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Routes to Make Natural Rubber Heal: A Review

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ABSTRACT

This review outlines latest developments in the field of self-healing rubbers and elastomers, analyzing their potential application to natural rubber (NR). Different validated healing concepts are presented and the possibilities of applying them to NR are discussed. Research in this field should aim at modifying the chemical structure of NR as to enhance physical or chemical reversible interactions either intermolecular or intramolecular. The realization of better mechanical properties at relevant working conditions and with milder healing conditions remains a challenge for all self-healing rubbers. This overview should be seen as setting the conceptual framework for new developments with a more clearly defined industrial focus.

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1. Introduction

Up and till recently, materials scientists have focused primarily on the design of materials which are robust and resistant to mechanical and chemical damage. The strategy has worked very well over the past decades and has led to the development of very strong materials. However, notwithstanding their high initial properties, these materials remain damage prone and will ultimately fail by the accumulated growth of local damage. Inspired by nature, self-healing man-made materials aim at extending their service lifetime by fully or partially restoring local mechanical damages.[1,2] The significant research devoted to the development of self-healing materials has led to many good reviews focused on a specific material class (*e.g.*, soft polymers) or application (*e.g.*, coatings)[3–10]; however, to the best of our knowledge, only one review deals with self-healing and recyclable rubbers and elastomers[11] and none has specifically focused on healable natural rubber (NR).

Self-healing materials can be broadly classified into two main groups: extrinsic and intrinsic, and the approaches differ in the type of healing moiety used in the repair of damage.[5] In extrinsic self-healing materials, a so-called healing agent is contained in discrete particles (capsules) embedded into a polymeric matrix and released upon damage.[5] The discrete healing agents are consumed in the actual healing reaction and hence, for a given damage site, healing is limited to a single event. Intrinsic self-healing polymers, on the other hand,

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make use of moieties forming an intrinsic part of the material itself.[9] In this case, the healing moieties are not consumed during the healing reaction and multiple healing reactions can take place at a given damage site. This reversible formation of bonds not only serves to heal mechanical damage, but at the same time opens new routes to reshaping and recycling of (crosslinked) polymeric products. Several concepts using different reversible dynamic groups such as H-bonding, disulfides, Diels–Alder chemistry, and metalorganic ligands have attracted significant growing attention in the field of intrinsic healing.[6,12–15] The early research in the field of self healing has mostly been based on the restoration of mechanical integrity, by bonding across interfaces created by fracture, cracking or cutting. Nonetheless, the self-healing field is evolving towards the healing of a broader spectrum of damage types[9] and recovery of other functionalities (*e.g.*, thermal and electrical conductivity).[16–19]

Elastomers are some of the most versatile engineering materials available. They have revolutionized consumer products ranging from simple bags and storage containers, sealing joints, impact protection, coatings and adhesives, to bladders and inner tubes in tires. Thanks to their inherent stable covalently bonded three-dimensional molecular network, elastomers can sustain large deflections with little or no permanent deformation. However, such irreversible covalent crosslinked networks theoretically block their self-healing capability; healing requires chain mobility and therefore seems to be in direct contradiction with the fixation needed to form a permanent network. Among all elastomers, NR stands out in the industry due to its exceptional properties. However, nowadays there is no satisfactory way to recycle vulcanized NR and most of the waste rubber is discarded in landfills. Thus, achieving self-healing properties in NR would be of paramount industrial and ecological interest for extending its lifetime and reducing waste.

In view of these considerations, this review offers an insight into the different potential routes to develop self-healing NR. In the first section, we summarize all concepts and achieved healing efficiencies in the self-healing rubbers and elastomers developed to date. We then discuss the possibilities of applying those developments and approaches to NR and NR composites, taking into account the type of damage and the intended recovery of mechanical integrity, as well as other functionalities. We conclude with some final remarks.

1.1 Natural rubber

NR is one of nature's unique materials. It is obtained from the sap ("latex") of several rubber-yielding plants by coagulation. The commercial market, however, is totally dominated by one plant, *Hevea Brasiliensis*. NR molecules consist mainly of *cis*-1,4-polyisoprene, with practically no evidence for any *trans* material in the natural product. The molecular weight of the natural polymer is very high but varies between lattices from different tree clones. Nonetheless, typical values of weight-average molecular weight (M_w) can range from 3.4×10^6 to 10.2×10^6 g/mol.[20–22] The very flexible backbone leads to a very low glass transition temperature (T_g) of about -64°C. Besides, due to its highly regular structure, NR is capable of crystallizing.[23] Crystallization may also be induced by stretching samples such as in a tensile test. As a result of this stress-induced crystallization, the tiny crystal structures formed act like reinforcing particles, and, unlike styrene-butadiene rubber (SBR) which does not crystallize, enable NR to exhibit high vulcanizate strengths. The presence of the methyl group in 1,4-polyisoprene enhances the activity of the double bond, making it rather more reactive than SBR or polybutadiene rubber (BR) to a wide variety of chemicals, including

vulcanization systems.[21] Nonetheless, the high unsaturation of the carbon backbone also supposes some drawbacks like susceptibility to abrasion, low oil and heat-resistant, attack by oxygen and ozone and by ultraviolet light.

Far East producers (Malaysia, Indonesia, Thailand, and Sri Lanka) account for about 80% of the NR market. In 2000, a total of around 7 million metric tons of NR were produced. Until 2017, this amount increased to more than 13.2 million metric tons. While global consumption has increased by 1.4%, summing up to 12.9 million tons during 2017.[24,25]

Compared to other synthetic rubbers, NR is the preferred polymer due to its superior building tack, better processing, hot tear resistance, high resilience, and excellent dynamic properties and fatigue resistance. This makes it the ideal material for tires and tire products, primarily for carcasses and sidewalls. Other product areas of interest are footwear, carpet and rug backing, surgical goods, adhesives, and textile thread.

2. Overview of reported self-healing elastomers

Developments of intrinsic self-healing rubbers and elastomers started with the pioneering work of Cordier *et al.* in 2008.[12] They reported the synthesis of an autonomous healing rubber based on supramolecular assembly. Since then, many different healing routes have been developed and new families of self-healing rubbery-like materials and crosslinked elastomers have evolved. The highly popular extrinsic healing approach for hard thermoset polymers has also been applied to rubbers by White *et al.*[26] in 2007 when they developed a healable polydimethylsiloxane (PDMS) elastomer using two microcapsule types, a resin capsule and an initiator capsule. However, several intrinsic problems can be encountered when adding capsules to rubbers. For example, the shell fragments, most of which poorly adhere to the rubber matrix, can cause crack-initiation and adversely affect mechanical properties. Since micro-meter sized capsules are micro-fillers, they can also influence rheological properties and cure behavior of rubbers. For these reasons in elastomers, intrinsic healing offers more advantages than extrinsic healing and will be the main focus of this review. Table 1 summarizes the different mechanisms explored using intrinsic healing approaches to develop self-healing rubbers and elastomers. The remainder of the manuscript will focus on discussing the different concepts used in relation to the type of functionality to be healed.

