

Self-repair of structural and functional composites with intrinsically self-healing polymer matrices: A review

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Abstract

Self-healing is a smart and promising way to make materials more reliable and longer lasting. In the case of structural or functional composites based on a polymer matrix, very often mechanical damage in the polymer matrix or debonding at the matrix-filler interface is responsible for the decrease in intended properties. This review describes the healing behavior in structural and functional polymer composites with a so-called intrinsically self-healing polymer as the continuous matrix. A clear similarity in the healing of structural and functional properties is demonstrated which can ultimately lead to the design of polymer composites that autonomously restore multiple properties using the same self-healing mechanism.

Keywords: B. Mechanical properties; B. Electrical properties; B. Thermal properties; Self-healing.

1. Introduction

Over the last decades the amount of studies reporting on polymer composite functionality and mechanical properties has grown significantly. Polymer composites showing for example thermal and electrical properties can be found in daily life in communication, lightning and aerospace applications [1, 2]. Although the field of multifunctional polymer composites is increasing rapidly, researchers are far away from reaching the diversity in functionalities that nature has established in its composites over the past millions of years. Wood is one of nature's finest examples of a multifunctional fibrous composite material. This well-known material consists of parallel hollow tubular cells reinforced by spirally wound cellulosic fibrils embedded in a hemicellulose and lignin matrix. The helix angle of the spiral fibrils is responsible

for a variety of mechanical properties such as wood stiffness and toughness, whereas the hollow tubular cells are capable of transporting nutrients from the soil to the top parts of a tree [3]. Also skeleton bones deliver optimal mechanical properties due to a smart combination of material selection and material shaping [4].

Besides a variety of mechanical and functional properties, wood and bone possess the capability to self-repair damage that is inflicted to their components [5]. Since both structural and functional polymer composites show a drop in performance when subjected to a certain cyclic or impact loading due to the formation of cracks or delamination, a bio-inspired system that autonomously restores the material properties is considered tremendously valuable. Therefore, in the past two decades, the self-healing capacity has inspired many researchers to design polymer composites that are capable of healing damage rather than preventing it [6, 7]. This field was pioneered by Dry who included hollow glass fibers containing liquid adhesive in a concrete matrix. The liquid agent is released upon local fracture, wets the crack surface and crosslinks thereby partially restoring the load bearing capacity [8, 9]. White et al. showed the recovery of tensile strength of an epoxy material by embedding polymeric microcapsules filled with crosslinkable liquid oligomer into the polymer matrix with dispersed Grubbs catalyst [10]. However, since it is quite challenging to obtain a uniform distribution of healing agent using particulate containers, Bond et al. developed a self-healing fiber reinforced composite by introducing glass fibers filled with healing agent. The resulting composite was capable of restoring a significant amount of its original flexural strength [11].

At the pioneering start of the field of self-healing composites, the employed healing strategies are extrinsic (i.e. are due to the inclusion of discrete entities containing the healing agents in an otherwise non-self-healing surroundings) and therefore in principle only a single healing event can occur at the same damaged site. This concept was further improved by Toohey et al. who developed a bio-inspired vascular system capable of repeated healing of an epoxy coating. The healing strategy, however, still relies on the inclusion of external healing agent [12]. In more recent years, the intrinsically self-healing route (i.e. the architecture of the polymer is such that local damage can be restored upon a mild proper trigger by the reformation of reversible chemical bonds) was shown as an attractive alternative. Due to the reversible character of the chemical bonds involved in the healing (and breaking) process, intrinsically

self-healing polymers can theoretically lead to an infinite amount of healing cycles as no external healing agents are required. However, where extrinsic healing systems are capable of healing polymers with large scale damages up to 35 mm as was recently reported by White et al.[13], intrinsic healing strategies are reported to be well suited for healing small scale damages, but restoration of larger damages remains a challenge because the contact between the failed surfaces is often lost. The intrinsic healing process depends on the ability of the matrix to acquire local mobility upon the stimulation of an external stimulus, such as temperature, light induction, electrical current and moisture exposure. Therefore, in contrast with their extrinsic counterparts, intrinsic healing materials are generally not fully autonomous. Intrinsic healing systems will require the input of extra energy which in some cases can be supplied by the damage event itself (e.g. impact damage in ionomers [14, 15]). Alternatively, damage has to be detected by a sensor or the composite has to be exposed periodically to its healing trigger. Still, the implementation of theoretically infinitely repeatable intrinsic healing in polymer composites is considered as a valuable addition to the development of materials that are designed to mend damage rather than preventing it [7, 16, 17].

The majority of studies that cover the intrinsic healing of polymer composites reported on the healing of structural properties (i.e. properties related to load bearing behavior, such as stiffness, strength and failure strain), whereas the field of general self-healing polymer functionality (including healing of non-mechanical properties such as thermal conduction, electrical conduction and magnetic shielding etc.) is emerging only in the last couple of years. However, damage (upon fatigue or impact loading) in either the polymer matrix (cracks) or at the matrix-filler interface (delamination) is responsible for a decrease in the properties of both structural and functional polymer composites, because the filler material is no longer capable of transferring its specific properties towards the matrix material. (In structural composites, reinforcing fibers and particles are customarily referred to as the ‘reinforcement’, while in functional composites, the added fibers or particles are referred to as ‘filler’. In order to maintain consistency of text, in this review we only use the term ‘filler’ to refer to the non-continuous non-polymer constituent in the composite.) Therefore healing strategies in both types of composites can be similar and will be most effective in the form of a polymer matrix capable of restoring either itself or the matrix-filler interface. For this reason the development of polymer matrices that can intrinsically heal themselves or restore the

adhesive properties at the composite interface is considered to be a major challenge within the field of self-healing polymers. This review aims to give an overview of the progress that is made on intrinsic matrix healing of both structural and functional properties in polymer composites. Firstly, the current developments in intrinsic polymer matrix healing are discussed, grouped by the triggering mechanism for the healing process. Secondly, the general concepts and influence of filler materials on structural composite properties (stiffness, strength) and their healing capabilities is covered. Finally, a similar approach is used to analyze the self-healing potential of functional (electrical, electromagnetic, electromechanical, magnetic and thermal) polymer based composites.

2. Intrinsically self-healing matrix polymers

In structural and functional composites, polymers, such as polyester, polyimide, polyurethane, epoxy or silicone rubber, are used as matrix because of their ability to bind and preserve the location of the filling materials, their low density, chemical inertness, low cost and versatility in fabrication methods. Traditionally polymer based composite systems were composed such that a maximum resistance to local mechanical, thermo-mechanical or chemo-mechanical degradation is obtained. Very often the optimization focused on creating a lasting chemo-mechanical bond between the polymer matrix and the fillers. This conventional optimization damage, virtually always starting in the polymer matrix or at the matrix-particle interface, was treated as an irrecoverable event. However, with the advent of intrinsically self-healing polymers, i.e. polymers which can restore mechanical bonding with itself or a different material due to reformation of chemical bonds under the appropriate stimulus (see Figure 1 and Figure 2), the design concepts for composites have changed significantly and irreversibly. Below, we describe the range of self-healing polymers and group them according to the trigger they need to heal cracks and interfacial delamination.

2.1 Heat triggered self-healing

Intrinsic self-healing polymers based on heat triggered reversible reactions have been studied extensively, because it is relatively practical to apply heat as stimulus compared to other stimuli such as light, electrical fields or moisture. Among the thermally activated self-healing polymers, the Diels-Alder/retro-Diels-Alder reaction (DA/rDA) has received most of the attention. The Diels-Alder

reaction is a reversible reaction that takes place between a conjugated diene and a substituted alkene, usually termed the dienophile to form a substituted cyclohexene system. The DA/rDA reaction can be used as healing mechanism in multiple polymer systems (e.g. polyamide, polyethylene and epoxies) and can be used to heal both the matrix and the matrix-filler interface. The latter one is schematically depicted in Figure 3. The healing temperature ranges from 100°C to 150°C and the healing times were reported in the range of 10min to 2h [18-26].

A second type of thermally activated self-healing was introduced by Canadell et al. who used remendable disulfide chemistry in a covalently cross-linked rubber [27]. In their work, an epoxy resin containing disulfide groups was cross-linked with a tetrafunctional thiol in a base-catalyzed addition reaction. Upon fracture, the mechanical properties of this material can be fully restored by re-contacting the fractured surfaces while heating at 60°C for 1h. A more recent study showed that the dominant healing mechanism is based on the thiol-disulfide exchange and that reaction is highly pH dependent [28]. An advantage of using disulfide chemistry as self-healing mechanism is that healing can be achieved at moderate temperatures, while keeping a reasonable level of bond strength.

Another example of self-healing by a thermal stimulus is the radical exchange reaction of alkoxyamine units that can be used to prepare a thermodynamic polymer cross-linking system [29, 30]. Based on this mechanism, Yuan et al. developed self-healing polystyrene with alkoxyamine side chains which function as cross-linker. In this system, fission and radical recombination of C-ON bonds takes place among alkoxyamine moieties when a thermal stimulus is applied. The healing efficiency of this system reaches values of 75.9% by heating upon 130°C for 2.5 hours [31].

