A review on self-healing polymers for soft robotics

Seppe Terryn[1,2]*, Jakob Langenbach[3], Ellen Roels[1,2], Antonia Georgopoulou-Papadonikolaki[4], Joost Brancart[2], Thomas George Thuruthel[5], Sophie Norvez[3], Ali Safaei[2], Pasquale Ferrentino[1], Sebastian Tutu[4], Fumiya Iida[5], Tonny Bosman[6], Francois Tournilhac[3], Frank Clemens[4], Guy Van Assche[2] and Bram Vanderborght[1].

Abstract: ***The intrinsic compliance of soft robots provides safety, allows to absorbs shocks and protects them against mechanical impacts. However, a literature study shows that the soft polymers used for their construction are susceptible to various damage types, including fatigue, overloads, delamination and cuts by sharp objects. An economical and ecological solution can be to construct future soft robotic systems out of synthetic self-healing polymers, incorporating a healing efficiency. This review paper, criteria are proposed that allow to validate the potential of a SH 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 many SH polymer types already available in literature are validated and compared. In addition, aside from a description of limited state of the art on self-healing soft robotics, the paper discusses the drives and limits in order 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 development of the novel field of "soft robotics" (*1*)(*2*), which is recently gaining a tremendous interest in the robotics community (*3*), in public media and in industries. In soft robots, parts of the body or in some cases the entire robot consist of a continuously deformable structure, which are in many cases made out of elastomeric polymers (*4*)(*5*), including silicones and polyurethanes. This soft body parts have a relatively large number of degrees of freedom, leading to interesting large-scale deformation modes (*6*). Most of these flexible devices are actuated through variable length tendons (7), which can be integrated tension cables or shape memory alloys cables (*8*), or pneumatically by placing their internal fluidic channels and chambers under pressure (*9*)(*10*) or under vacuum (*11*). Being made from flexible material, they have an intrinsic compliance that leads to interesting features, such as shock absorbance (*12*)(*13*), and safety (*14*)(*15*). Consequently, soft robots are suitable for applications in uncertain, dynamic task environments and for safe human-robot interactions (*16*). 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 intended for soft and delicate objects (*17*)(*18*), like fruits and vegetables that are susceptible to bruising (*19*), and even fragile corals (*20*). Consequently, they are already commercially available by companies like Softrobotics Inc (*21*) and Empire Robotics (*22*)(*23*), and will be (*24*) increasingly operative in the food packaging industry (*25*), agriculture and industrial pick and place of objects with irregular shapes (*22*)(*26*). Safe interaction with soft matter is also required in many biomedicines. Soft robotics, consisting of synthetic materials with compliance (elasticity modulus comparable to the one found in soft tissue in the human body (E = 10^3 – 10^7 Pa) (*27*), find many biomedical applications (*28*)(*29*), including minimal invasive surgery (*30*) prosthetics (*31*) and exoskeletons (*32*).

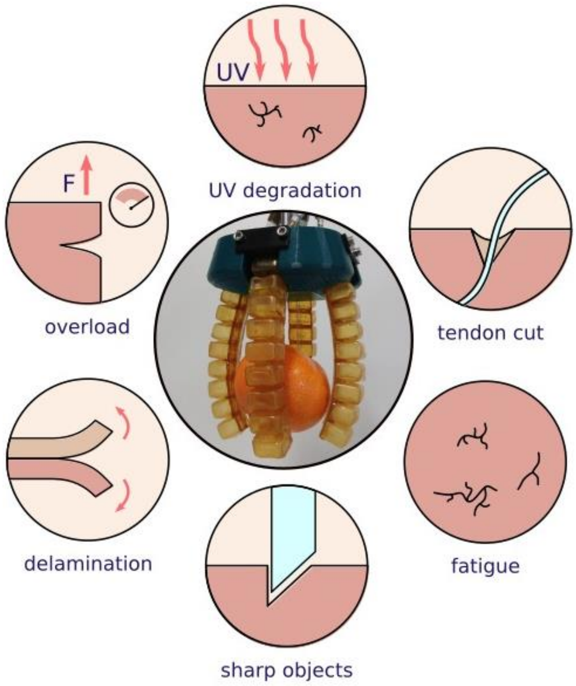

Figure 1: Damaging modes for soft robotics in unstructured and dynamic environments.

Due to their compliance, soft robots can be resilient to impacts and collisions with is illustrated in (*12*)(*13*). 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, these robots are prone to a number of damaging modes (Figure 1). First, the soft membranes 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 leads to a limited lifetime. This is the case for the commercial jamming gripper Versaball of Empire Robotics (*22*) that has its lifetime reduced from 50000 to 5000 grips in situations where sharp objects can be present. When actuating soft robotics using tendon mechanisms, the hard tendons, which are in many cases polyamine or Kevlar wires, can cut through the soft membranes (*33*). This **tendon cut** can occur gradually, due to abrasive damage resulting from friction between the tendon and the soft materials (*34*) or upon overloading the actuators, when the tendon slices through the soft membrane.

