacturing are increasingly used. In these manufacturing processes, solid pellets or filaments are reshaped into (complex) components and, consequently, they require reprocessability of the used polymer. If the SH polymer can be reprocessed, processing techniques providing a high design freedom will be available for future manufacturing of SH robotic components. In addition, SH polymers that can be reprocessed/recycled, further contribute to the development of a sustainable technology and eco-friendly soft robotics. Note that the self-healing action has to be performed at much milder conditions than the (re)processing to ensure mechanical stability of the robotic component.

Evaluation of self-healing mechanisms for soft robotics

Extrinsic healing: encapsulation mechanisms

In extrinsic SH systems, **healing agents**, often reactive chemical reagents, are stored in the polymer matrix through compartmentalization, usually in the form of **microcapsules** [57,70,84–89]. Upon damage, the containers break and the liquid healing agents are released, filling the fracture cavity (Fig. 2). The released monomeric agents start to polymerize and through solidification the crack is sealed and healed. Recently, progress was made towards the encapsulation in **nanocapsules** [90,91] which enhances the dispersion of healing agent in the polymer matrix and reduces the size an average (micro)crack

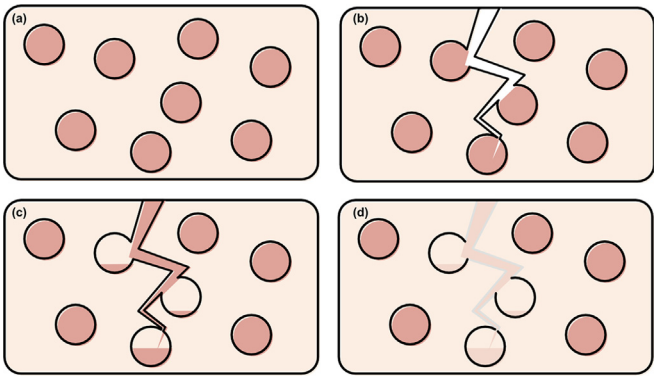

FIGURE 2

(a) SH mechanism that relies on healing agent encapsulated in micro- or nanocapsules dispersed in the polymer matrix. (b) Upon mechanical damage the capsules break (c) releasing the healing agent in the crack (sealing), (d) which repairs the damage upon polymerization (healing).

has upon breaking a capsule. Although high healing efficiencies can be obtained [88] the healing is limited to microscopic damage, because one capsule can only contain small amounts of healing agent and because only healing agent from capsules in the crack plane is released. This mechanism is mainly used to increase the lifespan of components by repairing fatigue microcracks before they propagate into larger defects. Larger damage can be healed by encapsulating the healing agent in **hollow fibres** [92,93] or **vascular systems** [94–96] potentially connected to an external healing agent reservoir [97,98]. This allows for the healing agent to be transported over larger distances, increasing the size of the damage that can be repaired. Using the encapsulation method, the local capacity for healing is finite. Once all containers in a certain location are broken and the healing agent is consumed, the local healing potential is depleted. Blockage of the channels by solidification of the healing agent, may limit the locally achievable number of healing cycles in vascular networks as well.

Healing using encapsulated healing agent works well for hard, brittle polymers, like thermosetting matrices. For the capsules or channels to crack open, their shells must be made from a brittle polymer that adheres well to the surrounding matrix. Furthermore, a necessary condition for the capsules or channels to rupture is that the matrix material has to be stiffer than the shell material [57]. If not, a propagating microcrack will have the undesirable tendency of deflecting away from the capsule or channel. Consequently, so far there are no records of a successful autonomous healing mechanism relying on encapsulated healing agents in elastomers (criterion C4). Alternatively to encapsulating liquid healing agent, solid thermoplastic particles, with a low melting temperature (e.g. 60 °C) can be embedded as solid healing agent in an elastomeric matrix [99–101]. However, these mechanisms are non-autonomous, as thermal activation is required (*e.g.* 80 °C) to melt the thermoplastic particles into molten polymer that flows into the cracks [100]. This mechanism allows to perform multiple healing cycles, though complete recovery of the initial properties cannot be achieved [99,100]. In addition, these composite materials are not reprocessable (C5).

Intrinsic healing

The advantage of intrinsic SH polymers is their theoretically infinite healing capacity [76]. Intrinsic healing mechanisms can be further subdivided depending on the type of interaction used to achieve healing, which can be **covalent** or **physical**. The healing ability of many intrinsic SH polymers relies on **dynamic covalent interactions** [102–108]. These dynamic covalent bonds have a reversible nature, they can break and reform, although a comparatively large amount of energy is required to break them, having bond strengths of 150–550 kJ mol^{-1}, in comparison to physicochemical bonds, like hydrogen bonds, having bond strengths of a few kJ mol^{-1}. The most common approach in intrinsic SH polymers is to use the dynamic covalent bonds as crosslinks, to construct a polymer network [106,109]. Networks with a relatively low crosslink density and flexible chain segments will exhibit an elastomeric behaviour, suitable for soft robotics application. SH polymers can also be designed by incorporating dynamic covalent bonds in linear polymer chains [110,111]. This approach does not lead to a network structure, which is required to achieve elastomeric properties. The high bond strength of the dynamic crosslinks in the network translates into a sufficiently high mechanical strength, as is often required in soft robotics. Because of this high bond strength, dynamic covalent SH polymers are generally non-autonomous, requiring energy provided by an external stimulus, usually in the form of heat [103] or light [112] to perform healing. Dynamic covalent bonds can be either **reversible** or **exchangeable bonds** depending on the underlying reaction mechanism that is respectively **dissociative** or **associative** (Fig. 3).

Intrinsic healing: dynamic dissociative covalent bonds

Intrinsic healability can be achieved using reversible covalent addition reactions, of which the **thermoreversible** Diels-Alder (DA) [4+2] cycloaddition reaction is the most studied example [113–118]. In this case, the crosslinks are formed by an equilibrium reaction between a diene and dienophile, both present as functional groups on the constituting monomers (or prepolymers). As the product or adduct formation is exothermic, the equilibrium will shift to a more bonded state with decreasing temperature. Upon macroscopic damage, the network locally cracks open, breaking reversible crosslinks, and a void is created between the fracture surfaces. Prior to the healing, the complementary fracture surfaces should be brought back in close contact, closing the void, while avoiding misalignment as much as possible. As long as the cracks are on a microscopic scale, this may be achieved by unloading the structure. The healing is activated by increasing the temperature (80–130 °C for furan-maleimide DA polymer networks) [119–127] shifting the equilibrium of the exothermal DA reaction from a major fraction of formed DA bonds at ambient temperature, towards the breaking of these bonds, resulting in a higher concentration of reactive diene and dienophile functional groups at the healing tempera-

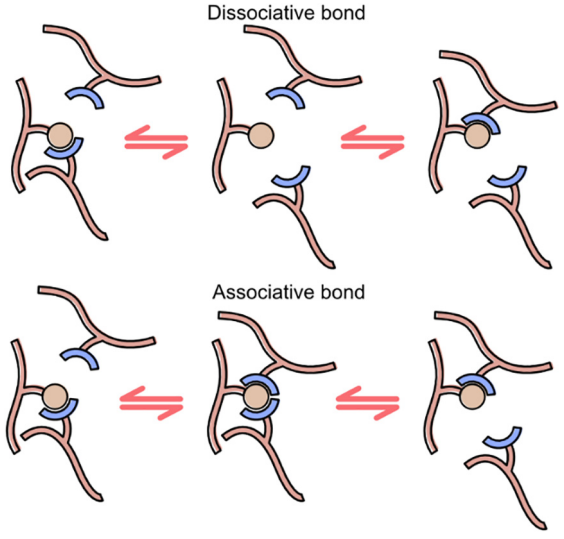

FIGURE 3

Schematic of the two types of dynamic covalent bonds: dissociative (=reversible) bonds can switch between an "open state" and a "closed state"; associative (=exchangeable) bonds can link new partners without change in connectivity.