3. Self-healing natural rubber. Recovery of structural integrity

As in other materials, mechanical failure in elastomeric materials will be accelerated significantly by accidental local damage (such as scratches and cracks) formed during early stages of the product lifetime. This local early stage accidental damage is often due to *quasi*-static or *quasi*-dynamic overload but impact damage is also decisive in many elastomeric applications both on the macroscale (*e.g.*, armor panels) and on the microscale (*e.g.*, protective coatings). The sections below describe the healing mechanisms to recover product integrity as a function of the initial damage.

3.1 Macroscopic (interfacial) damage

One key condition required to obtain full mechanical recovery by healing the interface between the two fracture surfaces of a crack brought in contact is to have a sufficient level of

Table 1. Examples of self-healing in rubbers and elastomers.

Elastomer	Healing mechanism	Ref.
Butadiene rubber (BR)	Diels–Alder	[27,28]
	Reversible disulfide crosslinks	[29]
	Hydrogen bonding	[30,31]
	Vitrimers chemistry	[32]
Natural rubber (NR)/Polyisoprene (IR)	Reversible disulfide crosslinks	[33,34]
	Hydrogen bonding	[35,36]
	Ionic functional groups	[37]
Epoxidized natural rubber (ENR)	Reversible disulfide crosslinks	[38]
	Molecular interdiffusion/polar interaction	[39–41]
Bromobutyl rubber (BIIR)	Ionic imidazole-bromide bonds	[42–44]
Chloroprene rubber (CR)	Reversible disulfide crosslinks	[45]
Nitrile rubber (NBR)	Ionic functional groups	[46,47]
Styrene-Butadiene rubber (SBR)	Ionic functional groups	[48]
	Diels–Alder	[49]
Thermoplastic elastomer (TPE)	Hydrogen bonding, brushes, two-phase separation	[50]
	Diels–Alder	[51]
Supramolecular rubber	Hydrogen bonding, vitrimers	[12]
Poly(dimethylsiloxane) (PDMS)	Diels–Alder	[52]
	Encapsulation (extrinsic)	26, [53–55]
	Thiol–silver interactions	[56]
	Disulfide metathesis, sunlight	[57]
Polyimide-based thermoplastic elastomer	Interface-wetting and chain diffusion	[58]
	Hydrogen bonding & π–π stacking	[59]
Polyurethane (PU)	Reversible alkoxyamine moieties	[60]
	Hydrogen bonding	[61]
	Diels–Alder	[62]
	Disulfide metathesis	[63–65]
	Heat transfer	[66,67]
	Chain-end interaction	[68,69]
Poly(urea–urethane)	Disulfide metathesis, hydrogen bonding	[70–72]
Acrylic elastomer (VHB 4910)	Hydrogen bonding, chain entanglements	[73]
Ethylene-Propylene-Diene Monomer (EPDM)	Diels–Alder	[74]
Organic–inorganic sol–gel hybrid	Disulfide exchange in dual network	[75,76]
Poly(butyl acrylate-co-acrylic acid)	Metal ion–ionomer interaction	[77–79]

chain dynamics to enable mobility through the named interface. This can be achieved either by molecular interdiffusion/rearrangements with or without external stimulus (polymer physics) or by the presence of dynamic bonds (chemical or physical reversible interactions).[80] In the first case, the polymer matrix is actually healed due to molecular diffusion along the polymer/polymer interface followed by chain entanglement, leading to the recovery of the mechanical properties of the healed material. Molecular interdiffusion and chain entanglement both depend on intermolecular forces, which are closely linked to the chemical composition of the polymer and the length of the molecules, including the dependence on the average molecular weight. Dynamic bonds, on the other hand, can be defined as any class of bond that selectively undergoes reversible breaking and reformation. This term usually encompasses two broad categories: supramolecular interactions (*e.g.*, $\pi-\pi$ stacking, hydrogen bonding, and metal-ligand coordination bonds) and dynamic covalent bonds capable of chain exchange reactions (*e.g.*, sulfur–sulfur and Diels–Alder). The reversibility of the dynamic bond allows repair to take place at the molecular level and fully restore the original interface, yet also in this case a sufficient interdiffusion/rearrangement of the chains is a must to obtain high healing levels. Although the different concepts to be discussed below have not yet all been explored in NR, they offer a good spectrum of possibilities to be successful based on their demonstrated validity in other elastomeric like polymers. Unless stated

differently, the healing efficiencies mentioned in Section 3.1 refer to the ratio of the failure load after healing at the indicated healing condition and the failure load of the undamaged as-prepared material, as measured under conventional *quasi*-static tensile testing conditions at room temperature. In most cases, the sample geometries do not comply with American Society for Testing and Materials (ASTM) standardized sample dimensions.

3.1.1. Entanglements

Entanglements naturally occur in long chain polymers. The interdiffusion of these molecular chains and subsequent formation of new molecular entanglements under certain conditions can also take place across cut surfaces brought in physical contact. Especially when heated, this diffusion can be labeled as self-healing behavior, as has been known to occur during crack healing of thermoplastics when heated above their glass transition temperature (T_g).[68] In this case, the healing is not of a chemical, but of a physical nature. Because of the resulting flow in the material, the structures inside the polymer matrix can reform physical entanglements after chain separation, restoring the mechanical properties of the matrix.[81] A requirement for this process is that the temperature must be at or above T_g of the material. Jud and Kausch[82] reported for poly(methyl methacrylate) (PMMA) that combinations of a healing temperature of 5°C above T_g and a healing time of more than 1 min were required to show partial healing. Full recovery of mechanical properties was possible if healing time or/and temperature were increased. The notion that healing is most effective at or above the T_g was reinforced by results by Wool *et al.* for glassy polymers and polystyrene (PS).[83–85]

The stages of healing according to the mechanism of Wool and O'Connor[83] are illustrated in Fig. 1.[80] Over time the rearrangement of the chains on the surface progresses into diffusion on a low level and then further into a seemingly random and complete diffusion of

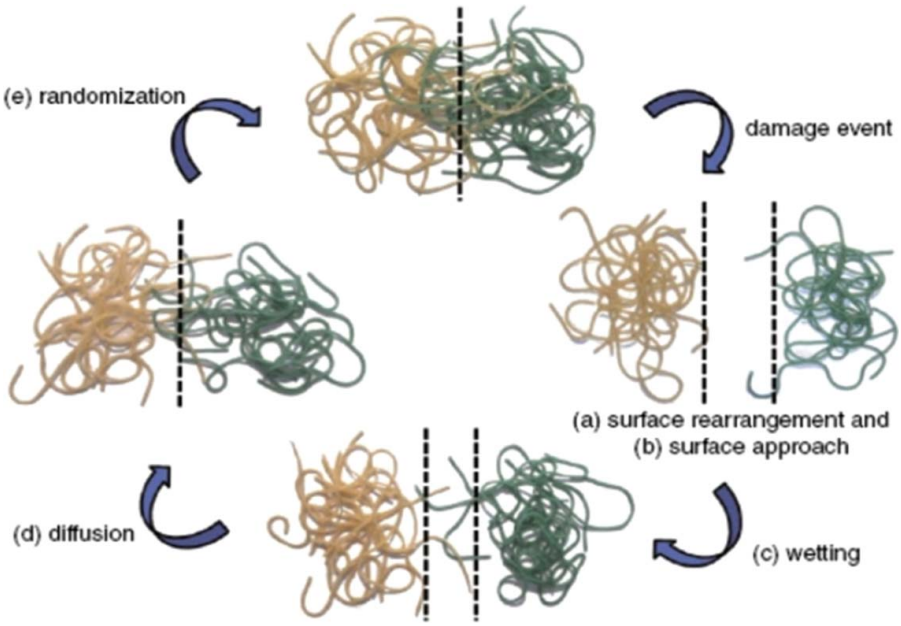

Figure 1. Stages of self-healing mechanism: (a) surface rearrangement, (b) surface approach, (c) wetting, (d) diffusion, and (e) randomization.[80]

the chains, making the material appear as one again.[3] A requirement for this behavior is proper wetting of the surfaces, *i.e.*, full contact of the cut interfaces. From this principle, it also follows that the time taken to reach full healing depends on a combination of the surface roughness of the crack as well as the binding force that is exerted on the surfaces when healing takes place.