Soft robots are almost entirely constructed out of flexible deformable material and a large part of their body undergoes cyclic deformation upon operation. Consequently, these parts are susceptible to **fatigue**, the formation of microcracks due to cyclic loading, which gradually propagate into larger macroscopic damages and eventually failure of the components (*35*). In soft pneumatic actuators, fatigue results in leaks and therefore a decreased efficiency, a change in actuator dynamics and eventually failure, like described for soft muscle in (*36*) and (*37*). 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 (*38*). 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 a rupture of the flexible membranes. These ruptures can occur when too high force or power output is requested or due to external impact or collision or when the parts unintentionally snag on an object or surface. In fluidic actuators the air chambers or channels can burst upon extensive over pressuring.

Many soft robots are produced through moulding or casting techniques (*5*). In many cases multi-step casting or moulding is required, in particular for manufacturing fluidic actuators (*10*), where hollow structures need to be produced and in the 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 pre-polymer, which glues the two parts together. However, this multi-step manufacturing technique introduces weak (multi-) material interfaces in the soft robots that rely almost fully on secondary interactions and are not chemically bonded. Upon extensive loading or multiple actuation cycles, these weak interfaces fail, and **delamination** occurs (*19*, *39*, *40*). 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 (*41*)(*42*). Being constructed out of polymers, soft robots will suffer from degradation over time when exposed to UV radiation. Although not reported in robotics papers, **UV degradation** of silicone (*43*) or polyurethane (*44*) will affect the properties of soft robots over time, depending on the light exposure time.

Aside from the mentioned classification, damages can be classified into two groups: 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 replace the damaged component in the robotic system. Although being manufactured out of relatively inexpensive materials, the cost of replacing a failed soft robotic component can be high. The 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 (*45*)(*24*) which 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, replacement of 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 and we get continuously injured. To compensate for this weakness, we possess a healing ability that allows us to heal small wounds, like scratches or cuts in our skin, and even larger injuries, like torn muscles or broken bones. When developing soft robotic components out of a synthetic material possessing a healing ability, similar to the one found in biological systems, would permit the healing of microscopic and macroscopic damages. This healing ability can 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 properties into synthetic materials to create **self-healing (SH) polymers** (*46*). Since White et. al. (*47*) first introduced the SH technology in 2001, a broad range of SH polymers has been developed, based on a variety of chemical principles (*46*, *48*–*50*).

In this review paper, for the large variety of SH polymers the potential for using them 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 validate and compare the SH mechanisms, five criteria were defined based requirements for future self-healing soft robotic systems. Based on this, limitations, general trends and trade-offs in material properties are identified. Next, the most promising SH polymers described in literature are listed and compared based on mechanical properties, healing stimulus and healing efficiency. At the end of the paper, the few self-healing soft robotic systems found in literature and their SH mechanisms are described and reviewed.

Classification of self-healing polymers

Although healing mechanisms have been incorporated in ceramics (*51*, *52*) and metals (*53*–*55*), most progress is made in SH polymers (*46*, *48*–*50*), due to their higher molecular mobility, which enhances healing and provides a flexible characteristic required for soft robotics (*56*). The many SH-mechanisms in polymers (*57*–*60*) can be classified as illustrated in Table 1. Two main SH approaches can be defined: autonomous and non-autonomous ones. **Autonomous** systems require no stimulus (other than the formation of damage) for healing. They most closely resemble biological systems, which deliver healing agents to compromised regions as soon as damage is initiated. **Non-autonomous** systems require some type of externally applied stimulus to activate their healing function. This stimulus can be in the form of heat, light, a mechanical or chemical stimulus. It has to be taken in consideration that in some conditions, the healing action may not happen autonomously at all 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. exposed to heat or sunlight).

Table 1: Classification of SH mechanisms.

Non-autonomous	**Autonomous**	
Thermoreversible	Hydrogen bonding	Healing agents encapsulated in:
Photoreversible	Metal-Ligand complex	Capsules
Exchange reaction		Tubes
Ionic bonding	Mechanochemical	Vascular systems
Intrinsic		**Extrinsic**

Alternatively, SH mechanisms can be classified as extrinsic or intrinsic (Table 1). **Extrinsic** SH materials have a healing ability built into the material system that is not original to the material, such as healing agents that are encapsulated in microcapsules or in vascular systems. These systems are often autonomous SH- materials, as the trigger used to activate the healing action is the damaging force that leads to the cracking 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.

Requirements of SH polymers for soft robotics

The integration of a healing ability will only reduce maintenance costs of the robotic system significantly if the recovery of functionality is performed completely autonomously, without human-intervention. Considering this, autonomous healing polymers are interesting, because their healing 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. In most soft robotic systems a power source, a battery or connection to the grid, and a control system is present. These can be used to provide the stimulus by an integrated system, e.g. a controlled heater. Another approach for untethered robotic systems is to use a *"healing station"*. Because of the finite battery capacity of robotic systems, they need to go regularly 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 incorporating of a relevant healing ability in soft robotics.

C1: Macroscopic damage can be healed completely. Fatigue in soft robotics, which is the formation of microcrack due to cyclic loading, is in general difficult to measure. Being unnoticed, these microcracks can propagate during cyclic loading into larger, macroscopic cracks (*38*, *42*, *61*, *62*). In addition, soft robotic components can get damaged by sharp objects. The resulting damages are macroscopic cuts, tears, scratches and perforations. To recover from these damaging modes, the SH-mechanism should be able to heal these relatively large damages.