ture [117]. Due to the decrease in crosslink density arising from the temperature increase and chemical shift, the molecular mobility increases, which further facilitates the establishing of contact between the fracture surfaces and aids sealing microscopic voids. Upon cooling, the shift of the equilibrium is reversed, resulting in the reformation of the dynamic covalent crosslinks in the network and across the fracture interface. At room temperature, the crosslink density converges back to the equilibrium value, completely restoring the initial material properties [125]. It has been proven that with this mechanism macroscopic damages can be healed with very high healing efficiency, measured through the recovery of the tensile strength of cut-through samples [120]. Multiple damage-healing cycles could be performed at exactly the same damaging location, with only a slight decrease in strength. Recently room temperature healing has been shown to be feasible in Diels-Alder based networks, taking days though [121]. Alternatively, other thermoreversible covalent chemistries, like diaryl-bibenzofuranone [128] imine [129] phenol-carbamate [130] and urea [131] bonds have been used to generate elastomers able to heal macroscopic damage with high efficiencies. The last three reaction mechanisms require mild heating only ($\leq$50 °C).

Conventional elastomers are crosslinked by irreversible covalent bonds, which implies that these polymers cannot be degelled, reshaped or (re)moulded. Recycling of these networks is impossible. Conversely, dynamic covalent networks with thermoreversible bonds are recyclable [125]. When heated above their gel temperature, a sufficiently high fraction of crosslinks will be broken, and the polymer network falls apart into (branched) chains. This results in macroscopic mobility and viscous flow. In these conditions the polymers can be reprocessed by casting or moulding, techniques currently used to shape soft robotic components [7,17]. Viscous flow at high temperatures, opens the opportunities for additive manufacturing techniques [132,133] to shape these thermoreversible elastomers, as recently illustrated by fused filament fabrication [122,134] and direct ink writing [120,135] of a soft actuators from Diels-Alder elastomers. In addition, thermoreversible elastomers can also be reprocessed by dissolving them in an appropriate solvent and subsequently performing a solvent casting [136].

Photoreversible bonds can be created and broken in a reversible fashion by means of irradiation with light having the appropriate wavelength [137]. When photoreversible bonds are used to crosslink networks, damage can be healed by exposing the material (locally) to UV light irradiation [138,139]. Examples of photoreversible reactions are the coumarin [2+2] cycloaddition reaction [140–142] and the anthracene [4+4] cycloaddition reaction [143–147]. Upon the occurrence of damage, photoreversible crosslinks are mechanically broken. After bringing the fracture surfaces back in contact, in most cases, the damaged site is first irradiated with UV-light with a low wavelength ($\lambda < 300$ nm), which leads to further breaking of reversible crosslinks in the network and a (local) increase in mobility and concentrations of reactive functional groups. The crosslinks are subsequently recreated by exposure to light with a higher wavelength ($\lambda > 300$ nm), healing the damage. Advantage of photoreversible reactions are typical high reaction rates and excellent temporal and spatial control over the activation stimulus, making local treatment feasible. However, the thickness of parts that can be healed is limited by the small penetration depth of the light required for healing. Coumarin based photoreversible elastomers have been developed in which damages with depths of 50–200 μm can be healed with high healing efficiencies [140,141]. Consequently, photoreversible SH polymers can find applications in soft pneumatic robotics [16] in which often thin structures are used. Reprocessing using light irradiation is difficult due to the limited penetration depth. A few photoreversible covalent bonds, like anthracene dimers, are also thermoreversible [145,146] opening opportunities for recycling and reprocessing using heat treatments. This thermoreversibility also allows performing healing procedures, in which debonding is achieved by heating, while bonding results from exposure to UV [146]. Following this approach, deeper damages up to 0.5 mm can be healed thermally and photochemically with high efficiencies [146].

Mechanoreversible bonds are covalent bonds that can be reversibly broken by mechanical force. Breaking these bonds creates reactive functional groups and surfaces that can rebind when the external force is removed. The healing is autonomous, since no external stimulus different than the stress release is required for the healing process. Although promising mechanoreversible mechanisms have been reported [148–150] to the authors' knowledge they have not been integrated and validated in healable elastomers. It could be argued that many reversible dissociative reactions are mechanoreversible, as it has been shown for Diels-Alder cycloadducts that mechanical force lowers the activation energy of the retro Diels-Alder reaction [151] and excessive mechanical force breaks the adduct bonds in a reversible fashion, allowing subsequent healing without thermal stimulation [121,152]. Similarly, anthracene photodimers have been shown to produce mechanoluminescence due to the colour difference between the colourless photodimer and the yellow anthracene monomer upon mechanical fracture [153]. The broken dimer bonds can then be restored photochemically.

Intrinsic healing: dynamic associative covalent bonds

Alternatively, to the dissociative mechanisms discussed in the previous section, intrinsic healing can also be achieved through **exchange reactions**. During this type of reaction, a covalent bond is broken while simultaneously the same type of bond is formed with a different reaction partner: the covalent bond is exchanged (Fig. 3). In vitrimers [154–156] which are dynamic networks that are crosslinked by exchangeable bonds, there is no net change in the number of bonds formed as a function of temperature, however, the rate of the exchange reactions accelerate as the temperature increases. At room temperature, most exchange reactions are slow and vitrimers with low crosslink densities behave like classical elastomers [154] with properties suitable for soft robotics. During the healing of a fracture, the exchange reactions should take place across fracture surfaces that are in contact, reinstating the local network across the fracture plane. At room temperature, in most cases, the kinetics are not sufficiently fast to perform healing. By increasing the temperature, the exchange reaction kinetics become faster, (additionally) increasing the mobility, which allows healing in a reasonable time frame (in the order of hours). A well-studied example are

the transesterification reactions [157,158]. In [158] a boronic ester based network is presented in which large damages can be healed with high efficiencies by heating to 80 °C for 24 h. Healing can be performed much faster at higher temperatures, as demonstrated for the hydroxyl ester based networks [159] which heal damage in 3 h at 160 °C. The thiol-disulphide exchange reaction [160,161] and the metathesis of disulphide [162–164] were used as well to create healable elastomers. The disulphide reaction has relatively fast kinetics and this allows combining high mechanical strength with high healing efficiencies [162]. At high temperatures, above the topology freezing transition, all mentioned exchange reaction are fast and the vitrimers show viscous flow [154]. Consequently, they can be reshaped and recycled using heat [165]. However, due to their relatively high viscosity at these elevated temperatures, high-pressure reprocessing techniques, including injection [157] and compression moulding [166,167] must be used.

The thiuram-disulfide reaction, which exchanges under the stimulation of visible light, was used to crosslink a photocurable elastomer [168]. Transparent samples of 1 mm thickness can recover completely from being cut in half by exposure to visible light for 24 h. Because of the ability to heal thick membranes and the reprocessability at high temperature, this SH-mechanism has high potential to integrate healability in soft (pneumatic) robotics. In [169] the metathesis reaction of disulphide in a highly flexible elastomer is catalysed by tri-*n*-butylphosphine, facilitating autonomous healing at room temperature with high efficiency, without the need of a stimulus.