Besides the aforementioned thermally triggered covalent self-healing systems, matrices can use supramolecular interactions, such as hydrogen bonding and π - π interactions, as a mechanism for intrinsic healing. In healing systems based on hydrogen bonding, mending will occur already at room temperature when the functional groups are brought into effective contact with each other. However, the healing efficiency decreases with increasing waiting time between the damage event and mending because the free hydrogen bonds can rearrange and associate with one another at the fractured surface instead of those

on the other side of the crack. Moreover, the elevation of the healing temperature can increase the molecular dynamics and accelerate the equilibrium, thereby decreasing the healing time [32-38].

A second system capable of supramolecular healing is based on π -electron-poor receptors and π -electron-rich pyrenyl end-groups. Here, the healing mechanism involves two steps. The first step is the disruption of the intermolecular π - π stacking cross-links upon an increased temperature. The second step is the rearrangement of chains and reformation of π - π stacking cross-links when the temperature is lowered. The healing temperature is reported to be around 100°C with healing time more than 2 hours [39-41].

Ionomers are another class of thermally activated supramolecular self-healing polymers that possess the ability to heal ballistic impact damage. In ionomers, ionic metal salts are bonded to the polymer backbone creating electrostatic interactions. The local heat that is released upon impact enables these bonds to reform and thereby heal the material. Studies on ionomer healing focused on the autonomous healing after high speed ballistic impact [42, 43] and on the stimulated self-healing after quasi static damage production [44-47].

Heat triggered self-healing polymers are excellent candidates as matrix material in polymer composites that can easily be exposed to a heat source. The heat triggered matrix material should be selected on the basis of the nominal working temperature of the desired application and the thermal fluctuations during product use. Hence, for some applications, it may be practically impossible to apply a proper thermal healing treatment and systems based on a different healing trigger might be more appropriate. Three other types of self-healing stimuli are presented below.

2.2 Photochemical triggered self-healing

Besides thermal activation, self-healing behavior can be triggered by photochemical reactions. Based on photochemical [2+2] cycloaddition of cinnamoyl groups, Chung et al. developed a self-healing polymer from 1,1,1-tris-(cinnamoyloxymethyl)ethane, which is a photo-cross-linkable cinnamate monomer [48]. In their study, healing was conducted by photoirradiation ($\lambda > 280$ nm) for 10 minutes. More recently,

Ling et al. and Oya et al. continued this line of research by synthesizing novel self-healing polymers based on [2+2] photocycloaddition [49, 50].

Another example of photochemically triggered healing was reported by Ghosh et al. who developed a self-healing oxetane-substituted chitosan polyurethane [51]. Upon fracture, four-membered oxetane rings open up thereby creating two reactive ends. When the crack plane is exposed to ultraviolet light ($\lambda=302$ nm), chitosan chain scission occurs, which forms crosslinks between the reactive oxetane ends and repairs the network in less than 1 hour.

Amamoto et al. showed two novel studies on self-healing polymers by photoinduced reshuffling of disulphide bonds. First, they introduced self-healing in poly(*n*-butyl acrylate) by including repeatable trithiocarbonate units [52]. These polymers are capable of healing macroscopic cracks almost completely after UV irradiation ($\lambda=330$ nm) for 48 hours. In a second study, they reported on macroscopic self-healing crosslinked polyurethanes based on radical reshuffling of thiuram disulfide units under the stimulation of visible light at room temperature [53].

Moreover, photochemical self-healing in metallosupramolecular polymers were reported by Burnworth et al.. Their low-molecular-mass polymers possess ligand end groups that are non-covalently linked through metal-ion binding [54]. Samples were healed by exposure to UV light leading to a temporary disengagement of the metal-ligand bonds.

Polymers that heal upon a photochemical trigger have a potential healing time that ranges from minutes to days, which can be advantageous over heat triggered polymers which generally need at least several hours for proper healing. Therefore, photochemical triggered self-healing polymers can be a good choice as matrix material when fast healing is required. However, due to light scattering at matrix-filler interfaces the penetration depth of light into a composite will be limited and the approach will be restricted to very thin, sheet like composite structures.

2.3 Electrically triggered self-healing

Matrix healing upon electrical stimulus was proposed by Chuo et al. who prepared an electrically triggered self-healing polymeric material based on the complexation reaction between ferrocene modified

poly(glycidylmethacrylate) and β -cyclodextrin groups [55]. A knife-cut crack on the surface of this sample mends almost completely after an electrical treatment of 9V for 24 hours followed by a resting period at room temperature for another 24 hours. The healing efficiency can be improved by an additional thermal treatment (85°C, 24 h) after the electrically induced repairing process. Although the number of studies on this topic is rather limited, self-healing based on electric stimuli has a great potential in electronic applications, because the healing will be instigated while the component is still functioning.

2.4 Moisture triggered self-healing

Another stimulus that triggers self-healing in polymers was reported by Zhang et al.. They synthesized an isocyanate containing methacrylate monomer copolymer system that repairs macroscopic cracks after a relative humidity treatment (95% at 30°C) of 12 hours and serves as a protecting fluorine-containing monomer component [56]. Healing is based on a zipper-like healing mechanism in which the isocyanate groups on both sides of the crack within the effective contact areas are coupled by reacting with environmental water. This process can be gradually extended to the ineffectively contacted areas which ultimately results in full closure and healing of the crack.

Taking the different self-healing stimuli into account, it is clear that heat triggered intrinsic self-healing is currently the most developed strategy. However, based on the actual application of a polymer composite, a different healing mechanism might be more appropriate in order to reduce the healing time or to create a system that heals while functioning.

3. Structural composites containing an intrinsically self-healing polymer matrix

Structural composites are optimized to give desirable mechanical properties, in particular (specific) stiffness and mechanical strength. The strength and stiffness of such composites depends on the properties of the constituent phases (polymer matrix and inorganic filler), their volume fraction and their configuration. To realize their full potential a perfect bonding between the matrix and the filler particles is required. As the inorganic fillers are based on strong irreversible (non-self-healing) covalent bonds, any self-healing has to come from the polymer matrix which (in principle) can restore the integrity of the

matrix as well that of the interfacial bond. Below we demonstrate how the principal mechanical properties are to be affected by a self-healing polymer matrix.

3.1 Stiffness recovery

The stiffness of a material is defined by the ratio between stress and strain (Young's modulus or modulus of elasticity) at the elastic regime of a tensile experiment and describes the resistance to elastic deformation of a material. To improve the typical low stiffness of polymers either particles or fibers of a high modulus material are integrated into the polymer matrix [2, 57, 58].

In particulate reinforced composites, the first factor that affects the stiffness is the weight percentage of the added particles. An increasing concentration of stiff particles in a polymer matrix improves the stiffness since the rigidity of fillers is much higher than that of matrix. This effect was described in many studies such as the work of Zhu et al. on polyimide/silica particle composites [59-63]. The polymer composite stiffness is less clearly affected by a change in particle size. For particles with sizes in the micrometer scale, the Young's modulus does not change with increasing diameter [61], but for nanometer-sized particles an increase in stiffness is observed when the average particle size is decreased [60]. Besides the particle size, the interfacial adhesion between the particles and the matrix has little effect on the stiffness as well. Since values for the stiffness are determined at relatively low deformation, there is insufficient dilation for interfacial adhesion parameters to have an effect on the Young's modulus [59, 62].

Besides adding particles, long continuous or short discontinuous fibers can also be used to increase the stiffness of a polymer matrix. The elastic modulus of common reinforcement fibers (glass, aramid, carbon) is typically a hundred times higher than that of conventionally used polymer matrices [58]. Based on the volume fraction of the fibers in the matrix, the overall stiffness of fiber reinforced polymer composites can be estimated by the 'rule of mixture':

$$E_c = \eta_L \eta_0 V_f E_f + (1 - V_f) E_m \quad (3.1)$$

where E_c , E_f and E_m are the stiffness of the composite, fiber and matrix respectively, V_f is the volume fraction of the fiber and η_L and η_0 are the length efficiency and orientation factor respectively [64]. The

fiber orientation factor has a value ranging from 0.2 (for randomly distributed fibers) till 1 (for unidirectional fibers). The length efficiency factor η_L depends on the critical fiber length (L_c) of the filler material which is described by:

$$L_c = \frac{\sigma_f d_f}{2\tau} \quad (3.2)$$

where σ_f is the maximum fiber stress (or ultimate fiber strength), d_f is the fiber diameter and τ is the interfacial shear stress which can be regarded as a measure for the interfacial adhesion between filler and matrix. When the fiber length is below L_c , η_L has a value near zero and the filler material does not contribute to the composite stiffness. The value for η_L increases with increasing fiber length up till the point where the fiber length is ten times L_c and η_L has a value of 1. At this level, an increase in interfacial adhesion does no longer adds to the composite stiffness. For this reason the interfacial adhesion has only a small effect on the stiffness of continuous fiber reinforced polymers. However, the effect of interfacial adhesion on short fiber reinforced composite stiffness is significant. A graphical description of the effect of interfacial adhesion on the composite stiffness is presented in Figure 4. In the case of complete debonding the fillers do not carry any load and the stiffness of the composite decreases with increasing filler content. In the case of perfect bonding, the stiffness of the composite increases with filler content according to the physical limit given by equation 3.1. In the case of partial debonding intermediate stiffness values are obtained. Several studies described interfaces that are modified to improve the adhesion between fiber and matrix which show higher elastic moduli than their unmodified counterparts [58, 65, 66]. A study by Thomason et al. on continuous glass fiber reinforced polyimides shows that the composite stiffness is unaffected by changes in the fiber diameter because the fiber length greatly exceeds the L_c [67].