Similar conclusions were obtained in a research by Skewis, who investigated the "tack strength" of various non-vulcanized rubbers as a function of contact time.[86] Here, "tackiness" is interchangeable with interfacial healing (primary phase of the healing process), as a result of short range chain entanglement and diffusion of small molecules. Wool *et al.* later showed that this tack strength is proportional to contact time to the power of $^1/_4$,[83] which they based on the tube model of molecular dynamics proposed by Doi and Edwards.[87] In intrinsic healing polymers, however, the tackiness is a must for full macroscopic healing to occur. The process of an interface/interphase formation involves short range physical and/or chemical interactions and molecule/chain diffusion. Such processes lead to the macroscopic mechanical phenomenon recognized as (self-) adhesion reflected in a low or high bonding energy depending on the level of interaction/diffusion achieved. The term "tackiness" coincides with such processes and definition, although it is traditionally applied to the elastomers field alone. For full healing to occur, long range motions (diffusion) are also necessary and these do not take place for conditions where the term "tackiness" has been used.[88]

3.1.2. Dangling chains and brushes

Molecular diffusion has been investigated and described in a number of researches, but not many researchers have investigated the possibility of diffusion of other molecular segments than the polymer backbone itself. Yamaguchi *et al.* designed polyurethanes (PU) in which the chemically controlled chain ends facilitated the autonomous healing of a fully cut polymer at $T > T_g$ in about 10 min.[68] It was hypothesized that the relatively long distance between the free end of the molecule and its first physical crosslink point ("the dangling length") facilitate the observed crack disappearance. In a later review paper, the healing efficiency of similar PU was presented and defined as the tear strength of the healed material over the virgin material.[69] The healing efficiency as measured in tensile testing was found to be 80% after only 10 min of healing at room temperature and they concluded that the material did not show macroscopic flow during healing. The authors also concluded that the molecular weight of the pre-polymer plays an important role, as a higher molecular weight pre-polymer led to longer "dangling" chains which in turn showed larger extension of the material before failure as well as healing. An optimal chain length can therefore be envisaged, after which the dangling chains will only obstruct diffusion.

In another context, the phenomenon of healing facilitated by dangling chains (brushed polymer) was investigated leading to high healing degrees at room temperature in a mechanically interesting thermoplastic elastomer.[58] In their work, the authors used a biobased aliphatic dimer diamine (DD1), which is known to be a large molecule. The synthesis of DD1 with a dianhydride (DA) led to a densely branched polyetherimide where 9-C aliphatic chains act as the dangling brushes. By varying the ratio of the DD1/DA and using multiple techniques, the authors unveiled the healing mechanism and showed the multiple healing steps

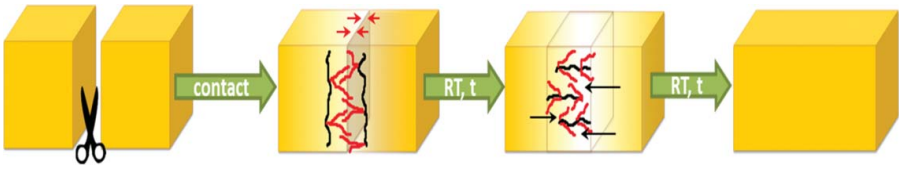

Figure 2. Stepwise healing process of a brushed polyetherimide system. Main chains are represented in black, whereas brushes are red.[58] © 2016, American Chemical Society. Reproduced by permission of Copyright 2016, American Chemical Society. Permission to reuse must be obtained from the rightsholder.

leading to a full interfacial recovery. Fig. 2 shows the proposed three-step healing mechanism unveiled by combining rheology and mechanical testing for this kind of branched systems. First, van der Waals interactions between the brushes allow for initial tack or interface adhesion between surfaces. Next, chain reptation occurs, leading to larger scale diffusion. Finally, randomization occurs, fully restoring the interface and its mechanical properties. The first step takes place in minutes, whereas the entire diffusion process takes days.

3.1.3. Hydrogen bonding

Weak interactions like hydrogen bonding seem to offer promising chances for the development of potential intrinsic self-healing elastomers. In hydrogen bonding, a hydrogen atom is connected to a strongly electronegative atom and is in the vicinity of another strongly electronegative atom with a lone pair of electrons. This creates a dipole–dipole attraction force, which is stronger than most other dipole–dipole forces, but not as strong as covalent or ionic bonds. As an example, N-H groups in the vicinity of C = O groups are able to form a hydrogen bond. If mobility is high enough to bring the dipoles into each other's vicinity after damage, the material will be able to self-heal at room temperature and since the hydrogen bonds form as soon as the dipoles come into near contact, the process is rather fast.[12,89] Healing will generally improve with an increase of dipoles in the system.

Hydrogen bonds can be both intermolecular and intramolecular, meaning that they can also be used as alternative crosslinks as has been traditionally used in polyurethane chemistry. First attempts to develop thermo reversible crosslinked NR by using supramolecular hydrogen bonding networks were done by Chino *et al.*[35] The hydrogen bonding moiety (amide triazole-carboxylic acid unit) was generated by the addition reaction of 3-amino-1,2,4-triazole (ATA) and acid anhydride. Later on, Peng and Abetz[90] presented a three-step polymer modification process based on epoxidation, hydrochlorination and sulfonyl isocyanate addition reactions to modify BR. The introduction of this type of hydrogen-bonding complex led to the formation of an effective thermo reversibly crosslinked supramolecular network formed in the rubber matrix. Recently, Gold *et al.* showed that transient bonds indeed form an alternative to permanent bonds in BR.[30] The rubber was modified to include urazole groups to enable transient bond crosslinks in combination with bissilane crosslinker to form covalently crosslinked bonds. The urazole groups were incorporated through reaction with the double bonds of BR with triazoline in tetrahydrofuran (THF). Each of these groups can form two hydrogen bonds with another urazole group. No self-healing tests were performed in this research, but the engineering stress of the BR containing just 0.5 mol% of bissilane crosslinker was shown to be approximately half of that of BR containing both 0.5 mol% bissilane crosslinker and 2 mol% urazole groups, whereas the engineering strain increased by about 33% with the inclusion of the urazole groups. Hence,