Intrinsic healing: physicochemical interactions

Physicochemical interactions are non-covalent bonds resulting from intermolecular interactions (Fig. 4). Due to a lower bond energy, these crosslinks are weaker and thus easier broken than covalent bonds, requiring less energy. High concentrations of these bonds in linear or branched polymers can lead to the formation of supramolecular networks, in which a high amount of physicochemical bonds (physically) cross-links the material [170–172].

Hydrogen bonds are widely used to crosslink elastomeric networks that have self-healing capacities [170,171,173]. The bond strength of hydrogen bonding interactions is typically several tens of kJ mol^{-1}, depending on the hydrogen donor and acceptor. This relatively low bond strength means that less energy is required to break the bonds. Hydrogen bonds can also reform relatively fast, making them popular for the development of autonomous self-healing polymers. The downside of low bond energy crosslinks is a negative impact on mechanical strength, strain recovery and creep behaviour. To enhance the mechanical strength and structural stability, the strength of the crosslinks can be enhanced by increasing the number of hydrogen bonds formed per crosslink, making use of multivalent hydrogen bonds [174]. An extensive study on complementary quadruple hydrogen bonding in supramolecular co-polymers was performed by Meijer et al. [175]. Leibler et al. [176] presented an impressive self-healing elastomer based on hydrogen bonds. The flexible polymer can be broken or cut and subsequently healed by bringing together the fractured ends for a few minutes to self-heal autonomously at ambient temperature. Moreover, it is possible to reconnect the fracture surfaces after a waiting times and still be able to heal but slower [177]. In general hydrogen bonded SH polymers can be easily reprocessed by increasing the temperature, which results in the breaking of the hydrogen bond crosslinks and leads eventually leading to viscous flow [176].

π–π stackings between π orbitals of aromatic rings [172] are attractive reversible non-covalent interactions that can be used to integrate healability [178]. However, the bond energy (8–12 kJ mol^{-1}) is lower than the hydrogen bond energy, and even when it leads to inter chain folding [179] only relatively weak crosslinks are generated, which limits material strengths and elastic recovery, both essential in soft robotics.

Self-healing polymers based on supramolecular, dynamic networks can also made using Ionic interactions [180,181]. **Ionomers** contain as much as 20% of charged or ionic species as a part of their polymeric structure. These ionic groups tend to cluster, forming physical crosslinks, and allowing reversible formation and reformation of the network structure. Compared to other types of physicochemical crosslinks, ionomeric clusters have a higher aggregation strength, benefiting tensile strength, fracture resistance and toughness. As the ionic (cluster) interactions require more energy to break, the healing of ionomers often demands external energy in the form of heat, however, lower temperatures (like 60 °C [182]) are required for healing than in dynamic covalent networks. Although classified as non-autonomous, in one example of a ballistic impact healing application, the damage event provided enough energy in the form of heat resulting from friction, for the material to effectively behaved as an autonomous self-healing material in this application [183,184]. This immediate sealing ability is interesting for the aerospace industry, where a small penetration of the pressurized hull of an airplane, for example caused by a bullet, can lead to a loss in pressure with disastrous consequences. Complexes of zinc-dimethacrylate [185] or ammonia-carboxylate [186] allowed for autonomous healing at room temperature, the latter relatively fast, in only 20 min.

Supramolecular network formation can also be achieved by **metal–ligand (coordination) complexes** that act as reversible physical crosslinks [170,187]. Similar to the clusters in ionomers, coordination complexes [188] are formed between the positively charged metal ions and the partially negatively charged groups on the ligand molecules. The charge on the ligand molecules is typically much smaller than the metal ion charge. As a dipole-ion interaction is weaker than an ionic interaction, the metal–ligand crosslinking complexes are much weaker. This allows healing macroscopic damages at room temperature without the need of an external stimulus. Similar to hydrogen bonded SH polymers, these weaker crosslinks permit reprocessing the material at mild temperatures, however, also make creep more likely. Highly stretchable elastomers based on metal–ligand complex crosslinks, having potential for soft robotics applications are presented in [189–191].

Finally, healing is possible in **thermoplastic elastomers** [192–194]. These copolymers are physically crosslinked by a **high-temperature transition phase** (melting of crystal phase or glass transition). Upon heating and cooling these physical crosslinks can be reversibly broken and reformed. This thermoreversibility allows healing damages by performing a heat-

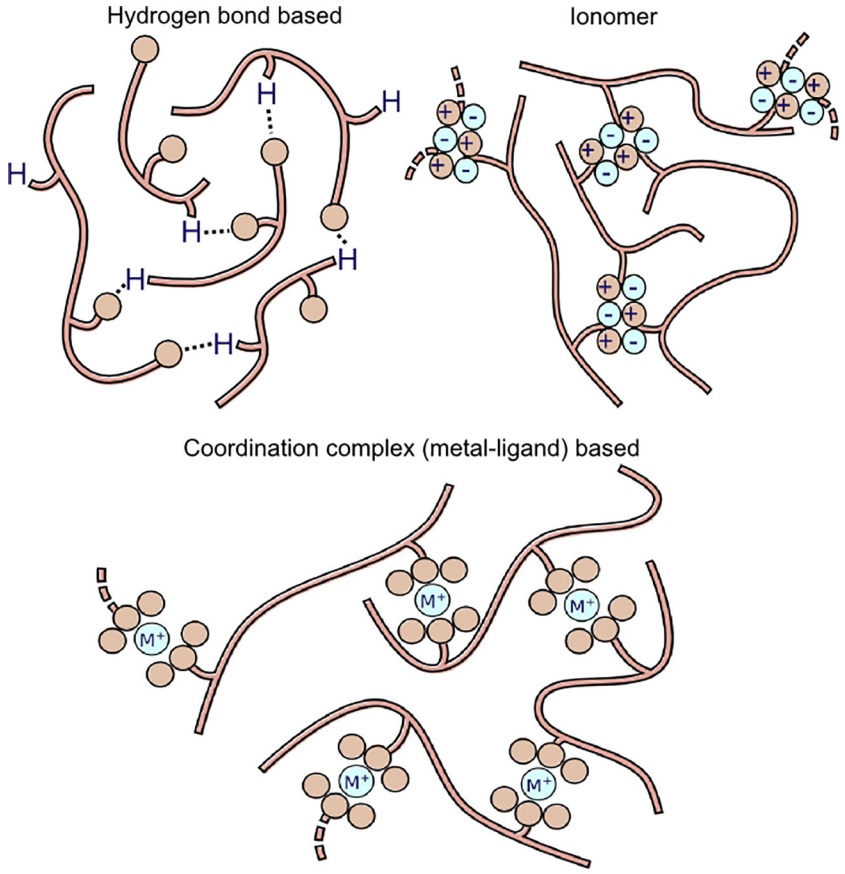

FIGURE 4

Physicochemical interactions can rely on hydrogen bonding, ionic interactions, or coordination metal–ligand complexes.

cool cycle. The main challenge of this SH mechanisms is to heat the polymer, while not losing structural stability. As the temperature window of the melting/glass transition can be narrow, most networks loose most of their structural stability upon healing due to a high portion of viscous response. To increase structural stability this mechanism can be integrated in an interpenetrating network (IPN) [195]. In the molten state these polymers can also be reprocessed.