Fatigue and impact damage are the most occurring types of damage in real-life applications of particulate and short fiber reinforced polymer composites. Fatigue damage results in cracks splitting either part of the polymer matrix or the matrix-filler interface and damage upon impact ranges from barely visible impact damage (microcracks or delamination) to large scale breakage like target penetration [7, 68]. In short fiber reinforced polymer composites the damage will initiate at the interface resulting in a reduction of τ and η_L leading to a drop in composite stiffness. Figure 4 shows the stiffness range that can potentially be recovered by healing of the interfacial adhesion between filler and matrix. To repair the composite's

damage and regain its structural properties, the focus should therefore be on healing the matrix and the composite interface which results in restoring the initial values of τ and η_L . Because of the small effect of interfacial adhesion on the stiffness of continuous fiber reinforced composites, healing of the filler-matrix interface does not contribute significantly to the recovery of the stiffness for these types of composites.

Studies that report on stiffness regeneration include the work of Yoshie et al. who reported on the recovery of tensile moduli of a self-mending polymer based on the Diels-Alder chemistry between anthracene and maleimide at both room temperature (17%) and 100°C (46%) [69]. Secondly, recovery rates of Young's moduli of almost 100 % were reported by Amamoto et al. who designed a polyurethane that heals using radical reshuffling of thiuram disulphide bonds under ambient conditions (Figure 5) [53]. A third example of stiffness regeneration was shown in the study of Zako and Takano. They developed a composite blend material that consists of a rigid polymer matrix in which melt processable thermosetting epoxy particles are introduced. Specimens were damaged and healed at 120°C. After healing the stiffness of the composite material was fully recovered [70]. The self-healing matrices described in the cited studies are considered good candidates for stiffness regeneration in particulate and short fiber reinforced composites. However, their influence on the healing of the filler-matrix interface is yet to be shown in future studies. For the recovery of stiffness in continuous fiber reinforced composites alternative strategies need to be considered. Furthermore, due to the reversible nature of the relatively weak chemical bonds in the matrix polymer, the polymer matrix has a tendency to flow when exposed to mechanical loads for long periods of time. So the dynamic nature of the self-healing polymer will restrict the use of such composites for continuously loaded structures.

3.2 Strength recovery

The strength of a material can be described by several parameters. The tensile strength is defined as the maximum stress that a material can sustain under tensile loading and is also called the ultimate strength. The stress at fracture and the stress above which plastic deformation occurs are called the breaking strength and yield strength respectively [2]. In line with polymer stiffness improvement, the polymer composite strength can be increased by introducing particles or fibers that have much higher strength values than the matrix.

The strength of micro and nano-particulate composites is mainly determined by the effectiveness of the stress transfer between the matrix and the particles [57]. As for composite stiffness, the strength depends on the weight percentage of filler that is present in the matrix. However, no clear trend can be derived from literature as studies show that an increase in filler concentration can initially improve the composite strength while it is reduced upon further increase of particle concentration [57]. This is exemplified by the work of Zhu et al. who reported on polyimide films with silica fillers that show an increase in tensile strength up to a silica weight fraction of 10% [63]. However, a decline of tensile strength is observed upon further increase of the silica concentration. This can be explained by the fact that the particle cluster size increases together with the weight fraction which suppresses the strength of the composite, since, in contrast to stiffness, there is a clear relation between the size of added micro- and nanoparticles and the strength of a polymer composite. Generally, a decrease in particle size will lead to an increase in tensile strength as is shown for epoxy/silica composites by Nakamura et al. [71]. A final crucial parameter is the strength of the interfacial particle/matrix adhesion which determines the stress transfer between the components. For polymer composites containing very well-bonded particles, the addition of particles will result into a higher material strength. Poorly adhered particles, however, have an ineffective stress transfer and therefore do not contribute to the reinforcement of the matrix which leads to a decrease in strength. This phenomenon was quantified by Zhang et al. who showed the effect of interfacial adhesion in polypropylene/silica nano-composites on the material's strength by treating the particles with various monomers [72, 73].

Short and continuous reinforcing fibers with high elastic moduli (carbon, aramid, glass) are used to enhance the strength of a polymer composite in a similar fashion as is described for stiffness modification. Therefore, the 'rule of mixture' can also be used to approach the strength of a composite based on the volume fraction of the fibers:

$$\sigma_c = \eta_L \eta_0 V_f \sigma_f + (1 - V_f) \sigma_m \quad (3.3)$$

where σ_c , σ_f and σ_m are the strength of the composite, fibers and matrix respectively. For strength, the length efficiency factor, η_L , is again related to the critical thickness L_c , as is described by equation 3.2. Therefore a similar graphical relation between the strength, volume fraction and interfacial adhesion, similar to that depicted in Figure 4 could be composed. Such a graph would indicate that the interfacial

adhesion between fiber and polymer also has a large effect on the strength of short fiber reinforced composites. However, for continuous fiber reinforced composites, this effect is much less. Additionally, delamination between fiber and matrix can have a significant effect on the crack-growth resistance and may therefore even increase the ultimate strength of a polymer composite [65, 74].

As is described for stiffness, the strength of short fiber reinforced composites will drop upon interfacial failure due to a reduction of effective stress transfer resulting from cracks and delamination in the matrix or at the interface. Therefore, studies on strength healing of these composites should also focus on the recovery of η_L and τ by intrinsic restoration of the polymer matrix or the matrix-filler interface. For this purpose mainly intrinsic covalent healing strategies, containing either thermo reversible or photo reversible chemistries, are used [75]. Healing of the strength of epoxy-amine thermoset composites by the addition of thermally reversible cross-linking gel based on Diels-Alder chemistry was reported by Peterson et al. [25]. Recovery of strength can be achieved by direct application of the gel (37%) and by incorporation as a secondary particulate phase (21%) [76]. A more recent study described strength recovery (41% healing efficiency) in an actual continuous glass fiber reinforced composite at the fiber-polymer interface by coating with DA functional groups (Figure 3) which results in restoration of stress transfer capacity between matrix and fiber [77]. A second thermo reversible route is the incorporation of disulphide bonds in epoxy thermosets which leads to the recovery of the material's tensile strength (>90%) [27] or adhesive strength (100%) [78].

Alternatively, self-healing of structural properties by photoreversible chemistry was introduced by Chung et al. in 2004, however, the healing efficiency was rather low [48]. Later, Ling et al. managed to achieve tensile strength recoveries up to 100% by embedding coumarin groups in the main chains of a polyurethane network [50, 79].

Instead of using covalent healing chemistry Hayes et al. showed the recovery of strength by blending conventional thermosets with thermoplastic material. Their study showed that including 20 wt.% of thermoplastic material results in a regain of 70% of the virgin properties of the matrix [80]. More recent, Luo et al. showed a strength recovery of more than 100% in a polymerization-induced phase separated thermoset/thermoplastic blend that is capable of differential expansive bleeding [81].

Similar to the studies that reported on stiffness recovery, the healing capabilities of majority of the matrices discussed was not yet investigated in actual composite materials. However, the work of Peterson et al. is an indication that the restoration of interfacial properties can actually lead to strength healing in both short and continuous fiber reinforced polymer composites. However, since the interfacial adhesion between matrix and filler has a larger effect for particulate or short fiber reinforced composites, it is expected that the development of such composites will be easier.

4. Functional polymer composites containing an intrinsically self-healing polymer matrix

Polymer based composites are also widely used as functional materials such as electrically conductive materials, electromagnetic interference shielding materials, electromechanical materials, magnetic materials or thermally conductive materials. Like structural polymer composites their properties generally (but not always) rely on the absence of damage in the polymer matrix and the absence of interfacial delamination. The opportunities for restoration of functional properties due to a self-healing polymer matrix are addressed below. The potential options are grouped according to the functional character of the composite.

4.1 Electrically conductive polymer composites

Electrically conductive polymer composites consist of a non-conductive polymer matrix and electrically conductive fillers and are widely used in various commercial applications due to their light weight, high manufacturability, corrosion resistance and good electrical conductivity [82-89].