C2: The healing can take place multiple times at a single location. Soft robots will meet various dangerous situations while exposed to an unstructured and dynamic environment and can be damaged multiple times. As for the human body, specific exposed locations will be more likely to be damaged, e.g. the contact surfaces of soft grippers are more likely to get perforated or cut. Consequently, damage can occur more than once at exactly the same location. The healing mechanism should allow multiple damage-healing cycles at a single location.

C3: The initial properties are completely recovered after healing. Soft robotic components are preferentially as good as new after a damage-healing cycle. To recover full performance, the initial material characteristics, including mechanical and healing properties, should be completely regained.

C4: *It is possible to obtain an elastomeric behaviour?* The healing ability will be introduced by constructing the flexible structural components of soft robots out of SH polymer. Therefore, the SH mechanisms should function in polymers with an elastomeric behaviour. Elastomers with a limited viscous contribution in the viscoelastic response are preferred, as an entirely elastic response excludes undesired phenomena like creep and stress-strain hysteresis (*56*) that have a negative effect on the energy efficiency and the dynamics of the soft robotic components. Although SH glassy thermosets (*63*) can be used to make healable stiff components in (soft) robotics, the focus of this review is on elastomers.

C5: The SH polymer can be reprocessed and recycled. In general, the components in soft robotics are of 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 filament are reshaped into (complex) components and consequently, they require reprocessability of the used polymer. If the SH polymer can be reprocessed, these processing techniques that provide high design freedom, will be available for future manufacturing of SH robotic components. In addition, if the polymers can be reprocessed, they have a high recycling potential and can contribute to the development of a sustainable technology and eco-friendly soft robotics.

Validation 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** (*47*, *58*, *64–68*). Upon damage, the encapsulation breaks, liquid healing agents are released, filling the fracture cavity (Figure 2). The monomeric release agents start to polymerize and through solidification the crack is sealed and healed. Recently, progress is made towards the encapsulation in **nanocapsules** (*69*, *70*), which enhances the dispersion of healing agent in the polymer matrix. Although high healing efficiencies can be obtained (*68*), the healing is limited to microscopic damages, 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** (*71*, *72*) or **vascular systems** (*73*, *74*), potentially connected to an external healing agent reservoir (*75*, *76*). This allows 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 capsules or tubes in a certain location are broken, the healing agent is consumed, preventing further healing. Blockage of the channels by solidified healing agent, strongly limits the locally achievable number of healing cycles in vascular networks as well.

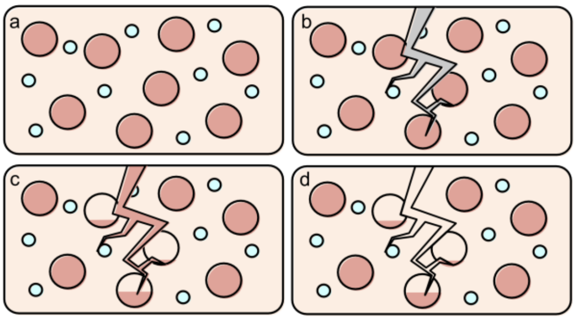

Figure 2: SH mechanism that relies on encapsulated healing agent in micro/nano capsules dispersed in the polymer matrix.

Healing using encapsulated healing agent works well for hard, brittle polymers, like thermosetting matrices. For the capsules or channels to crack open, their shells have to be made out of brittle polymer that adheres well to the surrounding matrix. Furthermore, a necessary condition for capsules or channels to rupture is that the matrix material has to be stiffer than the shell material (*77*). If not, a propagating microcrack will have the undesirable tendency of deflecting away from the capsule or channel. Consequently, up till now, it proved impossible to incorporate a working healing mechanism relying on encapsulated healing agents in elastomers.

The advantage of intrinsic SH polymers (*78*) is their potentially infinite healing capacity. Intrinsic healing mechanisms can be further subdivided depending on the type of interaction used to achieve healing, which can be covalent or physical based.

Intrinsic healing

The healing ability of many intrinsic SH polymers relies on **dynamic covalent interactions** (*79–85*). These dynamic covalent bonds have a reversible nature, they can break and reform, although a relatively large amount of energy is required to break them (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 (*83*)(*86*). 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 reversible bonds in linear polymer chains (*87*, *88*). This approach does not lead to a network structure, which is required to achieve elastomeric properties. The high bond strength of the reversible 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 mainly non-autonomous, requiring energy provided by an external stimulus, for most in the form of heat or radiation. Reversible covalent bonds can be **dissociative** or **associative** (Figure 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 (*89–94*). 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 educt formation is exothermic, the equilibrium will shift to a more bonded state with decreasing temperature. Upon macroscopic damage, the network locally cracks open because reversible crosslinks break and a void is created between the resulting 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. The healing is activated by increasing the temperature, 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 and the formation of a higher concentration of reactive diene and dienophile functional groups. Due to a decrease in crosslink density, the molecular mobility increases, which further enhances contact between the fracture surfaces and aids sealing microscopic voids. Upon cooling, the shift of the equilibrium is reversed, resulting in the reforming 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, restoring the initial material properties completely. It is proven that with this mechanism macroscopic damages can be healed with very high healing efficiency, measured through the recovery of tensile strength (*95*). Multiple damage-healing cycles can 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 a pneumatic finger, though taking days (*96*). Alternatively, other thermoreversible covalent chemistries, like diaryl-bibenzofuranone (*97*), phenol-carbamate (*98*) and urea (*99*) bonds have been used to generate elastomers able to heal macroscopic damage with high efficiencies. The last two reaction mechanisms require mild heating only (≤ 50 °C).