Intrinsic SH polymers with potential for soft robotics

An overview of the mentioned SH mechanisms and their evaluation with respect to the five soft robotics criteria is recapitulated in Table 2. In contrast to extrinsic SH mechanism, many intrinsic SH mechanisms have potential to be used for constructing healable soft robotics. Not surprisingly, many have been used to develop the first healable soft robotics prototypes (details in section *state of the art on healable soft robots*). Although heat is required, *thermoreversible intrinsic SH mechanisms* can be used to repeatedly heal macroscopic damages in elastomers with high healing efficiencies and relatively high mechanical strength. Because of the thermoreversible nature of their crosslinks these networks can be easily reprocessed. *Photoreversible SH polymers* have not yet been used in soft robotics because only damages with limited depths (<0.2 mm) can be healed. These materials might still be useful to introduce healing in thin robotic structures, like origami robots [196] or thin membrane or small scale pneumatic soft robots [197,198]. However, reprocessing is not always possible. Like thermoreversible mechanisms, *exchange reaction-based SH mechanisms* can be integrated in elastomers with adequate properties for soft robotics. These can be recycled though heating, however only through high-pressure moulding techniques. Physicochemically crosslinked elastomers allow to create autonomous healing in soft robotics; however, the force output of these systems will be limited due to their lower mechanical strength.

Based on this evaluation we provide a classification of publications presenting intrinsic SH elastomers suitable for soft robotics in Table 3. These were selected considering the following parameters. *(i)* The mechanical strength, which is preferentially high and defined by the ultimate stress (σ_{ult}) and the ultimate strain (ε_{ult}) at which fracture occurs. *(ii)* The healing efficiencies η_σ and $\eta\varepsilon$ are defined based on the recovery of respectively the ultimate stress σ_{ult} and the ultimate strain ε_{ult}, which are preferentially near 100%. *(iii)* The healing procedure parameters, like the healing temperature (T_H) and the time at this temperature (t_{HT}), preferably as low as possible and of short duration. $t_{recover}$ is the time the material must stay at a lower temperature to complete healing. For some thermoreversible systems this time is required to reform the crosslinks, which in some cases can take long due to slow reaction kinetics. For autonomous SH mecha-

TABLE 2

Evaluation of the self-healing mechanisms based on 5 criteria (C) for the integration in soft robotics.

Self-healing Mechanism	Stimulus	C1: Healing macroscopic damage	C2: Multiple healing cycles	C3: Recovery of initial properties	C4: Elastomer with high strength	C5: Reprocessable and recyclable	Ref	Ref Applied in soft actuators and robotics
Extrinsic								
Encapsulation							[70]	
Micro/nano capsules	/						[84–91]	
Hollow fibers	/						[92,93]	
Vascular network	/						[95,255]	
Vascular network + reservoir	/						[97,256]	
Solid healing agent	*Heat*						[99–101]	[99]
Intrinsic							[76]	
Dynamic covalent bonds							[102–108]	
Thermoreversible								
Diels-Alder	*Heat*						[113–119]	[120–127]
	/						[121][152]	[121]
Phenol-Carbamate	*Heat*						[131]	
Diarylbibenzofuranone	*Heat*						[128]	
Urea	*Heat*						[130]	[237]
Imine	/						[129]	[129]
Photoreversible							[137–139]	
Coumarin	*UV*						[140–142]	
Anthracene	*UV*						[143–145,147]	
	Heat+UV						[146]	
Mechanochemical							[148–150]	
	/							
Exchange reaction							[154–156]	
Transesterification	*Heat*						[157–159]	[223]
Thiol-disulphide	*Heat*						[160,161]	[164]
Metathesis of disulphide	*Heat*						[162–164]	[220][231]
	/						[169]	
Thiuram-disulfide	*Vis Light*						[168]	
Physicochemical interactions							[170–172]	
Hydrogen bonds	/						[170,174–176]	[207,226,257,258][236]
π–π stackings	/						[178]	
	Heat						[179]	
Ionomers	/						[185,186]	
	Heat						[182]	[182]
Metal-Ligand complex	/						[188–191]	[189,210]
Crystals	*Heat*						[192–194]	
Crystals (IPN)	*Heat*						[195]	[195]

Colour code	Criteria not met (major obstacle)	Criteria partially met. Limitations need to be taken in account	Criteria met (no major obstacles)

Refs. [70,76,84–93,95,97,99–108,113–131,137–150,152,154–164,168–172,174–176,178,179,182,185,186,188-195,207,210,220,223,226, 231,236,237,255–258] can be found at the end of the paper in the Reference list.

nisms that proceed at room temperature, t_{RT} represents the total healing duration at 25 °C. In both cases, $t_{recover}$ and t_{RT} are desired as short as possible. *(iv)* For photoreversible SH, λ is the specific wavelength of the irradiation for breaking and bonding of reversible bonds, and t_{exp} is the time of exposure.

For many mechanisms healing takes time, often in the order of hours. It is however important to mention that the $t_{recover}$ and t_{RT}, in Table 3, are the times needed to recover the mechanical strength almost entirely. In many soft robotics applications this full recovery is not needed to reactivate the system. In normal operation of the soft robots, the elastomers will be exposed to stresses well below the ultimate stress, while a (feedback) controller can address potential changes in elastic modulus. Consequently, operation can be resumed well before full recovery and the healing can be completed during operation [121,123]. Neverteless, the healing times are significant and an acceptable duration will always depend on the application. In soft robotics elastic recovery is prefered to be fast (order of 0.1–1 s) and complete. Although very important, this parameter is not included in our analysis due to insufficient data in literature. The same applies to the tackiness of SH elastomers for soft robotics, which will require more attention in future.

General trade-off in SH mechanisms for polymers

In Fig. 5, for all elastomers presented in Table 3, three performance parameters; the ultimate stress, the total healing time, and the maximum healing temperature are plotted. For the traditional SH classes (Table 1 and Table 2), a trade-off exists between healing temperature and ultimate stress [199]. In general, higher bond strengths lead to polymers that have greater mechanical strength and stability, as more energy is required to break the bonds. This means that more energy needs to be supplied by the healing stimulus, making the healing mechanism non-autonomous or slow at ambient temperature. Moreover, this

TABLE 3

SH polymers with high potential for soft robotics and their characteristics.