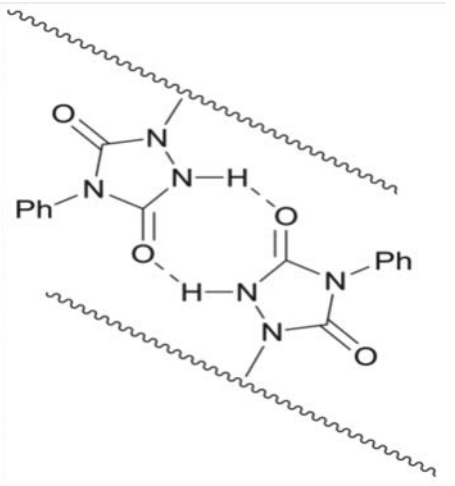

Figure 3. Hydrogen bonds between urazole groups, grafted onto BR. Ph stands for Phenyl substituent.[30]

the inclusion of urazole groups both improved mechanical properties and potentially enabled self-healing behavior through reversible hydrogen bonds, as shown in Fig. 3. Since NR is a polydiene polymer similar to BR, incorporation of urazole groups in both NR and epoxidized natural rubber (ENR) seems possible. At the same time, more exotic combinations may be formed in ENR, as the epoxy group may still be utilized in other reactions, as mentioned by Peng and Abetz.[90]

In a different approach, Wang *et al.*[31] prepared a set of rubbers by self-assembly of complementary BR oligomers bearing carboxylic acid and amine groups able to form reversible hydrogen bonds (see Fig. 4), and then further covalently crosslinked them by a tri-functional

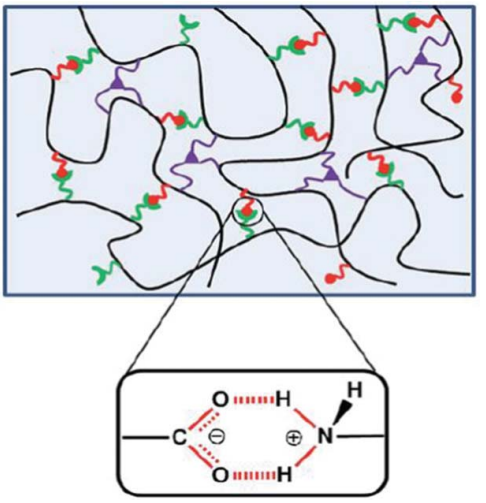

Figure 4. Hydrogen bonds between amine and carboxylic groups in BR.[31]

thiol via thiol-ene reaction. The degree of covalent crosslinking was tuned, leading to an increase in Young's modulus and maximum stress for a higher degree of crosslinking, at the cost of maximum strain. Healing was performed at room temperature on samples with three degrees of covalent crosslinking. However, these materials (as any other existing self-healing supramolecular material) are limited by the compromise between the degree of crosslinking (and thus strength/stiffness dimensional stability) and healing behavior, as healing times increased and healing efficiency decreased for higher degrees of crosslinking. It was also concluded that healing improved at higher temperatures (80°C) due to increased chain mobility.

3.1.4. Ionic interactions

NR is obtained by coagulation of the latex of the *Hevea Brasiliensis* tree. This latex contains, among other substances, rubber particles and vacuolar structures called "lutoids" comprising the protein Hevein responsible for the coagulation. Upon injury, the lutoids burst and the protein Hevein is released followed by the formation of Hevein-dimers under the influence of Ca^{2+} ions. This leads to the crosslinking of rubber particles containing binding sites for the Hevein protein on their surface, thereby causing an autonomous latex coagulation in a process comparable to extrinsic encapsulated man-made self-healing polymeric systems.[91] Similar to what happens in the crosslinking of Hevea proteins, in man-made ionomers, ionic groups aggregate to larger complexes contributing strongly to the intermolecular binding capacity. These ionic clusters, depicted in Fig. 5, are reversible linkages and act as physical crosslinking points. Therefore, it is possible to generate a dynamic system and to induce a self-healing mechanism.

Following this approach, promising results as to the self-healing capacity after macroscopic damage were found for carboxylated nitrile rubber (XNBR).[46] For non-vulcanized samples, a 50% restoration of its original *quasi*-static tensile strength was obtained, whereas the recovery ratio dropped to 15% for fully cured material. Also, Das *et al.*[42] converted Bromobutyl rubber (BIIR) into a highly elastic material with some self-healing capabilities by the inclusion of reversible ionic associates that exhibit physical crosslinking. They transformed the bromine functionalities of BIIR into ionic imidazolium bromide groups. In the same framework, Xu *et al.*[48] presented a simple reaction between carboxyl groups in carboxylated styrene-butadiene rubber (XSBR) and zinc oxide (ZnO), where the formed Zn^{2+} salt bondings connect separate XSBR molecules. The further self-aggregation of ion pairs of Zn^{2+} salts resulted in an ionic crosslinked network, whose rearrangements brought XSBR excellent reprocessing/recycling ability.

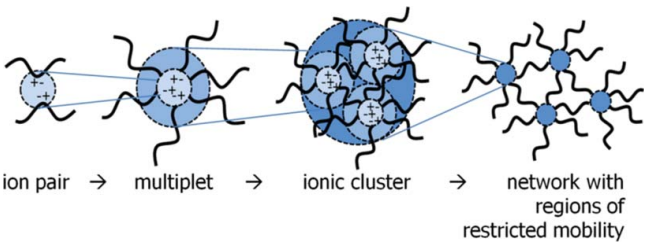

Figure 5. Schematic representation of the hierarchical formation of the ionomer morphology: ion pair – multiplet – ionic cluster – network with encircled regions of restricted polymer mobility.[78] © 2014, Royal Society of Chemistry. Reproduced by permission of Copyright 2014, Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

Despite these promising results, the opportunities for creating ionic associations on NR chains is limited because NR is non-polar and has no available functional groups to be converted into ionic groups. A practical approach to overcome this obstacle was found by Xu *et al.*[37] The key feature of their approach was the introduction of ionic crosslinks into the NR network through graft-polymerization of Zinc dimethacrylate (ZDMA). Their strategy was based on a controlled peroxide-induced vulcanization that allowed the generation of ionic crosslinks to construct a reversible supramolecular network without the formation of permanent covalent crosslinks. Though no direct evidence was put forward to confirm the graft ratio of ZDMA on NR, the experimental results strongly support the formation of an ionic supramolecular network and the resultant pronounced self-healing behavior (95% tensile strength recovery when the specimen is healed for 5 min at room temperature).

The earlier work of Xavier *et al.* on thermoplastic elastomers can also serve as inspiration for the development of NR-based self-healing ionomers.[92] In their work, styrene (S) was graft copolymerized with NR latex. The graft copolymer (S-*g*-NR) was then sulfonated and neutralized with Zinc acetate to obtain Zinc sulfonated styrene grafted NR (ZnS-S-*g*-NR), as shown in Fig. 6. The authors reported results of re-processability, by applying repeated cycles of mastication and press molding. The stress–strain properties of the ZnS-S-*g*-NR material remained almost constant after three cycles. This behavior was attributed to a morphological structure similar to that of conventional thermoplastic elastomers having a combination of hard domains and soft segments.