To analyze the electrical conductivity of filler-loaded polymer composites, the percolation theory is usually used. When the content of fillers is below the percolation threshold, a long-range connection of fillers does not exist, leading to a very low electrical conductivity. While above the percolation threshold, the electrical conductivity increases significantly due to the formation of a long-range filler connection. When the percolation threshold for a material with a fixed filler concentration is reduced an increase in electrical conductivity is observed. According to the statistic percolation theory [90], the percolation threshold is inversely proportional to the particle aspect ratio. Therefore carbon nanotubes are promising candidates as electrically conductive fillers. This is exemplified by the work of Sandler et al. who

reported percolation thresholds below 0.01% in a carbon nanotube/epoxy system [82]. Additionally, the work of Bilotti et al. showed that a further reduction of percolation threshold can be achieved by the addition of secondary nano-fillers [91].

Other systems using graphite, carbon black and carbon fibers as fillers are also investigated and research focuses on improving the processability and reducing the costs. An effective strategy that can be applied to these systems is to form a double percolation phenomenon by localizing fillers at the interface or within one of the phases of an immiscible polymer blend [92, 93]. Furthermore, processing conditions will affect the particle alignment and the electrical conductivity of composites. For example, Kitajima et al. fabricated anisotropic electrically conductive polymer composites by applying a strong magnetic field to orient fillers [94]. The resulting composites showed much higher electrical conductivity along the direction of the magnetic field.

When micro- or macro-cracks are formed in the system, the connection of fillers may break down. Since the electrical conductivity of composites depends on the connection of fillers, this leads to a full or at least significant decrease of electrical conductivity and unexpected failure of electronic devices. These problems can be overcome by introducing an intrinsic self-healing polymer matrix that can heal the crack and restore the connection of fillers. Following this concept, Li et al. fabricated electrically conductive self-healing films by depositing Ag nanowires on top of healable polyelectrolyte multilayer films consisting of a layer-by-layer assembled branched poly(ethylenimine) and poly(acrylic acid)-hyaluronic acid blend [95]. Cuts can be autonomically repaired when water is sprayed on the films thereby recovering the electrical conductivity. A second example electrical conductivity healing was given by Tee et al.. They prepared an electrically and mechanically self-healing composite consisting of a supramolecular polymeric hydrogen-bonding network with self-healing ability filled with chemically compatible micro-nickel particles with nanoscale surface features [96]. The result showed a full recovery of electrical conductivity within 1 minute at room temperature upon complete fracture (as shown in Figure 6).

Self-healing of electrical properties in stretchable wires was reported by Palleau et al. who combined the self-healing Reverlink polymer produced by Arkema with liquid metal [97]. In their experiment, 2D or

3D structures were made after cutting a straight sample. The self-healing polymer provided the mechanical recovery and helped to re-align the liquid metal channel. Once re-aligned, the liquid metal components merged together and formed a conductive channel again. Self-healing wires are particularly important for the growing field of stretchable electronics in which electronic components may undergo significant deformation and lead to unexpected failure. In addition, these self-healing structures offer a simple method to rewire circuits.

Another example of self-healing electrically conductive polymer composite was reported by Wang et al.. They fabricated silicon micro-particle (SiMP) anodes for high-energy lithium-ion batteries, which are coated with a self-healing polymer composite consisting of a randomly branched hydrogen-bonding polymer matrix and carbon black nanoparticles [98]. The self-healing conductive composite coatings assist to heal the cracks, which are generated during the cycling process, and as such extend the cycle life ten times longer than state-of-the-art anodes made from SiMPs while still retaining a high capacity.

Since the filler networks are generally responsible for the electrical conductivity in polymer composites, the most suitable healing strategy is to use an intrinsic self-healing matrix that brings the fractured surfaces in close contact and subsequently rebuilds the filler networks. In contrast to structural composites, healing of the matrix-filler interface is less important in electrically conductive polymers, because the interfacial adhesion has only a small contribution to the electrical conductivity of these composites provided complete debonding across the interface does not occur.

When designing a fully autonomous self-healing electrically conductive polymer, an electrically triggered intrinsic self-healing polymer would serve as ideal matrix material. By doing so, damage that is inflicted during operation will instantly be healed. However, the field of electrically triggered self-healing polymer is still rather unexplored.

4.2 Electromagnetic polymer composites

All electrical and electronic devices emit electromagnetic signals, which can interfere with the operational properties of either the emitting equipment or any other equipment around it. To overcome this problem, the equipment can be shielded by electromagnetic interference (EMI) shielding materials. The first

generation of EMI shielding materials were made of metals, but in recent years electrically conducting polymer composites have gained popularity for EMI shielding applications. EMI shielding polymer composites are lightweight, resistant to corrosion, flexible, and cost less than metals. The most important property of EMI shielding materials is the shielding effectiveness (SE). According to Simon's equation [99]:

$$SE(dB) = 50 + 10 \log_{10} \left(\frac{1}{\rho f} \right) + 1.7t \left(\frac{f}{\rho} \right)^{\frac{1}{2}} \quad (4.1)$$

where ρ is the volume resistivity in $\Omega \cdot \text{cm}$, f is the frequency in MHz, and t is the thickness in cm. According to this equation, the EMI SE is higher when the electrical resistivity is lower, and correspondingly the electrical conductivity is higher. Therefore the self-healing processes in EMI shielding polymer composites are very similar to those in electrically conductive polymer composites, which were discussed in section 4.1. The electrical conductivity can be restored after damage by introducing a self-healing polymer matrix to electrically conducting composites. Subsequently, the EMI shielding property can recover.

4.3 Electromechanical polymer composites

Polymers that possess the ability to convert electrical into mechanical energy or vice versa are used in composite materials for numerous applications, such as sensors, actuators and energy harvesting. The functionality of these so called electromechanical composites can be found either in the polymer matrix or in the added filler material. The driving force behind electromechanical polymer matrices can be electronic (driven by an electric field or Coulomb forces) or ionic (involving diffusion or mobility of ions). Electronically driven polymers operate at room temperature and show a rapid electroactive response (ms range), but the required voltages are high (± 200 MV/m). Ionic electroactive polymers already operate at low voltage levels (< 5 MV/m), but this is combined with a relatively slow response (in the order of seconds) [100, 101].

One of the most common electronically activated electromechanical functionalities is the piezoelectric effect. Piezoelectricity is found only in noncentrosymmetric materials and it is called ferroelectricity when such a material exhibits spontaneous polarization. Among the few polymers that show ferroelectric

behavior, poly(vinylidene fluoride)(PVDF) and its copolymers have shown to have the best overall electroactive properties. Therefore PVDF is used in the majority of the research and industrial applications that involve piezoelectric polymers [102]. Another class of electronically driven polymers is that of the dielectric elastomers. This group of polymers includes silicones and acrylics with rubberlike properties such as low tensile strength and high deformability [103]. Studies of Pelrine et al. describe high strain rates (>100%) for both silicone and acrylic polymers [104, 105].

Ionic electroactive polymers are used for the production of ionomeric polymer-metal composites (IPMC). IPMCs bend at low voltages due to an ionomer that provides mobility of positive ions between a fixed network of negative ions on metal clusters. Two types of ionomers are typically used for the production of IPMCs, being Nafion (DuPont) and Flemion (Asahi Glass). Both ionomers consist of a tetrafluoroethylene backbone with a sidechain containing a negative sulfonate end group that is responsible for ion mobility. The majority of follow-up research in this field is based these two commercial ionomers [106, 107]. Recent studies describe the influence of the ionomer sidechains [108] and the effects of softening and heating processes [109]. A second class of ionic electroactive polymers is conducting polymers. Their electromechanical response is based on the reversible insertion and expulsion of ions that occurs during redox cycling which induces a considerable volume change of the polymer. Frequently used conducting polymers are polyaniline, polypyrrole and polythiophenes [110, 111].

Besides using an electroactive polymer as matrix material, composites with electrochemical properties can be developed by adding functional fillers to a conventional matrix. These fillers range from inorganic metallic fibers to organic polymer particles. A common strategy is to enhance a matrix with semi-crystalline ferroelectric ceramic particles (0-3 composites) or fibers (1-3 composites) of which lead zirconate titanate (PZT) is the most frequently used example. These composites typically have a high electromechanical sensitivity, high pressure tolerance and good acoustical impedance [112]. Another strategy that increases the electromechanical performance of non-electroactive polymers is the addition of highly conductive fillers such as metal powders (e.g. aluminium and nickel) and carbon based materials which changes the composite resistivity value with several orders of magnitude [103]. Many recent studies describe the high potential of carbon nanotubes (CNTs), however, many problems will have to be

overcome before they will be used in industrial applications [113]. Another recent study describes the combination of PZT and aluminium particles in an electromechanical epoxy based material [114].