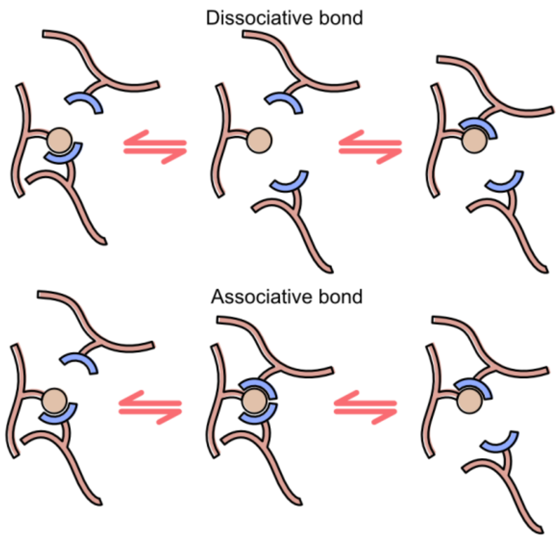

Figure 3: Schematic of the two types of reversible covalent bonds: dissociative and associative bonds.

Conventional elastomers are crosslinked by irreversible covalent bonds, which implies that these polymers cannot be melted, reshaped or (re)moulded. Recycling of these networks is impossible. Conversely, dynamic covalent networks with thermoreversible bonds are recyclable. 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 (*5*, *10*). Viscous flow at high temperatures, opens the possibility to additive manufacturing techniques (*100*, *101*) to shape these thermoreversible elastomers, as recently illustrated by fused filament fabrication of a soft actuators from Diels-Alder elastomers (*95*)(*102*). In addition, thermoreversible elastomers can also be reprocessed by dissolving them in an appropriate solvent and subsequently performing a solvent casting (*103*).

Photoreversible bonds can be created and broken in a reversible fashion by means of irradiation with light, having the appropriate wavelength (*104*). When used to crosslink photoreversible networks, damage can be healed by exposing the material (locally) to irradiation (*105*, *106*, *106*). Examples are coumarin [2 + 2] cycloaddition reaction (*107*–*109*) and anthracene [4 + 4] cycloaddition reaction (*110*–*113*). Upon 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 (λ >300 nm), which leads to further breaking of reversible crosslinks in the network and a (local) increase in mobility and reactive functional groups. The crosslinks are recreated by exposure to light with a higher wavelength (λ <300 nm), healing the damage. An advantage of photoreversible mechanisms is that photoreactions are usually very fast, that they can be selectively initiated, and that a controlled, local treatment is possible. However, the thickness of parts that can be healed is limited by the small penetration depth of the light required for the healing. Coumarin based photoreversible elastomers have been developed in which damages with depths of 0.05-0.2 mm can be healed with high healing efficiencies (*107*)(*108*). Although, photoreversible SH-polymers can find applications in soft pneumatic robotics (*9*), in which often thin membrane structures are used, reprocessing using light irradiation is not possible due to the limited light penetration depth. A few photoreversible covalent bonds, like anthracene dimers are also thermoreversible (*114*)(*113*), 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 (*113*). By excluding the need of short wavelength UV for debonding, damages with a higher depth (0.5 mm) can be healed with high efficiencies (*113*).

Mechanoreversible bonds are covalent bonds that can be reversibly broken by an external 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 (*115*–*117*) , to the authors' knowledge they have not been integrated and validated in healable elastomers. Sometimes, it is impossible to attribute a specific SH-mechanism to a single class. In (*96*, *118*) elastomers are synthesized based on the reversible DA-reaction that can heal damage at room temperature. Hence, the only trigger needed to start the healing process is the breaking of the (weaker) DA-links. Although this network is based on the (thermo)reversible DA-bonds, it has a mechanoreversible character.