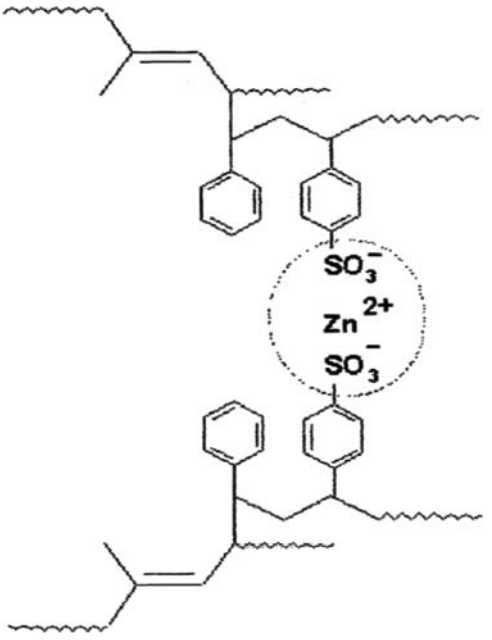

Figure 6. Proposed chemical structure of Zinc sulfonated styrene grafted natural rubber (ZnS-S-*g*-NR).[92]

3.1.5. Sulfur–sulfur exchange reactions

A further opportunity to obtain self-healing based on reversible bonds is by the introduction of dynamic disulfide groups into the polymer.[93] Disulfide groups are a versatile tool for the design of self-healing polymers because they can undergo different reversible reactions (metathesis reactions) such as disulfide exchange and thiol–disulfide exchange.[94] The pioneering work of Klumperman *et al.*[13] is based on the use of disulfide links incorporated in a disulfide-containing epoxy resin crosslinked with tetra-functional thiols, yielding elastomeric networks having a T_g around −35°C. They demonstrated that their material was capable of tensile strength healing due to annealing at 60°C after 1 hr, leading to a renewal of crosslinks across the fracture surfaces. In the original publication, they ascribed the healing mechanism to disulfide exchange reactions; however, in a later article, they concluded that thiol–disulfide exchange reactions were more likely to be responsible for the healing process.[95]

A study by An *et al.* reported a thiol-ene radical addition reaction.[96] They found that a material with an excess of S-H groups can be treated with iodine as an oxidizing agent, leading to disulfide linkages. These disulfide linkages were found to induce self-healing behavior at room temperature. The healing time appeared to be related to the size of the cuts introduced as well as to the disulfide crosslinks concentration, but no external stimuli (like contact pressure across the fracture surfaces) were imposed during healing. It must be noted that healing was enabled through disulfide crosslinks, but the cuts healed were all under 0.1 mm in width and therefore it was not possible to state that room temperature self-healing of disulfide containing polymers led to full restoration of the mechanical properties. If this technology is to be applied to NR, one should consider that at the curing temperature (~160°C), thiols are prone to oxidation.[29,75] In a typical thiol–disulfide exchange reaction, a thiol nucleophile reacts with a disulfide derivative under basic conditions providing the formation of the different component associations. Under aerobic conditions, the thiol species slowly oxidize into their corresponding disulfides, thus favoring disulfide metathesis more than thiol–disulfide interchange.

Xiang *et al.* introduced $CuCl_2$ as a new catalyst for the metathesis of sulfur bonds.[29] They experimented with this catalyst and found that metathesis of disulfides is possible in vulcanized BR, with an estimated content of 62% and 31% disulfide and polysulfides crosslinks, respectively. They reported self-healing behavior of their compound from temperatures above 110°C. They also indicated that the activation temperature of $CuCl_2$ would be lower in a polar environment, which is not the case for BR, nor would it be for NR. The assumed reaction is shown in Fig. 7. A healing cycle of 12 h at 110°C resulted in a 75% healing efficiency. In test specimens with the catalyst disabled, only 12% recovery of tensile strength was observed. By repeating the healing

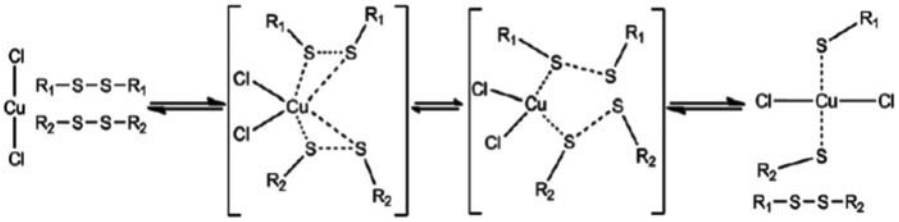

Figure 7. Reaction process of sulfide crosslink metathesis catalyzed by $CuCl_2$.[29] © 2015, Royal Society of Chemistry. Reproduced by permission of Copyright 2015, Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

process, the remaining tensile strength dropped to approximately 40% at the third cycle. They also concluded that healing efficiency should be higher, if the non-contact zones after fracture are eliminated. They estimate that these non-contact zones in their experiments make up for 6–10% of the total fracture area. Finally, they found that the tetrasulfide greatly improves mobility of the catalyst, which ensures a better distribution in the rubber. However, it was observed that $CuCl_2$ was not homogeneously distributed, which impairs the healing as less sulfide crosslinks will be able to recombine.

Although these results strictly speaking only apply to BR, the chances of this system working for NR are considerable, since the chemical composition of these materials is comparable. This would enable sulfur crosslink restoration at elevated temperatures for vulcanized NR. Room temperature self-healing of sulfur crosslinks, however, does not seem to be an option at present, since the catalysts required for these reactions are not able to withstand the vulcanization process. It must be noted that further research would have to be conducted to see whether adding these catalysts after vulcanization is an option. The research by Xiang *et al.* does not mention any healing at elevated temperatures without the use of the $CuCl_2$ catalyst. Disulfide and polysulfide bonds are known to degrade at temperatures above 60°C already over time (they are considered stable up to 50°C). So in this case, $CuCl_2$ would only act as a catalyst, but healing at elevated temperatures should be possible nonetheless.

Hernández *et al.*[33,34] reported sulfur-cured NR compounds with self-healing capability, without the need of additional catalysts and playing with the amount of sulfur. Macroscopic damage was introduced to rectangular samples by manually making a straight cut along the width using a fresh scalpel blade. Within 5 min after cutting, the rectangular damaged samples were carefully positioned inside a home-built healing cell such that the cut surfaces were in seemingly optimal initial contact. Based on earlier work,[13,33,75,95] the cut samples were healed at 70°C and 1 bar for 7 h. Healing, here understood as the disappearance of the cut and restoration of the mechanical integrity, was only observed for compounds with low sulfur content, resulting in a maximum recovery of tensile stress of ~80%.[34] Interfacial damage on samples to be evaluated by single edge notched tensile (SENT) test was also created for quantification of the healing efficiency. A testing protocol based on fracture mechanics was used. It was recently demonstrated that such an approach provides more realistic measure of the interfacial healing achieved compared to conventional tensile testing experiments.[97] The 50%-cured NR compound showed a recovery of the fracture energy of 63%.