Since both electromechanical polymers and self-healing polymers are able to regain a previously adapted form, it seems a logical step to combine these two material functionalities into one material. However, the amount of studies that report on the regeneration of electromechanical properties after fracture is rather limited. Still, Soroushian et al. report on the piezo-driven self-healing of fiber reinforced polymer composites. Here, the mechanical energy that is released upon fracture is converted into electrical energy by the PVDF based matrix. Healing of the composite is then achieved by a electrochemical reaction at the fiber-matrix interface [115]. A second study, that shows self-healing of electrical (as mentioned in chapter 4.1) and electromechanical properties was performed by Tee et al.. Their piezoresistive polymer composite with tactile pressure- and flexion bending sensitive properties can be used in electronic skin applications (Figure 7). The healing is based on supramolecular hydrogen bonding with high healing efficiencies, whereas the piezoresistive behavior is generated by adding μNi particles to the polymer matrix. This resulted in an almost full recovery of the composite functionality, however, the mechanical properties were not fully restored [96]. A final option that can be employed to prepare self-healing electromechanical composites could be through the use of ionomers. Since ionomers possess both electromechanical and self-healing properties, they are ideal candidates to serve as matrix material for multifunctional materials. Recently, James et al were the first to report a self-healing piezoelectric PZT-ionomer based polymer. They showed that the loss of sensorial functionality after high cyclic tensile fatigue can be partially recovered by thermal healing at 70°C [116]. Although the number of studies that report on self-healing electromechanical composites is still limited, it is expected that this combination of properties electromechanical crack closure and self-healing of contacted surfaces by an identical trigger will receive increasing attention in the near future.

4.4 Magnetic polymer composites

Magnetic polymer composites generally contain magnetic powders, such as Fe_3O_4 , CoFe_2O_4 , strontium ferrite and nickel [117-120], whereas epoxies, polyurethanes and polyimides are often selected as matrix material [118, 121, 122]. Although they possess inferior magnetic properties compared to cast or sintered

magnets, they have various advantages, such as a higher manufacturability and the possibility to produce complicated small and thin shapes with high precision. Therefore they are widely used for various applications, such as electronic and communications instruments, household tools and audio equipment [123]. Self-healing in magnetic polymer composites could be achieved by substituting conventional with intrinsically self-healing matrices, thereby creating more reliable and longer-lasting materials.

Magnetic gels are highly elastic hydrogels with magnetic fillers and they are an important group of magnetic polymer composites, which could greatly benefit from the self-healing effect. Controlled by the action of external magnetic fields, magnetic gels can perform elongation, contraction and coiling actions (as shown in Figure 8), which makes them suitable for actuator applications such as artificial muscles [124-126]. In these kinds of applications, the material will undergo significant deformation which may lead to unexpected failure. The mechanical damage can potentially be undone by introducing self-healing hydrogels, which are well developed [127-129], as polymer matrix in magnetic gels. This concept is exemplified by a study of Zhang et al.. They mixed Fe_3O_4 nanoparticles into a chitosan solution and subsequently added synthetic telechelic difunctional polyethylene glycol into the ferrofluid. The result is that a magnetic self-healing hydrogel can be fabricated quickly and straightforward at room temperature within less than 2 minutes. The resulting composite is capable of regenerating itself after multiple complete fractures under the influence of an external magnetic field [130].

Besides the studies on magnetic gels, the field of self-healing magnetic polymer composites is still rather unexplored. However, the authors believe that triggering of self-healing by applying a magnetic field, especially when damage detection (e.g. by integrated sensors) can be achieved, is a research field that shows great promise.

4.5 Thermally conductive polymer composites

Thermally conductive polymer composites, consisting of a polymeric matrix and high thermally conductive fillers, such as carbon fibers, carbon nanotubes, aluminum oxide, zinc oxide, silicon carbide, boron nitride and metal powders, are widely used as thermal interface materials (TIMs), which play a key role in thermal management of the electronic industry [131-135].

Both modelling and experimental results indicate that the formation of thermally conductive chains leads to an increase in thermal conductivity of composites. For example, Devpura et al. proposed a model on percolation phenomenon based thermal conductivity [136]. On the other hand, an experimental study by Hu et al. described the addition of carbon nanotubes into a silicone composite filled with spherical Nickel particles [137]. They found out that even small quantities of carbon nanotubes can effectively improve the heat conduction performance of the composites by forming carbon nanotube-nickel sphere chains. Their work shows that a large increase in the thermal conductivity can be obtained by percolation phenomena, which is also justified in many recent studies [138-140]. Upon crack formation the thermally conductive chains can be cut off, which leads to a significant decrease in the thermal conductivity of the composite.

The adhesion at the interface between the polymer matrix and the fillers is essential to the thermal conductivity of composites. Many studies showed that the surface treatment with coupling agent can improve the matrix-filler interfacial adhesion, which increases the thermal conductivity of composites [141-143]. Thermal boundary resistance (R_b) is a measure of an interface's resistance to thermal flow. Every et al. built a thermal conductivity model of spherical particle loaded composite material which took R_b into account, as shown in equation 4.2 [144],

$$(1-V)^3 = \left(\frac{\lambda_m}{\lambda_c}\right)^{(1+2\alpha)/(1-\alpha)} \times \left[\frac{\lambda_c - \lambda_f(1-\alpha)}{\lambda_m - \lambda_f(1-\alpha)}\right]^{3/(1-\alpha)} \quad (4.2)$$

in which λ_c , λ_m and λ_f are the thermal conductivity of composite material, matrix and filler, respectively, V is the volume fraction of filler, α is a non-dimensional parameter with reference to the boundary resistance, which is defined by equation 4.3,

$$\alpha = \frac{2R_b\lambda_m}{d} \quad (4.3)$$

in which d is the diameter of filler. When $\lambda_f \gg \lambda_m$, equation 4.2 can be deduced to

$$\frac{\lambda_c}{\lambda_m} = \frac{1}{(1-V)^{3(1-\alpha)/(1+2\alpha)}} \quad (4.4)$$

If crack formation occurs at the matrix-filler interface, the boundary resistance will increase significantly leading to a decrease of the composite's thermal conductivity, as shown schematically in Figure 9. As in its reference figure for mechanical stiffness (Figure 4), figure 9 shows that upon full delamination the properties of the composite decrease with filler fraction and reach a value well below that of the matrix.

Only for the case of perfect interface heat transfer, the properties of the composite increase with the filler content to reach values that are substantially above that of the polymer matrix.

Interfacial failure is a key failure mechanism in the use of TIMs. Hence TIMs and the components contacted to them usually have a mismatch in coefficient of thermal expansion (CTE) which leads to mechanical stress. After some thermal cycles, CTE mismatch may induce delamination between components and TIMs, which leads to an increase in thermal contact resistance and subsequent failure of the whole device [145-147].

In general, the functionality of TIMs will be damaged in three ways: cracks cutting off the thermally conductive chains, cracks separating matrix and fillers and delamination between components and TIMs. To introduce cohesive and adhesive self-healing ability to TIMs could be an effective way to solve this problem. Although much work has been done on both self-healing polymers and TIMs, only a few attempts have been made to fabricate self-healing TIMs. Lafont et al. prepared TIMs consisting of boron nitride or graphite particles and two types of self-healing polysulphide-based thermoset matrices [148]. The composites exhibit recovery of both cohesion and adhesion properties under a mild healing temperature (65°C). After multiple healing cycles, most of the samples show full recovery of initial adhesive strength. On the other hand, the samples behave differently on cohesion recovery: 20-100% recovery can be achieved depending on filler concentration, filler type and matrix type.

Since thermally conductive polymer composites invariably will be exposed to a range of temperatures during use, heat triggered self-healing polymers are the most appropriate matrix materials. In the case of unexpected local failure of thermally conductive polymer composites, the resulting change in the temperature in the region surrounding the crack or the delamination can trigger the healing process and allow the thermally conductive polymer composites to recover their original performance thus increasing the reliability of the device. Although the development of self-healing thermally conductive polymer composites is still in its infancy, it is expected that self-healing thermally conductive polymer composites have real potential applications in the electronics and lighting industry [149].

5. Conclusion

This review gives an overview of the emerging field of self-healing behavior of polymer composites. Healing of both structural and functional composites, that combine an intrinsic self-healing polymer matrix with either reinforcing or functional fillers, is discussed. In polymer composites, damages in the matrix or at the matrix-filler interface lead to the loss of both structural and functional properties. By applying intrinsic self-healing polymer as matrix, those damages can be healed upon the stimulation of an external stimulus and subsequently both structural and functional properties can be partially or even fully restored. In some examples, the external stimulus is supplied by the damage event itself or comes from the working environment, thereby creating an autonomous healing process. In composites where the filler networks are mainly responsible for the composites' properties (e.g. electrically conductive and electromagnetic polymer composites), healing can already be achieved by an intrinsic self-healing matrix that can restore the fractured surfaces when they are brought into close contact thereby rebuilding the filler networks. In other composites (e.g. structural composites and thermally conductive polymer composites) both the filler networks and the matrix-filler interface need to be healed by the polymer matrix in order to restore the original properties.

As discussed, the majority of recent studies regarding self-healing composite materials focus on the restoration of structural properties, such as stiffness and strength. Research into the self-healing of functional properties (electrical, electromagnetic, electromechanical, magnetic and thermal conductive) is still in its early stage development. However, as the demand for functional polymer composites is increasing, it is expected that the focus of researchers will broaden to the development of materials that are capable of healing both structural and functional properties in the upcoming years.