Intrinsic healing: Dynamic associated 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 covalent bond is formed at with a different reaction partner; the covalent bond is exchanged. In vitrimers (*119*–*121*), which are dynamic networks that are crosslinked by exchange reactions, there is no net change in the number of bonds formed as a function of temperature., however, the dynamics of the exchange reactions accelerated as temperature rises. At room temperature most exchange reactions are slow and vitrimers with low crosslink densities behave like classical elastomers (*119*) with properties suitable for soft robotics. During 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. However at room temperature, in most cases, the kinetics are not sufficiently fast to perform healing. By increasing the temperature, the exchange reaction kinetics becomes faster, while increasing the mobility, which allows healing in a reasonable time frame (in the order of hours). A well-studied example is the transesterification (*122*, *123*). In (*123*), a boronic ester based network is presented in which large damages can be healed with high efficiencies by heating to 80 °C for 24 hours. Healing can be performed much faster at higher temperatures, like demonstrated for the hydroxyl ester based networks (*124*), which heal damage in 3 hours at 160 °C. The thiol-disulphide exchange reaction (*125*, *126*) and the metathesis of disulphide (*127*–*129*) 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 (*127*). At high temperatures, above the freezing topology transition, all mentioned exchange reaction are fast and the vitrimers can flow and behave like viscoelastic liquids (*119*). Consequently, they can be reshaped using heat based reprocessing techniques, including injection (*122*) and compression moulding (*130*, *131*), and have a high recycling potential (*132*).

The thiuram-disulfide reaction, which exchanges under the stimulation of visible light, was used to crosslink a photo-curable elastomer (*133*). Transparent samples of 1 mm thickness can recover completely from being cut in half by exposure to visible light for 24 hours. 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 (*134*), the metathesis reaction of disulphide in a highly flexible elastomer is catalysed by tri-n-butylphosphine, which leads to the ability to heal autonomously at room temperature with high efficiency, without the need of a stimulus.

Intrinsic healing: Physicochemical interactions

Physicochemical interactions are weaker, non-covalent bonds resulting from intermolecular interactions (Figure 4). 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 (*135*, *136*)(*137*).

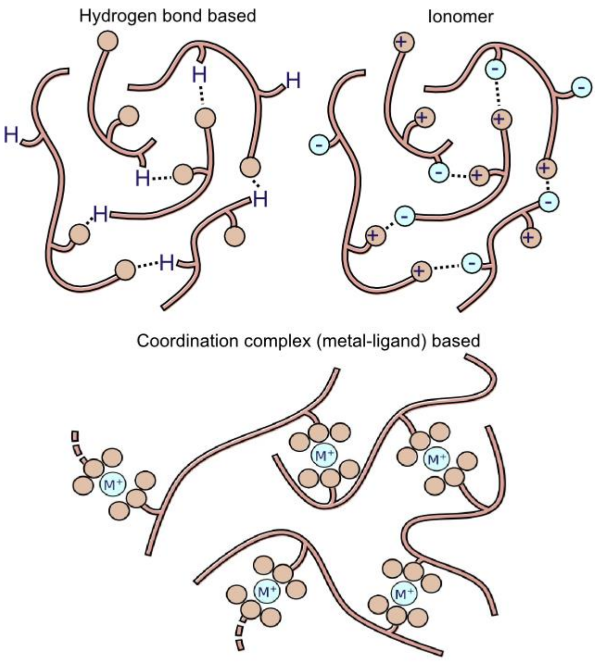

Figure 4: Physicochemical interactions can rely on hydrogen bonding, ionic interactions ore coordination metal-ligand complexes.

Hydrogen bonds are widely used to crosslink networks that have self-healing capacities (*135*, *136*, *138*). The bond strength of hydrogen bonding interactions varies from a few kJ mol^{-1} to several tens of kJ mol^{-1} depending on the hydrogen donor and acceptor. This low bond energy, compared to the covalent bonds (150 – 550 kJ mol^{-1}), means only little energy is required to break and reform, and consequently they can be used to develop autonomous self-healing polymers. The downside of low bond energy crosslinks is a negative impact on mechanical strength, creep behaviour and strain recovery. To enhance the mechanical strength and structural stability, the crosslink strength can be enhanced by increasing the number of hydrogen bonds formed per crosslink, by creating through the use of multivalent hydrogen bonds (*139*). An extensive study on complementary quadruple hydrogen bonding in supramolecular co-polymers was performed by Meijer et al. (*140*). Leibler et al. (*141*) 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. In general hydrogen bond SH-polymers can be easily reprocessed by increasing the temperature, which results in breaking of the hydrogen bonds crosslinks and leads eventually to viscous flow (*141*).

Self-healing polymers based on supramolecular, dynamic networks can also made using **ionomers** (*142*, *143*). Ionomers contain as much as 20% of charged or ionic species as a part of their structure polymeric structure. These ionic groups tend to cluster, acting as physical crosslinking points and allowing reversible formation and reformation of the network structure. Compared to other types of physicochemical crosslinks, ionomeric clusters are stronger, requiring more energy to break. As a result, the healing of ionomers demands external energy in the form of heat. Although classified as non-autonomous, in one example the damage event may provided enough energy, generally in the form of heat as a result of friction heating, so that the material effectively behaved as an autonomic self-healing material in this ballistic impact healing application (*143*). 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. The healing of ionomers relies partly on the elastic response ("snap back") of the (hot) polymer immediately after the projectile has left the part. Because this snap back and the friction heating is less present in other damaging events, like cutting the material, the autonomous self-healing is limited in these conditions.