The dynamic character of the di- and poly-sulfide bonds naturally present in covalently crosslinked NR was found to be responsible for the healing ability and the full recovery of mechanical properties, provided the material was employed in a non-fully cured starting state. The breakage of the sulfide bridges at a given temperature during the healing process allows for a substantially higher mobility than in a fully crosslinked polymer with irreversible crosslinks, facilitating chain interdiffusion across the damaged interphase. Hernández *et al.* also demonstrated that the underlying disulfide metathesis healing mechanism is based on temperature-driven sulfur radical reactions. In addition, that study revealed that the ratio between di- and poly-sulfide bridges is an important mechanistic parameter, although other limiting factors on healing seem to be sulfur content, crosslinking density, post-curing storage time, and contact time between damaged surfaces before healing treatment.

Using alternative crosslinking systems, a recent study by Imbernon *et al.* showed disulfide healing in an ENR system crosslinked by dithiodibutyric acid (DTDB).[38] The crosslinking relies on these di-acids carboxylic groups to react with the epoxides within ENR, whereas

healing is enabled through DTDB's disulfide bonds. In this work, recovery of properties was not measured by measuring the tensile load recovery of a sample containing a single crack, but "healing" was determined by grinding the crosslinked rubber, after which it was remoulded. After the remoulding, the maximum stress decreased significantly though (approx. 45% drop), whereas the maximum strain stayed at about 85% of the initial failure strain.

Disulfides not only respond to thermal stimulus but also to visible light.[8,98,99] Amamoto *et al.*[64] prepared macroscopic self-healing crosslinked PU based on radical reshuffling of thiuram disulfide (TDS) units under the stimulation of visible light at room temperature without solvent. Since the S–S bonds in the incorporated TDS units homolytically dissociate in visible light, the radical reshuffling reactions enable the reorganization of the linking units in the covalently crosslinked polymers and self-healing of significantly damaged polymers. Thus, the method based on photo-induced scission and reformation of chemical bonds in a metathesis manner is also appealing for the development of self-healing NR compounds.

3.1.6. Diels–alder chemistry

Diels–Alder moieties allow for the implementation of self-healing capabilities to existing polymeric networks without significantly compromising the original properties.[100–102] An important property of Diels–Alder reactions is that they can be thermally reversible with a good choice of reactants under certain temperature conditions. A commonly used Diels–Alder reactant combination is formed by furan/maleimide.[103] Trovatti *et al.*[28] and Bai *et al.*[27] implemented this combination in BR in search of recyclable tires; they added a furan heterocycle as pending group in BR (by means of a thiol-ene reaction of furfuryl thiol) and added maleimide as dienophile to crosslink the system. The reaction scheme is displayed in Fig. 8.

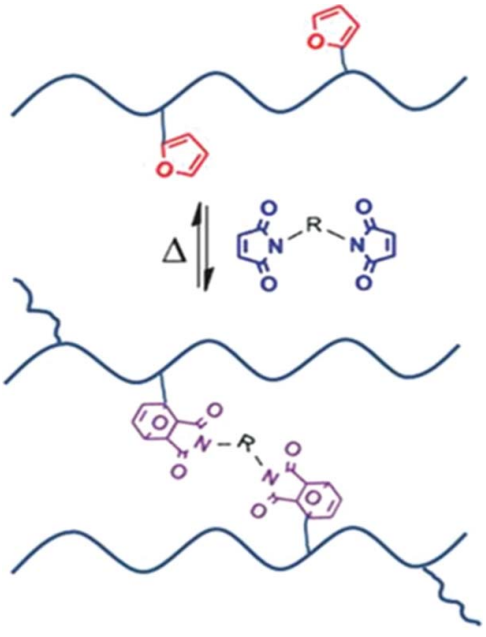

Figure 8. Diels–Alder reaction scheme using heterocycle furan as diene and maleimide as dienophile in BR.[28] © 2015, WILEY-VCH Verlag GmbH & Co. Reproduced by permission of Copyright 2015, WILEY-VCH Verlag GmbH & Co. Permission to reuse must be obtained from the rightsholder.

According to Trovatti,[28] the forward reaction is dominant around 60°C which allows for a maximum use temperature of 60°C. The reverse reaction is dominant above 100°C, implying that there is increased mobility and theoretically the forward reaction should occur again when cooled below 60°C again. This process should also be possible using NR and may work well for the development of self-healing NR. Considering that the forward Diels–Alder reaction occurs at 60°C, this may lead to self-healing without any intervention in some applications.

A similar healing reaction, but in an poly(styrene-block-butadiene-block-styrene) (SBS) rubber system was described by Bai *et al.*[51] They grafted furfuryl groups to the SBS rubber which were crosslinked by introducing bismaleimide into the toluene solution. After stirring, the solution was casted and dried at 80°C for 12 h. The resulting film was then cut and remoulded under 10 kPa of pressure at 160°C for 5 min, presumably breaking the Diels–Alder crosslinks. The remoulded film was then cooled for 2 days, after which tensile tests showed only a slight decrease in modulus and tensile strength, indicating the reformation of the Diels–Alder crosslinks.

ENR could also be modified to include furan rings in the backbone structure.[103,104] This can be done either by acid titration or ageing. Furanation of ENR, however, results in formation of THF. Unfortunately, this moiety is not a diene and therefore will not undergo a Diels–Alder reaction upon introduction of a dienophile into the system.

3.1.7. Vitrimers chemistry

Vitrimers, introduced in 2011 by Leibler *et al.*,[105] and recently reviewed by Du Prez and Winne,[8,106] are a new class of materials made of an organic network formed by exchangeable covalent bonds as crosslinking points instead of reversible bonds. This network is able to change its topology via exchange reactions that are associative in nature and thermally triggered, resulting in the thermal malleability of the network.

In the field of rubbery materials, vitrimers chemistry appears as an excellent way to combine the good mechanical properties of covalently crosslinked elastomers with full recyclability and repairability. Lu *et al.*[32] have reported vitrimers properties in a peroxide crosslinked BR network by addition of an olefin metathesis catalyst (Grubbs catalyst). The resulting material was fully processable but still insoluble. This approach is potentially applicable to all olefin-containing rubbers like NR and SBR. However, Grubbs catalysts are expensive, which can be a serious limitation for industrial applications. Moreover, it is likely that rubbers like NR will not maintain, after olefin metathesis, the well-defined *cis*-configuration that makes them outstanding materials.[11]

3.2 Network damage

The focus of the previous section was on the restoration of localized macroscale damages involving the creation of new interfaces (*e.g.*, cracks or scratches) and the subsequent loss of stiffness and strength. Even though healing of optically detectable microscopic and mesoscopic damage is important, the healing of invisible internal damage (*e.g.*, chain scission, reduction of average molecular weight, or induced crosslinking) to the polymer network is of equal importance. Besides, the healing quantification of this type of damage will be more reproducible than the healing efficiency calculations of completely separated fracture surfaces that show a large amount of scatter for nominally identical testing conditions.