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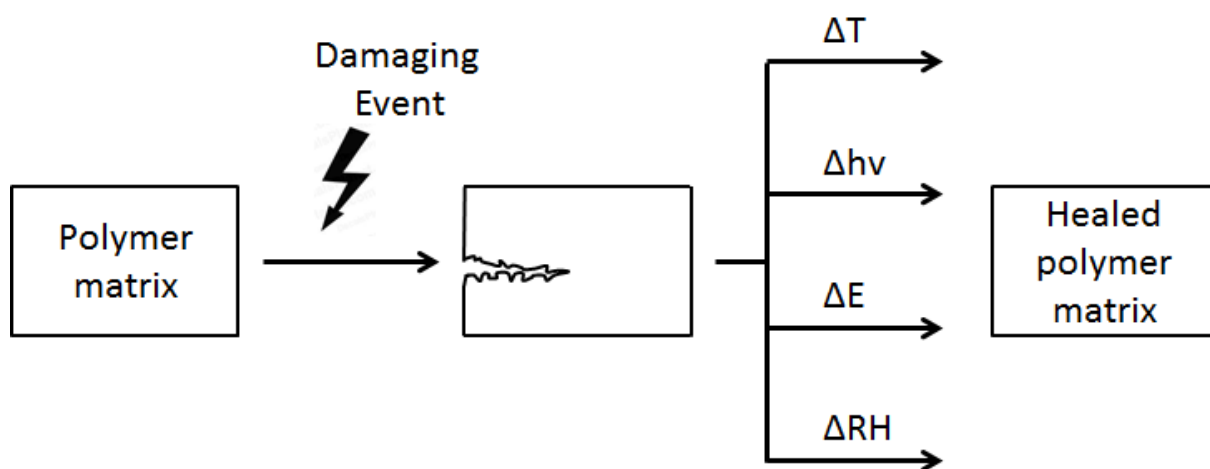


Figure 1 Schematic representation of intrinsic self-sealing by external stimuli; thermal, photochemical, electrical and moisture activation.

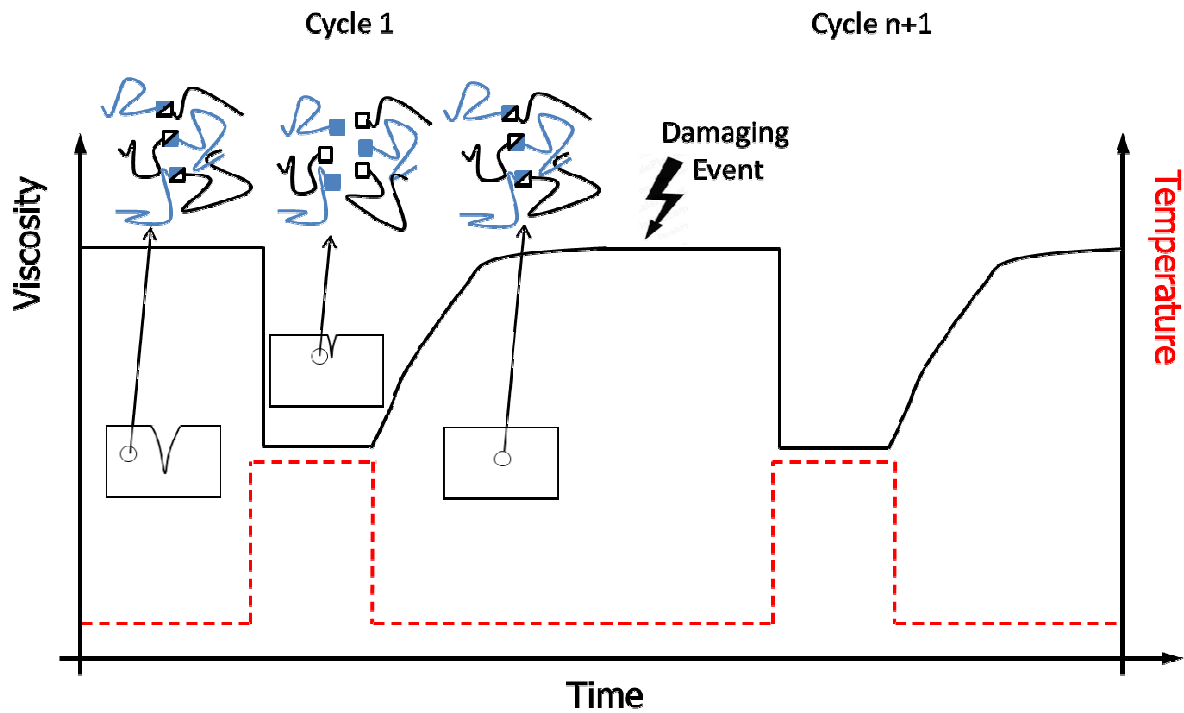


Figure 2 General concept of matrix healing using intrinsic healing concepts. Figure shows a sudden drop in viscosity upon heating linked to local temporary network mobility necessary for flow and damage repair. Upon cooling the local properties (e.g. viscosity) are restored to initial values so the material can be further used. Figure also shows the multiple healing events possible with intrinsic healing concepts [7].

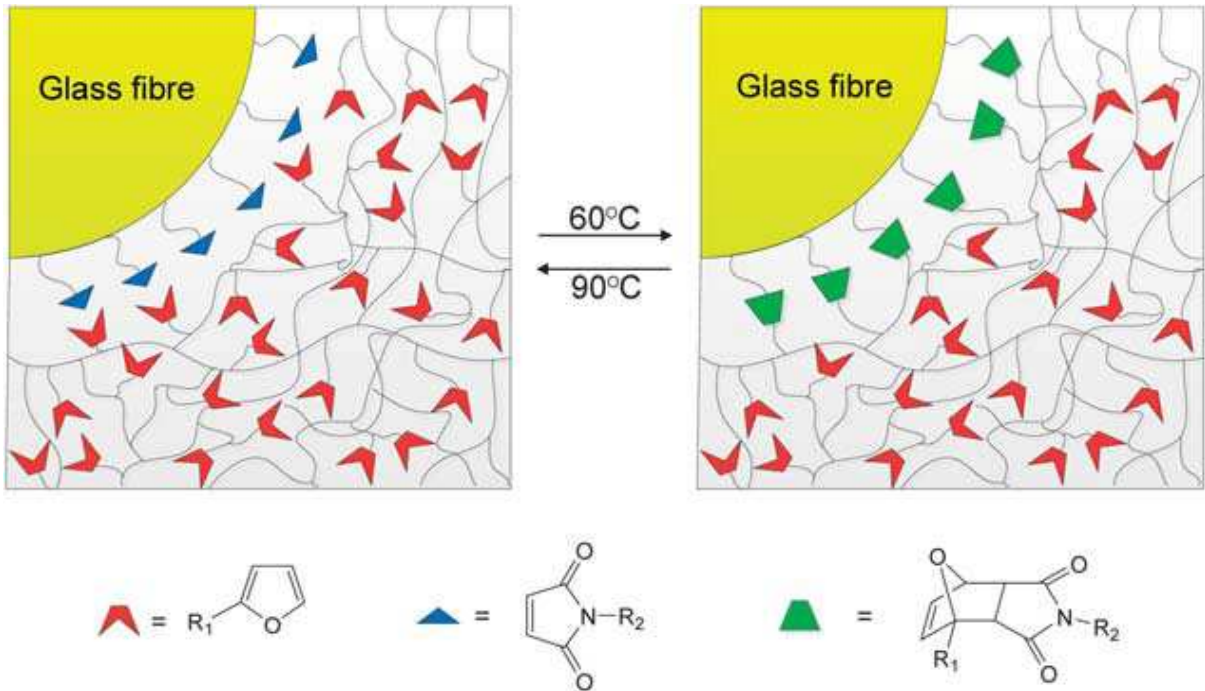


Figure 3 Self-healing of composite strength via a reversible Diels-Alder reaction at the fiber-matrix interface. Glass fibers are functionalized with maleimide functionalized groups (blue figures) and placed in a furan group (red figures) containing polymer network. The resulting composite is capable of thermoreversible interface healing resulting in restoration of stress transfer between fibers and matrix [75, 77].