Thermoreversible SH mechanisms	Ref	σ_{ult} (MPa)	ε_{ult} (%)	T_H (°C)	t_{HT}	$t_{recover}$	η_σ (%)	η_ε (%)
Dissociative covalent								
Diels-Alder	[119]	26	250	130	10 m	1 h (60 °C)	69	65
	[120]	22.5	295	140	10 s (NIR)	3 d (25 °C)	92	93
	[123]	0.4	144	90	1 h	3 d (25 °C)	96	98
Phenol-Carbamate	[130]	2.9	240	80	2 h	3 h (25 °C)	98	96
Diarylbibenzofuranone	[128]	0.75	830	50	12 h	/	90	90
Urea	[131]	0.93	301	37	12 h	/	76	87
Associative covalent								
Transesterification	[159]	5.5	750	160	3 h	/	82	91
	[158]	2.0	275	80	24 h	/	90	85
Thiol-Disulfide	[160]	0.47	65	60	1 h	/	99	97
Disulfide	[162]	22.9	846	100	10 m	/	91	99
Physicochemical								
Hydrogen	[259]	37.1	702	120	4 h	8 h (60 °C)	92	96
	[260]	0.3	33	50	5 m	/	100	97
Host-guest interaction	[261]	13.5	17	120	30 m	/	85	94
Ionic binding	[182]	7.2	500	60	24 h	/	83	90
Combined mechanisms								
Transester + Metal-ligand	[262]	9.2	650	80	24 h	/	98	98
HB + disulfide bonds	[204]	20	500	90	24 h	/	94	90
HB + β-sheets	[211]	23	300	50	2 s	/	95	75
HB + π- π stacking	[263]	1.1	69	45	12 h	/	100	93
Autonomous SH mechanisms	Ref	σ_{ult} (MPa)	ε_{ult} (%)		t_{RT}		η_σ (%)	η_ε (%)
Dissociative covalent								
Diels-Alder	[121]	0.11	365		7 d		80	91
Associative covalent								
Disulfide	[169]	0.23	105		24 h		95	96
Thiuram disulfide	[168]	0.4	202		24 h and visible light		100	90
Transesterification	[264]	4.2	56		72 h (85% RH)		95	93
Physicochemical								
Hydrogen	[265]	1.92	780		24 h		92	90
	[176]	3.5	600		3 h		88	87
Metal-Ligand	[190]	1.4	770		3 h		99	100
	[191]	0.67	320		48 h		76	/
Ionic binding	[266]	0.65	325		20 m		100	100
	[186]	1.2	1100		24 h		92	/
	[267]	0.17	1650		24 h (in water)		95	94
Combined mechanism								
Metal-ligand + Capsules	[268]	3.2	90		10 h		90	/
π- π stacking + Pt complex	[269]	0.3	1400		24 h		100	100
HB + transesterification	[270]	1.6	325		24 h		100	/
HB + Metal-ligand	[210]	9.4	600		15 s		98	92
HB + disulphide	[206]	0.81	3100		24 h		95	97
	[205]	4.2	128		48 h		88	85
HB + Ionic	[271]	1.35	1800		24 h		88	85
Photoreversible SH mechanisms	Ref	σ_{ult} (MPa)	ε_{ult} (%)	λ (nm)		t_{exp}	η_σ (%)	η_ε (%)
Dynamic covalent								
Coumarin	[140]	1.2	640	254	350	1 m 90 m	100	80
	[141]	12.1	457	254	365	10 m 30 m	84	90

Refs. [119,120,121,123,128,130,131,140,141,158–160,162,168,169,176,182,186,190,191,204–206,210,211,259–271] can be found at the end of the paper in the Reference list.

results in a stronger competition with the breaking of irreversible bonds, reducing the healing efficiency. Conversely, the total bond energy of hydrogen bond crosslinks and coordination complexes is much lower [200] and less energy is needed to break them. Therefore, these physicochemical networks can heal damage at lower or ambient temperature. However, the lower total bond energy has negative consequences for the mechanical properties. Autonomous, intrinsic SH polymers have lower mechanical strength and, in some cases, creep behaviour and self-adhesion are non-negligible and permanent plastic deformations can lead to non-optimal strain recovery. The general trade-off between the requirement of a healing stimulus and the mechanical strength, described by σ_{ult}, is clearly visible in Table 3 and Fig. 5. In general SH polymers that rely on thermo- and photoreversible crosslinks have σ_{ult} in the 1–100 MPa range, while autonomous SH-polymers have σ_{ult} in the 0.01–10 MPa range.

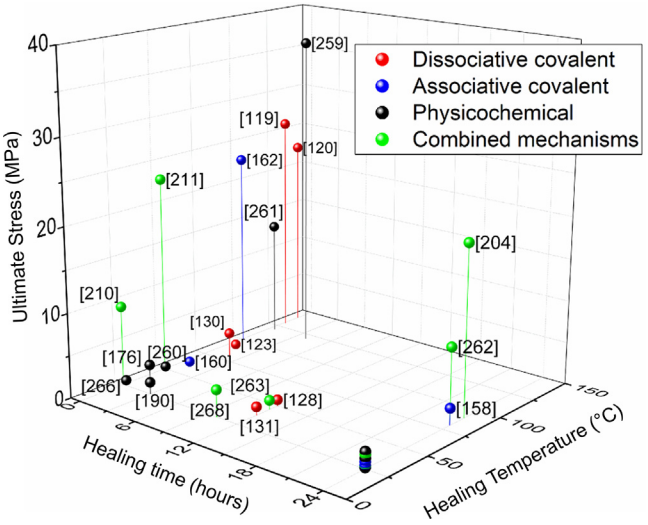

FIGURE 5

Overview of three performance parameters of intrinsic SH elastomers with potential for soft robotics: healing temperature, healing time, and the mechanical strength, represented by the ultimate stress. For the traditional SH classes, a general trade-off exists between the mechanical strength, represented by the ultimate stress, and the healing temperature/healing time. Refs. [119,120,121,123,128,130,131,158,160,162,176,190,204,210,211,259–263,266,268] can be found at the end of the paper in the Reference list.

Combining multiple SH mechanisms in a single polymer

In search for a combination of fast healing at low temperatures and excellent mechanical properties, SH polymers have been developed that combine multiple of the above-mentioned mechanisms [201]. Double dynamers contain both strong reversible covalent bonds, for mechanical strength, and reversible physicochemical bonds, to achieve fast initial healing [202] (Table 3 and Fig. 5, combined mechanisms). Sordo et al. reported a hybrid network with a fixed amount of hydrogen bonds and a tuneable number of covalent ester bonds [203]. The combination of di- and tetra-epoxy resins allowed for tuning the number of chemical cross-links and therewith the mechanical properties, with σ_{ult} up to 3.7 MPa. The rubber shows full self-healing at ambient temperature after 24 h and 78% after the first hour due to the fast reformation of hydrogen bonds. Hydrogen bonds and disulphide bonds were combined by Liu et al. [204] resulting in relatively tough SH polyurethane elastomers (σ_{ult} = 20 MPa) and healing at mild temperatures of 90 °C. Aromatic disulphides are also combined with hydrogen bonds in SH polyurethanes, as presented in [205] and [206] the latter able to recover mechanical strengths of 0.7 MPa within two hours after damage. Alternatively to integrating multiple reversible or dynamic crosslinks in a single network, the development of interpenetrating networks (IPNs), also called double networks, allows combining stronger dynamic bonds (for strength) and weaker physicochemical bonds (for fast healing) in a single material, each being present in one of the interpenetrating networks [207–209].

The two most impressive SH elastomers were developed by Wang et al. [210] and Sitti et al. [211] both relying on combined mechanisms. Wang et al. [210] used hydrogen bonds and ferric oxide – catechol (metal–ligand) complexes to form what they refer to as a hierarchically structured supramolecular elastomer. This highly structured network has decent mechanical stability (σ_{ult} = 9.4 MPa) and exhibits excellent healing within 15 seconds. Sitti et al. [211] combined high mechanical strength (23 MPa) and fast healing in a network composed of synthetic proteins that are physically crosslinked by reversible crystalline phases and contain extensive hydrogen bonding. Their mechanical strength is recovered within a single second after placing the fracture surfaces back together at 50 °C. Examples like these, prove that by combining the best of different SH mechanisms, superior SH polymers can be created.

Limitations of artificial self-healing polymers

The wound healing process of a cut in human skin is highly complex [212] and involves multiple stages, including hemostasis (blood clotting), inflammation, proliferation (growth of new tissue) and maturation. The artificial SH mechanisms discussed above, which involve at most two stages, are much less complex. In synthetic polymers, the powerful hemostasis step, which relies on complex cell division and growth, has not yet been achieved due to mass conservation. Microscopic cavities at the fracture interface can be closed by sufficient molecular mobility or filled by a released healing agent. However, synthetic material cannot grow to fill large damages. Consequently, the healing is limited to recombining fracture surfaces that are brought back in contact on a microscopic level.