Supramolecular network formation can also be achieved by **metal-ligand complexes** that act as reversible physical crosslinks (*135*, *144*, *145*). Similar to ionomers, clusters, often referred to as **coordination complexes** (*146*), 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. Compared to ionomeric crosslinks, the metal-ligand crosslink complexes are much weaker. This allows healing macroscopic damages at room temperature without the need of an external stimulus. Like for hydrogen bond SH-polymers, these weaker crosslinks permit to reprocess the material at mild temperatures. A highly stretchable elastomer based on metal-ligand complex crosslinks is presented in (*147*) and has potential for soft robotics applications.

An overview of the mentioned SH mechanisms and their relationship to the five soft robotics criteria are presented in Tabled 2. Many intrinsic SH mechanisms have potential to be used to construct healable soft robotics.

General trade-off in SH-mechanisms for polymers

Every SH-polymer class mentioned above has its advantages and disadvantages: a fully autonomous SH-polymer with excellent mechanical strength and stability, complete recovery and no creep behaviour has yet to be developed. In general, higher bond strengths in the crosslinks, like the ones present in dynamic covalent and ionomeric networks, lead to SH-polymers that have good mechanical strength and stability at room temperature. However, in order to break the bonds, external energy is required, making their SH-mechanism (in general) non-autonomous or slow at ambient temperature. The total bond energy of hydrogen bond crosslinks and metal-ligand complexes is much lower (*148*) and less energy is needed to break them. Therefore, these physicochemical networks can heal damage at ambient temperature. However, the lower total bond energy has negative consequences for the mechanical properties. Autonomous, intrinsic SH-polymers have in general lower mechanical strength and stability. In some cases, creep behaviour is non-negligible and permanent plastic deformations can lead to non-optimal strain recovery.

Table 2: Validation of the SH-mechanisms based on 5 criteria (C) for integration of a healability in soft robotics.

SH-Mechanism	Stimulus	C1: Healing macroscopic damage	C2: Multiple Healing cycles	C3: Recovery of initial properties	C4: Elastomer behavior	C5: Reprocessable and Recyclable	Ref	Ref Applied in soft robotics
Extrsinsic								
Encapsulation							*(58)*	
Micro/nano capsules	/						*(64–67, 70, 77, 149–151)*	
Hollow fibers	/						*(71, 72)*	
Vascular network	/						*(74, 152)*	
Vascular network + reservoir	/						*(75, 153)*	
Intrinsic							*(78)*	
Dynamic covalent							*(79–85)*	
Thermoreversible covalent								
Diels-Alder	*Heat*						*(89–95, 102, 103, 154)*	*(96)(102, 155–159)*
Phenol-Carbamate	*Heat*						*(99)*	
Diarylbibenzofuranone	*Heat*						*(97)*	
Urea	*Heat*						*(98)*	*(160)*
Photoreversible covalent							*(104–106, 106)*	
Coumarin	*UV*						*(107–109)*	
Anthracene	*UV*						*(110, 114, 161)*	
	Heat+UV						*(113)*	*(162)*
Mechanochemical covalent							*(115–117)*	
	/							
Exchange reaction							*(119–121)*	
Transesterification	*Heat*						*(122–124)*	*(163)*
Thiol-disulphide	*Heat*						*(125, 126)*	*(129)*
Metathesis of disulphide	*Heat*						*(127–129)*	*(164)*
	/						*(134)*	
Thiuram-disulfide	*Vis Light*						*(133)*	
Physicochemical								
Hydrogen bonds								
	/						*(135, 139–141)*	*(165, 166)*
Ionomers								
	/						*(143, 167)*	
Metal-Ligand complex								
	/						*(147, 168–170)*	*(171)*

Combining multiple SH-mechanisms in a single polymer

To obtain both adequate self-healing and mechanical properties, more recently SH-polymers have been developed that combine above-mentioned mechanisms. Double dynamers contain both reversible covalent bonding and reversible physicochemical bonding (*172*). In (*173*), a vitrimeric co-polymer was designed with both photoreversible and thermoreversible covalent crosslinks. This combination allows controlling the required healing temperature through UV-irradiation. As the location and intensity of light can be more easily controlled, this combined SH-mechanism can be interesting for applications where only very local healing is required. Another promising technique that allows incorporating a SH-property while having relatively high mechanical strengths are double-networks (*174*)(*175*).

Sordo et al. reported a hybrid network with a fixed amount of hydrogen bonds and a tuneable number of covalent ester bonds (*176*). The combination of di- and tetra-epoxy resins allows to tune the number of chemical cross-links and therewith the mechanical properties. The rubber shows full self-healing at ambient temperature after 24 hours and 78% after the first hour due to fast reformation of hydrogen bonds.

Another interesting thermally self-healing network is described by Fuhrmann et al. (*177*). The polymer can switch on (visible light) and off (UV-light) the healing capacity by light irradiation. Hence, damage can be healed locally while the other part is locked for exchange reactions.

Several self-healing double networks based on disulphide and hydrogen bonds were reported (*178–180*). Particularly Liu et al. described a polyurethane network with high mechanical strength (Young's modulus of 112 MPa) and self-healing ability at mild temperatures (*180*).

Intrinsic SH-polymers with potential for soft robotics

From a detailed literature study, a list of SH polymers with potential for soft robotics was created and summarized in Table 3. Based on the 5 criteria, the following parameters are provided where described in literature:

Mechanical strength:
- σ_{ult}: ultimate stress at which fracture occurs.
- ε_{ult}: ultimate strain at which fracture occurs.