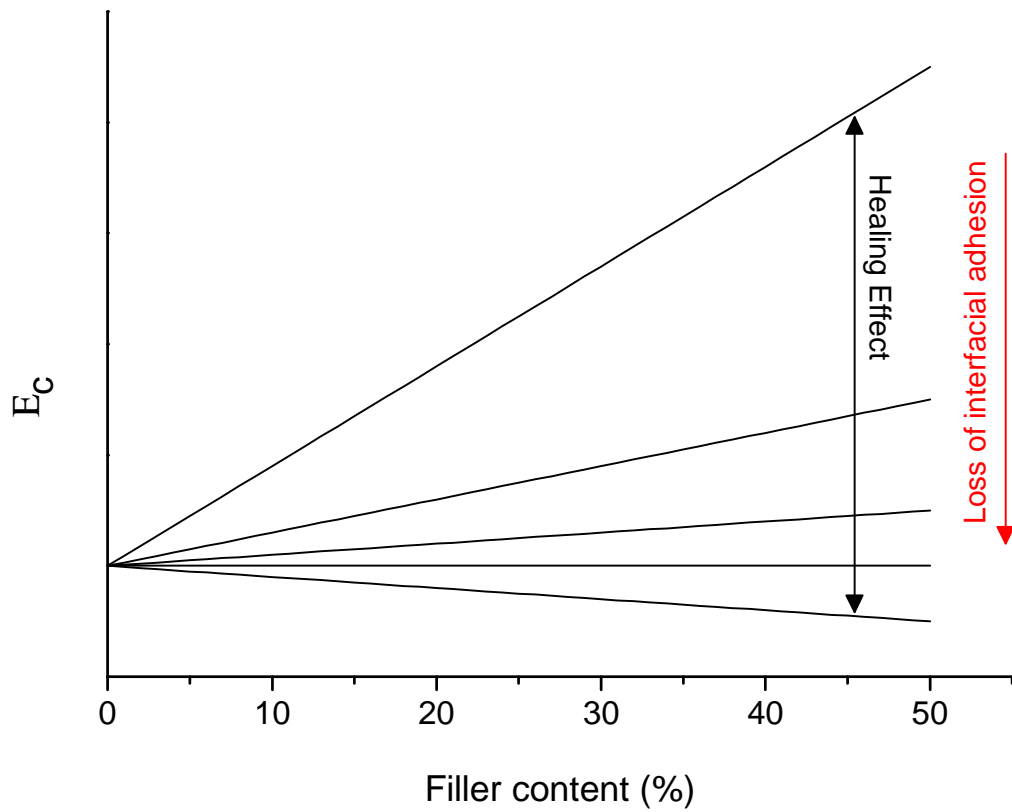


Figure 4 Graphical representation of the relation between filler content, interfacial adhesion and the elastic modulus in a short discontinuous fiber reinforced polymer composite material. The relation is plotted for various values of τ resulting in values for η_1 ranging from 0 to 1 which directly shows the range of stiffness that can be healed by restoring the fiber-matrix interface. A similar model could be composed for the strength of a polymer composite.

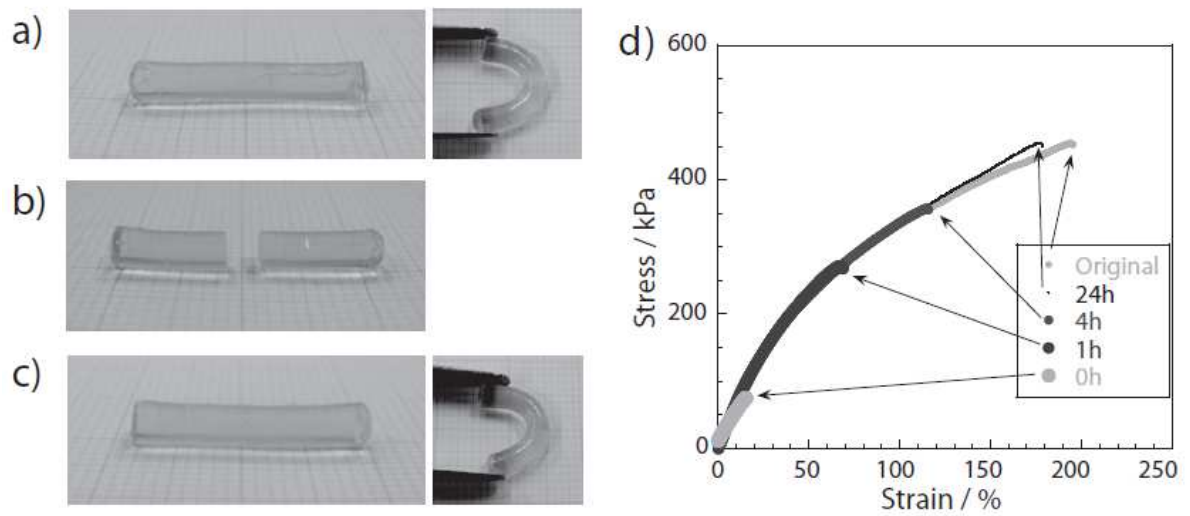


Figure 5 Recovery of structural properties in a self-healing polymer matrix using photochemical reversible thiuram disulfide bonds. The polymer matrix is displayed prior cutting and self-healing (a), after cutting (b) and after 24h of self-healing (c). (d) shows a stress, strain curve in which the regeneration of mechanical properties is plotted at different stages of the self-healing process [53].

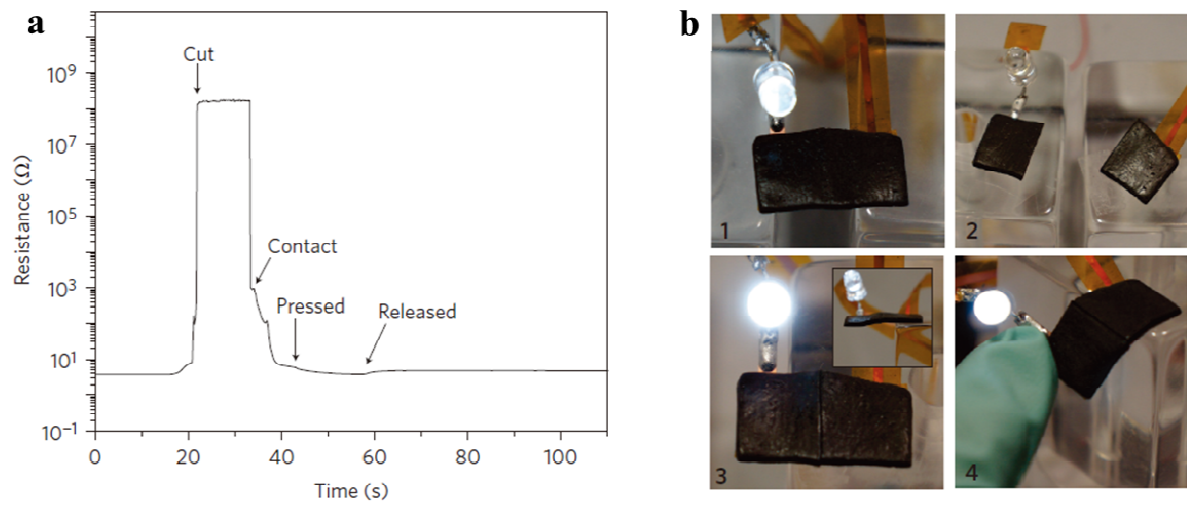


Figure 6 Electrical conductivity healing characterization of self-healing composite. (a) Resistance measurement shows electrical conductivity healing at room temperature. (b) Demonstration of the healing process using an LED in series with a self-healing composite conductor. 1, undamaged; 2, completely severed (open circuit); 3, electrical healing (inset shows conductor being self-supporting); 4, healed film being flexed to show its mechanical healing after only 5 min at room temperature [96].