For relatively small damages in elastomers, the elastic response of the material after damage, allows the fracture surfaces to come back in contact, allowing healing. However, for larger damage the fracture surfaces must be brought in intimate contact by external intervention. In future soft robotic system this can be done by the robot that places itself in a configuration in which the fracture surfaces are pressed together. Aiding mechanisms have been developed to alleviate this problem on the material level, according to the close-then-heal (CTH) two step principle [55]. By integrating extrinsic shape memory polymer muscles [99] wires [213] or fibres [100], or shape memory alloy wires [214] or springs [215] in a SH elastomeric matrix, shape memory assisted self-healing (SMASH) can be performed [61,215]. Upon heating, the integrated shape memory effect brings fracture surfaces back together, prior to binding them back together [213] or curing using a healing agent [99,100,214]. Magnetic particles have been added to SH materials to close large damages using an applied magnetic field [216,217]. Although not yet adopted in soft robotics, both SMASH and magnetic-field assisted healing are promising to aid healing of large damages. Recently, researchers investigated the use of stem cells for creating growing and living, self-healing robots [218].

In many soft robotics applications, low or medium mechanical moduli and strengths are acceptable or even preferred [8,68]. However, many intrinsic SH networks, suffer from slow or incomplete elastic recovery due to a high viscous component in the viscoelastic behaviour because of the dynamic character of their crosslinks, which will have a negative impact on the dynamics of soft robots and can be detrimental for applications in which high actuation speeds are desired. On the other hand, undesired creep caused by the dynamic crosslinks can compromise the structural stability, specifically in applications where soft robots are under load for a longer period. As not many report

on these effects and their acceptance is dependent on the soft robotics application, they are not included in this first comparative study.

For all materials in Table 3, healing can be performed on temperatures that deviate from the one presented (T_H for non-autonomous and 25 °C for autonomous systems). In general, lower temperatures lead to lower kinetics and increase the healing time. Conversely, higher temperatures lead to faster healing. The maximum healing temperature is defined by the temperature at which networks lose mechanical stability, which is the degelation temperature for dissociative or physicochemical systems or the topology freezing transition for associative systems. In addition, in soft robotics application this temperature can be limited by other components in the system, such as electronics.

State of the art on healable soft robots

Although many SH mechanisms have tremendous potential to integrate healability, only a limited number of publications demonstrates their use in soft robotics. In 2013, Shepherd et al. [219] presented a soft pneumatic gripper that is resistant to punctures, induced by a needle due to a SH behaviour of a silicone/Kevlar composite (Fig. 6a). The author stated that the damage resilience stems from a combination of the Kevlar fibres preventing crack propagation, the composites elastic behaviour that returns the actuator in the original shape and the silicone's tendency to self-adhere. This healing principle is limited to small damages, yet interesting since many failures of soft actuators are due to small punctures and perforations.

Recently, our group at the Vrije Universiteit Brussels reported on various soft grippers and soft robotic hands based on Diels-Alder polymers with the capacity to heal macroscopic damages [121–123,125,126] (Fig. 6b–d). These prototypes, which are pneumatically actuated [125,126] or tendon driven [123] demonstrated that Diels-Alder elastomers have mechanical properties, which are suitable for soft robotic applications. The soft robotic prototypes can recover from large realistic damages, with near-complete restoration of initial characteristics after being subjected to a healing process. Even very drastic damages, like cutting the actuators completely in half, could be healed entirely. For these Diels-Alder soft robotic components [122,123,125,126] the healing was controlled by heating (80–90 °C) the entire soft robotic part in a healing station (*e.g.* an oven). In search to avoid the need of external heating, a soft robotic gripper constructed out of a novel Diels-Alder network was reported that can heal large damages autonomously at room temperature [121] (Fig. 6e). However, to allow efficient room temperature healing in Diels-Alder polymers, high molecular mobility is required, which resulted in a highly flexible behaviour, with a limited mechanical strength. Consequently, the power and force output of the soft gripper is limited, emphasizing the trade-off between mechanical properties and healing temperature. The dynamic nature of crosslinks in Diels-Alder elastomers can be exploited in manufacturing, as demonstrated by the folding & binding technique [125,220] a technique that is particularly interesting for soft origami [196] and pneumatic robotics [16]. 3D polygon soft robotic structures are formed out of 2D sheets, by subsequently folding and binding through heat-cool cycles.

As presented in Table 2, many of the intrinsic SH polymers can be reshaped when heated to a temperature at which extensive debonding of the reversible crosslinks leads to a loss of structure stability and a resulting viscous flow behaviour. The solid–liquid transformation at elevated temperatures in Diels-Alder elastomers allows to use these reversible networks for fused filament fabrication (FFF) 3D printing, as demonstrated in feasibility studies in [134,135] and by Roels et al. [122] (Fig. 7a), who printed three passive soft fingers that are used in a soft gripper for food manipulation. Damages are healed by heating the entire part to 90 °C. Zhang et al. [120] printed a shape-memory (SM) polyurethane with reversible Diels-Alder crosslinks using direct ink writing into complex shapes. Both the SM actuation and SH are temperature controlled in this multi-responsive material by locally irradiating of a NIR laser. Although actuation is slow, the combination of SM and intrinsic SH [221,222] has recently gained interest in the robotics community [15,223]. Among others [224]Coa et al. [207] have reported on the use of covalent–noncovalent interpenetrating networks in robotics. The double network is a humidity responsive SM hydrogel that was used to construct soft SM actuators. In these systems, macroscopic damages can be healed with high efficiency, but actuation is relatively slow. In [195] a semi-IPN is made by mixing linear, semi-crystalline ε-polycaprolactone into methacrylate-based monomers to print a shape-memory-actuated gripper using stereolithography (SLA) (Fig. 7b). The double network can be actuated by a heat stimulated SM effect. Actuation is slow but large damages can be healed entirely by heating the gripper to 80 °C, for only 5 min. SLA was also used in [164] to manufacture a soft pneumatic muscle, constructed out of a disulphide based supramolecular network with healing capacities (Fig. 7c). The muscle can recover entirely from being cut in halve by healing it for 2 h at 60 °C. However, due to the low mechanical modulus of ~17.4 kPa, its force output is limited. SupraPolix presented that FFF can be used to print elastomers using hydrogen interactions into high resolution 3D parts with fast healing capacities at room temperature [225] (Fig. 7d). Lopez Diaz et al. [226,227] constructed an artificial muscle based on the commonly used McKibben design out of a hydrogen-bonded network, allowing to heal punctures and cuts without the need of a temperature increase in 24 hours, but with a limited healing efficiency of around 65 %.