Hernández *et al.*[33] studied a uniform molecular network damage (due to multiple straining cycles of the entire sample) imposed to 50% and 90% sulfur-cured NR

compounds. Healing of the cyclic strained samples not showing macroscale damage was done by pressure-less relaxation for 3 h at 70°C. For both rubbers, the instantaneous elastic modulus appeared to be completely recovered in the first cycle. However, the global tensile behavior differed after the thermal healing treatment. For the 50%-cured NR, the potentially higher availability of reversible bonds directed to full recovery of the original properties, thanks to the overall mobility, while for the 90%-cured rubber, the rupture of permanent bonds was irreversible, causing permanent damage. Healing was quantified according to the difference in instantaneous tensile modulus between the 1st and 10th loading cycle. Such an approach was selected in order to only consider the effect of reversible bonds on the recovery of mechanical properties since the residual permanent bonds (related to the instantaneous modulus of the 10th cycle) do not contribute to the network healing. A full recovery (96%) obtained for the 50%-cured NR confirmed the larger amount of reversible bonds available in partially cured systems. Hernández *et al.*[33] also used broadband dielectric spectroscopy (BDS) for monitoring the network damage of these compounds, demonstrating that the polymer architecture in the healed material slightly differs from that in the original one.

More recently, and following a different approach, Liu *et al.*[36] incorporated a combination of two types of sacrificial bonds to maximize the mechanical properties of a chemically crosslinked *cis*-1,4-polyisoprene (IR) network. They incorporated weaker hydrogen bonds and stronger metal-based units. To confirm the existence of hydrogen bonding as sacrificial bonds, cyclic tensile tests were performed with stretching to a predefined 300% strain. A significant hysteresis behavior was observed in the first loading–unloading cycle, associated with the rupture of the hydrogen-bonding network. After heating at 80°C, the hydrogen bonds exert a nearly complete self-recovery, without residual strain. Flex-cracking tests were also conducted. The sacrificial hydrogen bonding and Zn-based bonds had opposing effects on flex-cracking resistance. The introduction of hydrogen bonding led to deteriorated flex-cracking, while the Zn-based bonds improved it significantly. The incorporation of Zn-based units is believed to increase the energy necessary to break the sacrificial bonds at the crack tip.

The rearrangement of ionic supramolecular networks during cyclic deformation was also studied by Xu *et al.*[37] They applied multiple loading cycles with sequential increasing strains (ε_{max} = 50, 100, 150, and 200%) to a NR/ZDMA ionic compound, showing typical stress softening behavior with hysteresis and large permanent residual strain. They claim that in every cycle, the rupture and rapid reconstruction/redistribution of ionic crosslinks during deformation restricts the complete recovery of the supramolecular network although more scientific evidence would be necessary to complement this hypothesis.

3.3 Ballistic impact damage

In contrast to static and fatigue damage, impact damage is very hard to describe and to quantify as the impact damage is a dynamic response of both the material and the impacting object (not only its velocity and kinetic energy, but also its shape and impactor material). Ballistic impact creates a high temperature region due to friction and strain energy dissipation around the bullet impact zone. The complete hole closure indicates a high level of interdiffusion at the damage zone, following the elastic recovery of high deformation imposed by the bullet.

Ballistic healing, in particular of ionomers, has received a relatively large amount of attention in the literature[80,94] as the discovery was made in the early stages of the development of

the field of self-healing materials and it was the first reported example of intrinsic self-healing.[107–109] In this case, self-healing occurs through a heat generated frictional process, which heats the polymer to the viscoelastic melt state and provides the ability to rebound and repair damage, thanks to the reformation of existing ionic clusters in the matrix. Inspired by this healing mechanism, Rahman *et al.*[39,40] developed a strategy for blending different ionomers based on poly(ethylene-co-methacrylic acid) (EM) partially neutralized with sodium (Na) or zinc (Zn) salts with ENR. Healing was checked by both optical and scanning electron microscopy and also by depressurized air flow tests. A pressurized burst test can be used to determine the degree of healing of samples showing more or less complete hole closure. The burst pressure of healed samples in relation to the burst pressure of pristine samples is taken as a measure of healing efficiency. Complete self-healing behavior was found for all the ENR/EMNa blends. They argued that the adhesion of dismantled surfaces results from the chain interdiffusion in the crate zone as well as intermolecular interaction in the polymers. However, only partial self-healing phenomena were observed in all compositions of ENR/EMZn blends. This incomplete healing was due to the rearrangements of coordinated complexes of Zn^{2+} ions and the existence of some level of chemical interaction between the epoxy functionality of the rubber and the acid groups in EMZn, leading to a significant reduction in molecular mobility.

In an attempt to systematically investigate the self-healing behavior of ENR regarding the effect of epoxidation level and curing degree, Rahman *et al.*[41] in a later work developed ENR crosslinked with dicumyl peroxide (DCP) with self-healing behavior at room temperature. The authors concluded that not only the mobility of macromolecular chains but also the level of epoxidation (25 and 50%), along with the presence of epoxides ring-opened polar moieties, played a significant role on the successful intermolecular diffusion and hole closure following the bullet impact. Self-healing was observed for ENR-50, but not for ENR-25 after ballistic impact; the higher level of epoxidation promoted stronger intermolecular interactions among polar groups. These results were also confirmed by T-peel tests. This test can give an indication about the ability of two adjacent surfaces of the same substance to give a strong connection preventing their separation at the place of contact. Such a phenomenon is usually ascribed to self-adhesion. In this study, the authors claim that simple interdiffusion was not sufficient for an efficient self-adhesion, but intermolecular forces, as in ENR-50, were necessary to restore full joint strength. It is worth mentioning that the ENR used in this study is only slightly crosslinked. It would be expected that, as the crosslinking density increases, the interdiffusion process could be hindered, and thereof, the level of healing be decreased. This puts in evidence once more the compromise between repairability and performance. In other words, a high molecular weight ENR well crosslinked, in principle, could not be healed by this process.

4. Natural rubber composites. Recovery of multiple functionalities

In a polymer-based composite, any self-healing ability has to come from the polymer matrix, since most filler materials are based on strong irreversible (non self-healing) covalent, metallic, or ionic bonds. The inclusion of either reinforcing or functional fillers to intrinsic self-healing polymers might generate some novel self-healing composite materials, which not only will have enhanced mechanical properties but also can be healed via multi-channels. In this sense, the incorporation of magnetic, photo-thermal, and/or electrical nanoparticles into self-healing polymeric matrices can be considered as an alternative external stimulus for

the self-healing process.[99] The following sections describe healing processes of different functionalities in rubber-based composites.

4.1 Mechanical integrity

Rubbers with reversible non-covalent crosslinks are unlikely to survive the high stresses as encountered in current industrial applications. The addition of reinforcers absolutely increases their mechanical properties, but usually, this is accompanied by the disadvantage that the reinforcing agent tends to destroy the non-covalent crosslinks, retarding the reconstruction of the network and thus its self-healing ability. The inclusion of nanofillers like graphene or carbon nanotubes (CNTs) in small amounts appear as a good alternative to defeat this trade-off by improving the mechanical/structural performance and generating heat within the matrix so the healing process after damage can be accelerated.