Healing procedure parameters:
- T_{Hmax}: maximum temperature.
- t_{HT}: time at highest temperature.
- t_{RT}: time at room temperature before loading.
- λ: specific wavelength of the irradiation for breaking and bonding of reversible bond.

Healing efficiency:
- η_σ: efficiency based on the recovery of σ_{ult}.
- η_ε: efficiency based on the recovery of ε_{ult}.

The general trade-off between the requirement of a healing stimulus and the mechanical strength, described by σ_{ult} and ε_{ult}, is clearly visible in Table 3. 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.

Table 3: SH polymers with high potential for soft robotics and their characteristics

Thermoreversible SH-mechanisms	Ref	σ_{ult} (MPa)	ε_{ult} (%)	T_{Hmax} (°C)	t_{HT}	t_{RT}	η_σ (%)	η_ε (%)
Dynamic covalent								
Diels-Alder	(*181*)	26	250	130	10 min	1 h (60 °C)	68.9	65.2
	(*182*)	1.47	325	130	4 h	3 days	38	71
	(*95*)	22.5	295	140	10 s (NIR)	3 days	92	
Phenol-Carbamate	(*98*)	2.9	240	80	2 h	3 h	98	
Diarylbibenzofuranone	(*97*)	0.75	830	50	12 h	/	90	90
Urea	(*99*)	1.2	301	37	12 h	/	83	87
Exchange								
Transesterification	(*124*)	5.5	750	160	3 h		80	>85
	(*123*)	2.0	275	80	24 h	/	90	85
Thiol-Disulfide	(*126*)	60	10	180	2 h	/	80	
	(*125*)	0.47	65	60	1 h	/	100	97
Disulfide	(*127*)	22.9	846	100	10	/	100	99
Physicochemical								
Hydrogen	(*183*)	37	700	120	4 h	12 h (60 °C)	91.8	
	(*184*)	0.3	30	50	5 min		~100	~100
Host-guest interaction	(*185*)	13.5	17	120	30 min	15min (NIR light)	85	>85
π- π stacking	(*186*)	12	3.5	70	12 h	12 h (70% RH, RT)	~100	~100
Combined mechanisms								
Transesterification + Metal-ligand	(*188*)	9	650	80	24 h	/	~100	~100
HB + disulfide bonds	(*180*)	20	500	90	24 h	/	>90	>85

Autonomous SH-mechanisms	Ref	σ_{ult} (MPa)	ε_{ult} (%)	t_{RT} (h)	η_σ (%)	η_ε (%)
Dynamic covalent						
Diels-Alder	(*96*)	0.11	365	7 d	80	91
Exchange						
Disulfide	(*178*)	0.81	3100	24 h	95	97
	(*134*)	0.23	105	24 h	95	96
Thiuram disulfide	(*133*)	0.4	202	24 h and visible light	100	90
Transesterification	(*189*)	4.2	56	72 h (85% humidity)	95	93
Physicochemical						
Hydrogen	(*190*)	1.92	780	24 h		90
	(*191*)	3.5	600	3 h	>80	>80
Metal-Ligand	(*169*)	1.4	770	3 h	>95	
	(*170*)	0.6	320	48 h	>90	80
Host-guest interaction	(*192*)	~0.5	>4500	12 h	~100	~100
Ionic binding	(*193*)	0.7	300	20 min	~100	~100
	(*194*)	1.2	1100	24 h	92	
	(*195*)	0.02	1500	24 h	100	~100
	(*196*)	0.2	1700	24 h (in water)	>95	>95
Combined mechanism						
HB + transesterification	(*197*)	1.6	325	24 h	100	
Capsules + Metal-ligand	(*198*)	3.2	90	10 h	90	>80
π- π stacking + Pt complex	(*187*)	0.3	14	24 h	~100	~100

Photoreversible SH-mechanisms	Ref	σ_{ult} (MPa)	ε_{ult} (%)	λ (nm)		t_{exp}		η_σ (%)	η_ε (%)
Dynamic covalent									
Coumarin	(*107*)	1.2	640	254	350	1 min	90 min	100	80
	(*108*)	12.1	457	254	365	10 min	30 min	84	90

Limitations of artificial self-healing polymers

The wound healing process of a cut in our skin is highly complex (*199*) and involves multiple stages, including hemostasis (blood clotting), inflammation, proliferation (growth of new tissue) and maturation. Compared to this, the artificial self-healing mechanisms discussed above, which are single or dual step processes, are relatively uncomplicated. In artificial self-healing polymers, the powerful hemostasis step, which relies on complex cell division and growth, cannot be achieved because of the mass conservation law. In artificial self-healing polymers, cavities on the microscopic level at the fracture interface can be filled by an increased molecular mobility or by means of a released healing agent. However, synthetic material cannot grow to gradually fill large gaping damages. Consequently, the healing is limited to recombining fracture surfaces that are brought back in contact on a macroscopic level. In reaction to this limitation, recently researchers investigated the use of stem cells for creating living, self-healing robots (*200*).