In 2017, Wallin et al. [228] presented a soft bending actuator developed from silicone (polydimethylsiloxane) using SLA, which interior is filled with thiol-ene resins (Fig. 8a). When the membrane of the actuator is pierced, the resin flows out and is exposed to sunlight, leading to photo-polymerisation and the sealing of the hole. In [210] a soft photo- and magnetoresponsive actuator is presented with a self-healing ability due to a combination of metal–ligand coordination bonds and hydrogen bonds. In a publication of Metin Sitti [211] it is illustrated that the mechanical properties of a network, composed of synthetic proteins that are physically crosslinked by crystalline phases with hydrogen bonding, allow to construct pneumatic muscles that can repeatedly lift weights that are 3000 times heavier than its own mass (Fig. 8b). Damages in the soft material of the muscle are healed at 50 °C in only seconds. Wang et al. [210] developed healable robotic butterfly, which wings actuate relatively fast (within a second) in response to the presence or absence of near

FIGURE 6

(a) A soft bending actuator, constructed out of a silicone/Kevlar composite, that is resistant to small punctures due to self-sealing based on the self-adhesion of silicone (reproduced with permission from [219]), (b) A soft pneumatic hand [125] and pleated pneumatic artificial muscle [127] that are given an intrinsic healing capacity by constructing them out of Diels-Alder elastomers. Cuts and perforations are healed by subjecting the parts to 80 °C for 40 minutes. (c and d) Different types of soft grippers, pneumatically actuated [126] or tendon driven [123] that are constructed out of multiple Diels-Alder polymers. Large cuts, including ones that damage more than one material section, as well as damage due to delamination at multi-material interfaces, can be healed by heating the parts to 90 °C for 30–40 min. The performance of these robotic components is not influenced by a damage-heal cycle. (e) A soft pneumatic robotic hand manufactured out of a Diels-Alder based network that can autonomously heal at room temperature [121]. Large damages, like cutting fingers in halve are healed without decreasing the systems performance.

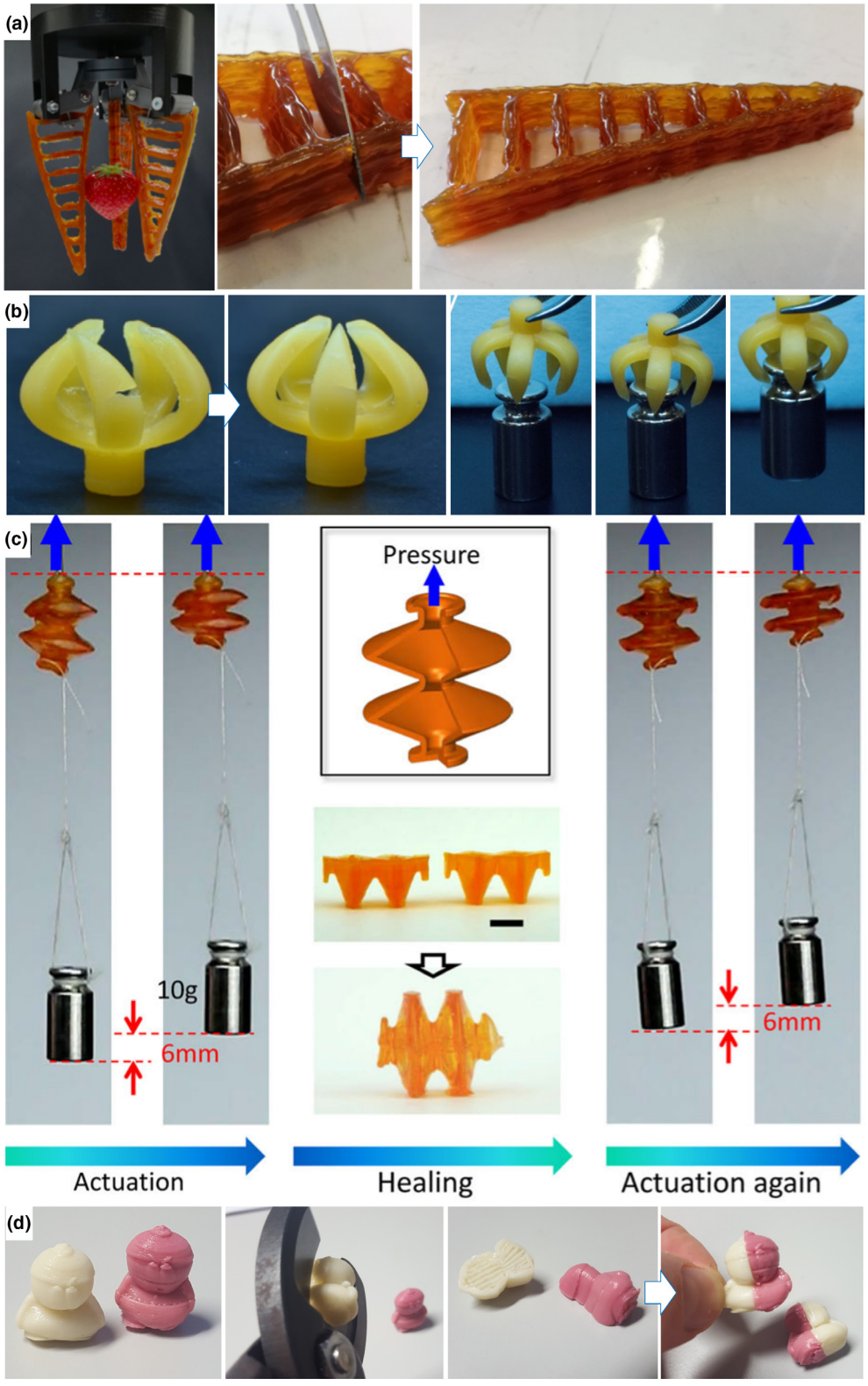

FIGURE 7

(a) A soft gripper, of which the three passive fingers have an intrinsic healing ability as they are 3D printed out of Diels-Alder elastomers using fused filament fabrication [122]. The reversible characteristic of the Diels-Alder reaction allows reprocessing the network through heat treatments, which allows reshaping the Diels-Alder polymer filament into complex 3D robotic components. Large cuts can be healed completely by exposing the gripper to a temperature of 90 °C for 30 min. (b) A gripper based on a double network polymer formed by incorporating a semi-crystalline polycaprolactone into a methacrylate-based shape memory polymers system (reproduced with permission from [195]). This gripper can be actuated by a shape memory effect that is triggered by heating the gripper above 80 °C. Damages can be healed at 80 °C in 5 min. (c) A pneumatic muscle that is 3D printed out of a disulphide based supramolecular self-healing elastomer using stereolithography (reproduced with permission from [164]). After being cut in halve and healed at 60 °C for 2 h, the muscle recovers its functionality. (d) 3D printed high resolution parts, out of hydrogen based self-healing filament using a fused filament fabrication technique [225]. Healing the two halves together can be performed at room temperature in about 1 h.

FIGURE 8

(a) A soft pneumatic bending actuator manufactured out PDMS using stereolithography (reproduced with permission from [228]). During the manufacturing process, uncured thiolene resin is encapsulated. The actuator is hydraulically actuated by pressurizing the unreacted resign. When the membrane is perforated, the thiolene resin escapes. In contact with oxygen and in the presence of visible light the thiolene resin polymerizes and acts as a healing agent, sealing the damage. (b) Squid-inspired synthetic proteins were used to generate supramolecular networks that are physically crosslinked by crystalline phases with extensive hydrogen bonds (reproduced with permission from [211]). The networks have high mechanical strength and can heal large damages at 50 °C in the order seconds. These elastomers were used to develop the first protein-based self-healing actuator. (c) Wang et al. developed multi-stimuli responsive actuators with healing capacities relying on both hydrogen bonds and ferric oxide – catechol (metal–ligand) complexes (reproduced with permission from [210]). The combination of these physical crosslinks allows healing at room temperature as illustrated in a butterfly prototype that is actuated by local heating through irradiation of near-infrared light and due to mismatch in the coefficient of thermal expansion between different layers in the material. (d) A self-healing dielectric actuator, in which the dielectric layer is a Fe(III)-pdca (metal–ligand) based self-healing elastomer [189]. Defects in the dielectric medium are healed before they propagate, preventing dielectric breakdown (reproduced with permission from [189]).

infrared irradiation (Fig. 8c). The prototype is constructed out of a strong network (σ_{ult} = 9.4 MPa) relying on extensive hydrogen bonds and ferric oxide–catechol (metal–ligand) complexes. The combination of these two types of reversible crosslinks, allows healing large damage within seconds. The same research group [229] developed light-responsive actuators (bending angle over 90° within 1.6 s) from a material containing extensive hydrogen bonding and low melt point crystalline crosslinks, with a robust mechanical strength (12.5 MPa) and superfast healing speeds (2 s) at 18 °C.