Studies that report on self-healing rubber/graphene composites include the work of Kim *et al.*[66] They synthesized PU/graphene nanocomposites to introduce the light-induced self-healing by modified graphene as well as to reinforce the PU. They state that healing occurred thanks to the intermolecular diffusion of rubbery chains which was accelerated by thermal energy generated by near infrared (INR) absorptions. The healing effect, measured by the recovery of toughness, was most pronounced with 0.75 wt% of graphene, while further addition of filler physically disturbed the chain interdiffusion, thus reducing the self-healing efficiency. Secondly, Huang *et al.*[67] reported a TPU fabricated with few layers of graphene. In addition to its enhanced mechanical properties, this self-healing material could be healed repeatedly via different methods including infrared (IR) light, electricity, and electromagnetic wave with excellent healing efficiencies higher than 98%. They ascribe the improved healing performance to two intrinsic properties of graphene: i) good IR absorbing capacity; ii) excellent thermal conductivity, which would help efficiently transfer the Joule energy from the IR absorption into the PU matrix. Thus, during the healing process, graphene worked as a nanoscale heater and transfer unit to generate the required energy and then transport it to the matrix efficiently. A third example of an elastic nanocomposite material with self-healing ability, combining the unique features of hydrogen-bonded polymers and graphene oxide (GO) as a macro-crosslinker, was shown in the work of Wang *et al.*[110] By adding as little as <2 wt% of GO to the supramolecular polymer, they obtained an elastic material with similar mechanical properties to that of conventional rubbers while possessing very fast healing properties at room temperature. Their described concept of using GO as both crosslinker and filler to derive highly efficient self-healing materials can be applicable to a wide range of other supramolecular systems or dynamic covalent bond containing functional polymers. This approach could also be applied to self-healing ENR where hydrogen bonds could be formed between the oxygen functionalities on the surface of GO and the epoxy groups on the isoprene units.[111] In another context, GO was added to PU via *in situ* polymerization based on Diels–Alder chemistry.[112] On the basis of the recovery of tensile strength, the prepared composites showed excellent thermally healable ability with an efficiency of 71%.

Besides the aforementioned graphene-filled composites, rubber/CNTs composites have also caught attention recently. Le *et al.*[43] studied the self-healing behavior of BIIR filled with CNTs. They modified the rubber matrix by introducing ionic groups after the reaction of butyl imidazole and BIIR. These groups contributed to the formation of an ionic network and to the pronounced self-healing behavior of the composites, due to the improved

rubber–filler interactions. They also demonstrated that the self-healing process could be locally triggered by Joule heating. Later on, they blended imidazole modified BIIR with NR and added CNTs.[44] The favored localization of the CNTs in the NR phase improved the electrical properties of the blends and did not deteriorate the mechanical self-healing of the BIIR phase. Another example of enhancement of mechanical properties without reduction of the healing capability was reported by Kuang *et al.*,[49] adding multi-walled carbon nanotubes (MWCNTs) to SBR on the basis of Diels–Alder bonding. Furfuryl-modified SBR and furfuryl-functionalized MWCNTs were reacted with bismaleimide to form a covalently bonded and reversibly crosslinked SBR/MWCNTs composite. The nanofiller played dual roles of being simultaneously the reinforcing and the carrier for the healing agent.

4.2 Thermal and electrical conduction

Graphene/NR composites with a conductive segregated network were prepared by latex mixing by Zhan *et al.*[113] Self-healing properties based on the recovery of the electrical conductivity after several tensile cycles (elongated up to 50% and then retracted to its original length) were analyzed. The authors followed the changes in conductivity with filler content (0–10 phr), before and after a post-processing thermal treatment. They reported that the electrical conductivity of all composites increased with the thermal treatment, while it decreased after four tensile cycles, due to the damage occurring at the weak electrical network. The destroyed network was healed via a post thermal treatment achieving conductivity values similar to those of the undamaged samples thermally treated.

Moving from latex to solid-state processing, Hernández *et al.*[114] aimed at restoring more than one functionality in cut NR/graphene composites. They evaluated the restoration of electrical and thermal conductivity in a mechanically damaged sample. Different healing trends as function of the graphene content (0–2 phr) were found for each of the functionalities: (i) thermal conductivity was fully restored independently of the graphene filler loading; (ii) electrical conductivity was only restored to a high degree once the graphene content was above the percolation threshold; and (iii) tensile strength restoration increased more or less linearly with graphene content but was never complete (see Fig. 9).

Functionality	Damaged sample	Healed sample	Minimal requirements for healing	Graphene content effect on healing
thermal			1-Surface contact	Independent
electrical			1-Surface contact 2- Percolation path	Percolation threshold set as lower limit
mechanical			1-Surface contact 2- Rubber-filler interactions 3- Load transfer at the interface	Gradual increase

Figure 9. Schematic representation showing the minimal requirements to be met for restoring thermal, electrical, and mechanical functionalities.[114] © 2017, IOP Publishing. Reproduced by permission of Copyright 2017, IOP Publishing. Permission to reuse must be obtained from the rightsholder.

A dedicated molecular dynamics analysis by dielectric spectroscopy of the pristine and healed samples highlighted the role of graphene–rubber interactions at the healed interphase on the overall restoration of the different functionalities. Based on the results, they suggested that the dependence of the various healing efficiencies with graphene content is due to a combination of the grapheme-induced lower crosslinking density, as well as the presence of strong polymer–graphene interactions at the healed interphase.

5. Future developments and final remarks

The objective of this review was to examine different healing concepts and discuss their potential in the development of self-healing NR and NR composites, considering both structural and functional recoveries. From hydrogen bonding to Diels–Alder reactions, all the healing premises presented in this state-of-the-art in principle can be applied to NR. Nonetheless, the fact that NR is a non-polar elastomer with no functional groups into its main chain or attached to side-chains reduces the possibility for any physical or chemical reversible interaction to take place easily. The challenge, therefore, is to chemically modify its structure by grafting polar groups during polymerization and/or during mixing of the rubber compound. The inclusion of disulfide groups as healing moieties is also feasible in sulfur-vulcanized NR. However, the sulfur crosslink restoration would only take place at temperatures higher than room temperature, with unavoidable side-reactions that create permanent crosslinks occurring as well.

Most of the developments here discussed refer to low molecular weight rubbers and/or with low crosslinking degree. Achieving simultaneously good repairability and mechanical performance in highly crosslinked networks, and scaling up to mass production still remains a challenge. Future research should then be focused on preparing NR with higher mechanical properties at working conditions and with milder healing conditions. A combination of crosslinks of different nature (*e.g.*, covalent and non-covalent) in the rubber network seems a viable option. The inclusion of nanofillers playing a dual role of reinforcing and carrier of the healing agent would also be beneficial. This is an absolutely promising result for the tire industry in which safety, performance, and longer fatigue life are crucial factors. In addition, many rubbers usually undergo a large variety of dynamic loading conditions in real life service, thus it seems more relevant for the quantification of healing efficiency to assess healing processes through cyclic deformations and fatigue tests to ensure already at an early stage of the material development the safety and reliability of various applications. Moreover, these types of tests are also relevant for studying the potential reshaping/reprocessing performance of self-healing elastomers.

Likewise, research on the restoration of more than one functionality is still in its early stage development. However, as the demand for functional rubber 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. Nonetheless, self-healing of these materials will require the independent restoration of different functionalities, which requires different healing mechanisms to take place simultaneously or in close succession. Self-repairable electronic circuits and flexible stretchable conductors are just some examples of potential applications. Even more, the ultimate challenge would be to sense damage before real damage occurs.

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