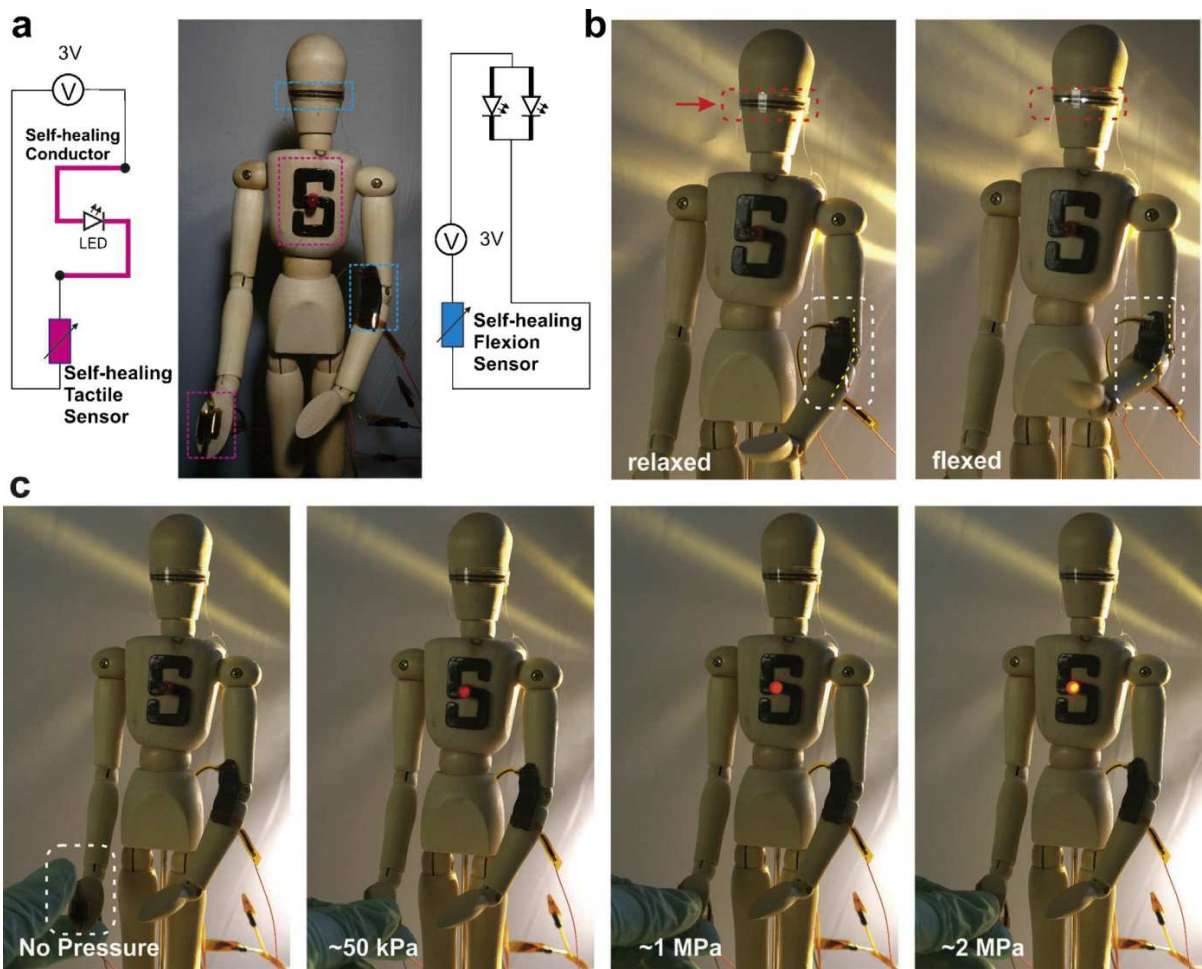


Figure 7 Example of piezoresistive recovery in a fully articulated wooden mannequin. (a) A self-healing flexion and a self-healing tactile sensor were mounted on the elbow and palm of the mannequin respectively. LEDs in the eye and body region are used to transduce mechanical deformation into visible light. (b) shows the LED lights up with increasing elbow flexion. (c) shows LED lightening with increasing palm tactile pressure[96].

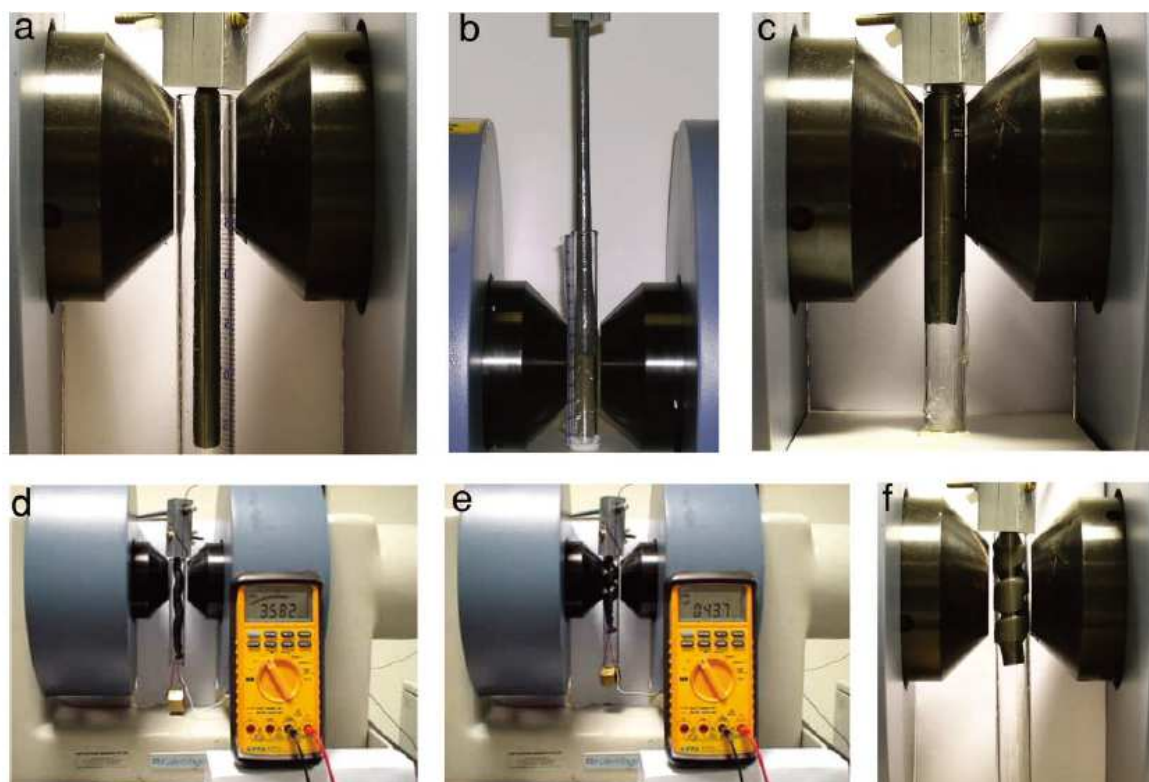


Figure 8 Performance of magnetic gel (20 wt.% Fe in silicone) controlled by external magnetic fields. (a) Relaxed mode without magnetic field; (b) elongation mode; (c) contraction mode; (d) and (e) coiling mode, the ohmmeter shows the resistance change of the sample during coiling process; (f) hybrid mode at $B = 1T$. [124]

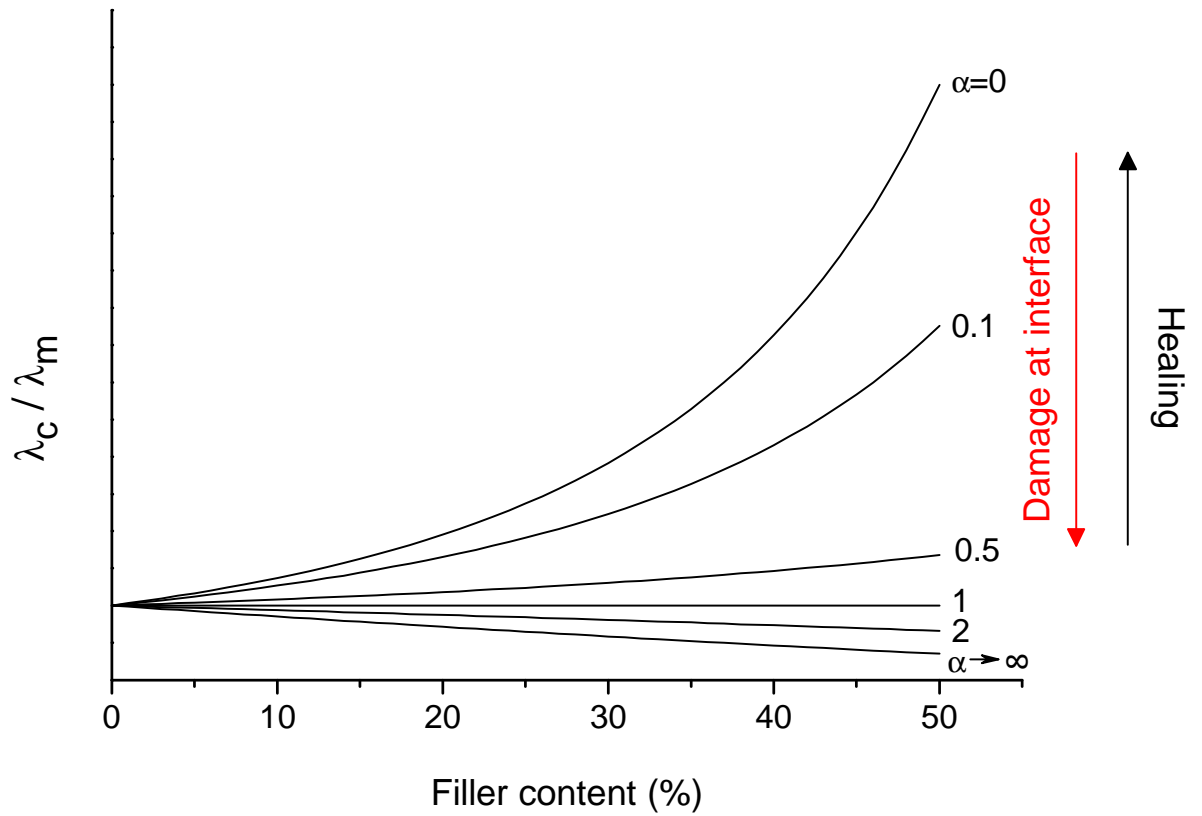


Figure 9 Graphical representation of the relation between filler content, thermal boundary resistance and the thermal conductivity of spherical particle loaded composite material. The relation is plotted for various values of R_b resulting in values for α ranging from 0 to ∞ which directly shows the range of thermal conductivity that can be healed by restoring the fiber-matrix interface.