Liu et al. [230] combined ionic and hydrogen bonds in a hydrogel. Although being hyperflexible (σ_{ult} = 40 kPa), it is used in a low force soft gripper that can heal autonomously at temperatures as low as −20 °C. Recently, He et al. [231] used the metathesis of disulphide in a liquid crystal elastomer actuator, that is thermally actuated by hot water flowing through internal channels and is used as artificial muscle and in a soft gripper. The actuators that can generate relatively high contraction forces, heals at 180 °C.

SH mechanisms have been implemented in dielectric elastomer actuators (DEA) [189,232]. A DEA consists of a highly stretchable dielectric layer that is sandwiched between two stretchable electrodes (Fig. 8d). When these electrodes are charged, the dielectric layer is squeezed leading to a decrease in

thickness and a large increase in surface area. This actuation principle has potential for future soft robotic applications [233] such as grippers [232,234]. The dielectric layer is very thin and therefore susceptible to physical damage and manufacturing imperfections. A hole in the dielectric layer can lead to near-contact between the electrodes, which leads to sparking (dielectric breakdown) that most of the times destroys the actuator. This can be prevented if the small defect is healed before actuation. Therefore, DEA have been manufactured with a SH dielectric layer using an open-cell silicone foam filled with silicone oil [235] a liquid dielectric [234] a metal–ligand based [189] hydrogen based [236] and urea based [237] SH polymer.

Alternatively, to performing healing on the material level, damage in a robotic system can be dealt with by incorporating resilience mechanisms in robotic systems [238]. One way to integrate this resilience is to add the ability to learn how to compensate for damage by a self-thought adapted behaviour [239–241]. These resilient systems contain trial and error learning algorithms for compensatory behaviour, allowing the robot to adapt its functionality as a reaction to damage in one of its body parts. As such, the damaged robot can continue its task, with an adapted behaviour that compensates for the damage and with a reduced performance. The rise of modular and self-reconfigurable robotic systems [242] will facilitate self-repair in robotic systems in the future, by replacing failed modules with new ones completely autonomously. Although this approach allows full recovery of the robotic system, extending the lifetime of the overall system, it generates damaged modules, which if not fully recyclable, are not eco-friendly.

Future perspectives and challenges

Including a healing capacity will only be a reliable and sustainable solution to the vulnerability of soft robots in future applications, if the healing is performed fully autonomously, without external or human interventions, which are in general cost inefficient. As illustrated in this review, this goal currently pushes material researchers to obtain SH polymers with improved mechanical behaviour and autonomous healing in application conditions. However, on a system level, the embodiment of stimulus-providing devices (*e.g.* an integrated flexible heater), permit to achieve a robot that heals without external intervention using SH polymers that are classified as non-autonomous. To react autonomously to partially or complete damage, the robot should be able to detect the damage, using integrated sensors. The healing is most effective when the SH polymers are in unloaded conditions, especially at the start of the healing process. Consequently, the detection of damage should lead to the scheduling of a healing period in which the system is at rest.

Soft sensors are already integrated in soft robotic actuator designs to establish feedback motion controllers and state estimation [243,244]. Similarly, there have been reports on flexible damage detection sensors [245–247] and flexible heaters [79,80]. The integration thereof, does not compromise the flexible characteristic of the body of the robot. However, being flexible, these soft sensors and electronics are also prone to the damaging conditions previously mentioned in this review. Adding a healing ability to these integrated components is essential to develop soft robots that are entirely healable. With these future applications in mind, conductive SH polymers [248–251] have been used to construct self-healing electronics [252] including sensors and heaters [253]. However, creating healable soft sensors that are reliable, specifically for application environments in which the conditions slightly vary, remains a challenge.

To achieve the final goal of a soft robot that detects and heals damage autonomously, multiple technologies like SH polymers, SH sensors, health monitors, smart motion controllers and potential integrated stimulus providing devices must be combined in a single intelligent system. Although, the recent fast progresses in the subfields are promising, combining them is a challenge for the coming years. On a material level, for the SH polymers described in this paper a thorough analysis of the dynamic behaviour based on the static and dynamic loads these materials will experience during actuation, is still lacking in literature. Based on the determined dynamic properties such as elastic recovery, viscoelastic and creep behaviour, a more complete evaluation of the SH polymers can be made, as undesired dynamic effects can be detrimental for many soft robotics applications.

Conclusion

Robotics is a highly multidisciplinary field in which various technologies are imported from other research domains. Fields like power supplies, sensors, processing and communication systems are brought together in robotics. Recently, smart materials also have been introduced, integrating additional functionalities, new actuation methods and embodied intelligence, particularly in the emerging soft robotics community [254]. Literature shows that the latest developments in self-healing (SH) materials have pushed the mechanical and healing properties to a higher level, allowing to construct 3D objects capable of healing macroscopic damages. As a result, SH elastomers recently made their first appearance in soft robotics academia, in which they can offer a solution to the vulnerability of these soft systems. The susceptibility of soft robots to damages cause by sharp objects, fatigue, tendon cut, overloading and interfacial debonding will be an obstacle to the effective use of soft robots, particularly when functioning in dynamic, unstructured environments. This stressed the need for a healing ability which allows to recover from these damages and consequently reduce maintenance in future robotics and their ecological impact.

This paper builds the bridge between the self-healing polymer research field and the soft robotics community, as proof of concepts found in literature clearly demonstrate that a high level of transdisciplinary collaboration is required in this new line of research. Because this combination is cutting edge, the capabilities of the materials and requirements of the soft robotics applications are not yet attuned. To address this, we proposed five basic criteria for effective integration of a healing function in soft robots. Although the reports on SH robotics are still limited, a careful investigation of the different SH mechanisms based on these five criteria, makes it clear that many recently published SH elastomers meet the requirements. Potential candidates were listed and compared, based on performance parameters, including mechanical strength, the required stimulus, healing time

and healing efficiency. There exists a general trade-off between mechanical strength/stability of the elastomeric network and the intensity of the healing stimulus or the healing duration. This is translated into soft robotic prototypes that can heal autonomously but have a limited force and power output due to their hyperelastic bodies and others that have a higher mechanical performance but require thermal or UV irradiation in order to heal. Driven by combining high mechanical strength and autonomous healing, researchers started integrating multiple SH mechanisms in a single elastomeric network. This led to a next generation of SH elastomers, with mechanical moduli in the tens of MPa scale and extraordinary healing capacities at mild or room temperatures. Some of these are already used to construct impressive proof of concepts of healable soft robotic actuators.

Although the soft robotics poses several requirements for SH polymers, it is a very suitable application field. Not only because the clear need for a healing function to deal with the vulnerability of the flexible bodies, but also because the robotic system provides a framework where additional systems required for autonomous healing, such as a controlled stimulus providing device and sensors for health monitoring, can be conveniently integrated. Through the adoption of SH polymers in robotics, the SH technology can find its way to other industries like automation, automotive and machines.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Anton W. Bosman is employed by SupraPolix BV and hold shares in SupraPolix BV.

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