State of the art on healable soft robots

Although many self-healing mechanisms have tremendous potential to integrate a healability, only a limited number of publications demonstrates their use in soft robotics. Recently, researchers at the Vrije Universiteit Brussels, constructed various soft grippers and soft robotic hands out of Diels-Alder polymers and provide them with the capacity to heal macroscopic damages (*102*, *155*, *157*, *158*). These prototypes, which are pneumatically actuated (*157*, *158*), or tendon driven (*155*), demonstrated that Diels-Alder elastomers have mechanical properties, which are suitable for soft robotic applications. The soft robotic prototypes can recover from large realistic like cuts, with near complete restoration of initial characteristics after being subjected to a healing process. Even very drastic damages, like cutting the actuators completely in halve, could be healed entirely. For these Diels-Alder soft robotic components (*102*, *155*, *157*, *158*), 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 exclude the need of external heating, the researchers also reported on a soft robotic gripper, constructed out of a Diels-Alder networks, that can heal large damages autonomously at room temperature (*96*). However, to allow efficient room temperature healing in Diels-Alder polymers, high molecular mobility is required, which resulted in a highly flexible characteristic, with a limited mechanical strength. Consequently, the power and force output of the soft gripper is limited, which emphasizes the trade-off between mechanical properties and healing temperature.

In 2013, R. Shepherd et al. (*201*) presented a soft pneumatic gripper that is resistant to punctures by a needle due to a self-sealing behaviour of a silicone/Kevlar composite. 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. Hence this healing principle is limited to small damages, yet interesting since many failures of soft actuators are due to small punctures and perforations. In 2017, J. T. Wallin et al. (*202*) presented another SH-technique for soft pneumatic actuators. A soft bending actuator developed from silicone (polydimethylsiloxane) using stereolithography (SLA) was filled with thiol-ene resins. 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 by the network formed.

In (*203*) a soft photo and magnetic responsive actuator is presented with a self-healing ability due to a combination of metal-ligand coordination bonds and hydrogen bonds.

SH-mechanisms have been implemented in dielectric elastomer actuators (DEA) (*204*). A DEA consists of a highly stretchable dielectric layer that is sandwiched between two stretchable electrodes. 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, such as grippers (*204*, *205*). 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. DEA have been manufactured with a SH-dielectric layer using an open-cell silicone foam filled with silicone oil (*206*), a liquid dielectric (*205*) or a metal-ligand SH-polymer (*147*).

Recently, soft sensors and electronics are integrated in soft robotic actuator designs in order to establish feedback controllers. Adding a healing ability to these components is essential to develop entirely SH-soft robots. With these future applications in mind, conductive SH-polymers with high potential for soft-sensing applications have been synthesized (*144*, *207*, *208*).

Alternatively, to performing healing on the material level, damage in a robotic system can be dealt by incorporating resilience mechanisms in robotic systems (*209*). One way to integrate this resilience is to add the ability to learn how to compensate for damage by a self-thought adapted behaviour (*210–212*). These resilient systems contain trial and error learning algorithm 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 (*213*), will facilitate self-repair in robotic systems in the future, by replacing failed modules with new once completely autonomously. Although this approach allows full recovery of the robotic system, extending the lifetime of the overall system, it generates damaged modulus, which if not fully recyclable, are not eco-friendly.

Conclusion

Various technologies used within robotics are imported from other domains and robots are often seen as integrators. Fields like power supplies, sensors, processing and communication systems are brought together in robotics. Recently, novel smart materials are introduced, integrate addition functionalities, new actuation methods and embodied intelligence, specifically in the recently emerged soft robotics community. In addition, recent developments in the self-healing polymers have pushed the mechanical and healing properties of these materials to a higher level, which allows to use not only use them for coating applications but also to construct healable objects, able to heal macroscopic damages.

This review paper aims bridge between the self-healing materials research field and the soft robotics community. From a first literature study it is concluded that soft robots are volnurable and can be damaged through various damaging modes, including fatigue, delamination, overloading, tendon cut and by sharp objects. This stressed the need for a healing ability which allows to recover from these damages and consequently reduce maintenance in and the ecological impact of future robotics. However, to provide an economical and ecological solution for the volnurability of soft robots, the SH polymers that can be used need to meet five basic criteria, proposed in this review. Based on these, SH mechanisms with limited potential are excluded. For the remaining, based on performance parameters, including mechanical strength, healing efficiency and healing times, examples with exceptional suitable properties for soft robotics were sought in the literature, listed and compared. Throughout the paper, it discussed how the underlying chemistry impacts the performance parameters, which are provided in overview tables. From this extensive analysis it is conclude, that taking in account some limitations and trade-offs in material properties, many SH mechanisms can be directly used to construct healable soft robotic components.

This interesting multi-disciplinary combination is recently picked up by a limited amount researchers. A state of the art of the first publications on the self-healing soft robots is included. Because this combination is cutting edge, the capabilities of the materials and requirements of the soft robotics applications are not yet attuned, meaning that further research is needed to improve the system capabilities of self-healing soft robots. As such, this paper discusses the drives and limits in order to spur the interdisciplinary research field.

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