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Evolution of self-healing elastomers, from extrinsic to combined intrinsic mechanisms: a review

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The evolution of self-healing polymers has resulted in a myriad of healing designs that have given way to complex systems capable of supporting multiple cycles, among other features. This progression enables us to propose the implementation of a timeline that classifies self-healing polymers in generations based on the healing mechanism, and correlated with historical development. The first generation employed the encapsulation of external healing agents; the second one, based on intrinsic mechanisms, applied reversible chemistries; and the third generation was inspired by natural examples such as plants and human skin, in which the healing agent is embedded in vascular networks. Despite great efforts and, with a few exceptions, polymers with high healing efficiency and high mechanical performance are not common. To improve this situation, a combination of different mechanisms is currently emerging, giving birth to the fourth generation of self-healing materials. This article, focused on self-healing elastomers, provides a rigorous overview of this new generation, in which the combination of covalent bonds and non-covalent interactions provides an optimal balance between mechanical performance and repairability. The implementation of this concept leads to materials with real commercial potential in functional applications, such as coatings, sensors, actuators, controlled release of drugs, seals, gaskets, hoses, and even high-performance applications such as tires and railway components.

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1. Introduction

The history of humankind has been classified in periods according to the use given to materials to meet their basic needs. In all cases, the discovery of new materials and the advancement in the manipulation of those already known implied a real revolution in social structures. With the impressive development attained between the 20th and the 21st century, humanity began to require new materials with properties on demand. Among these properties, self-healing has arisen as an unstoppable development in the last 20 years.

Self-healing materials are attractive in the current environmental context, where there is a need for reducing waste and extending the lifetime of products. Besides, in the framework of the circular economy,[1,2] certain polymers, such as elastomers or thermosets, are inappropriate because, despite great efforts,[3,4] their reprocessing remains a challenge. Due to their importance in industrial applications, it has become mandatory to make them compatible with the circular economy model. Precisely, one possible path to achieve it is by conferring them with self-healing capability.

One can find in the literature some important reviews on the development of self-healing materials.[5–7] However, there are just a few in the field of elastomers[8–11] and to the best of our knowledge there is no specific one considering the combination of healing moieties, a new trend that has shown exponential growth in recent years. This review initially presents a brief overview of the evolution of self-healing, divided into generations, and later compiles the advances in the last five years in the field of self-healing rubbers. We define four generations and structure the review based on the nature of the involved bonds and interactions: non-covalent, covalent or combinations between them. The review ends with a final outlook and some future perspectives.

2. A brief history of self-healing polymers

2.1. Self-healing key concepts

Inspired by nature, self-healing materials have the ability to repair or restore damage, replicating mechanisms found in living organisms such as plants and human skin. To ensure the success of self-healing, three concepts have been defined by van der Zwaag:[12] (a) localization, (b) temporality and (c) mobility. We include a fourth key concept: (d) mechanism (Fig. 1), in order to classify the different generations of self-healing materials.

The concept of localization refers to the position and/or scale of the damage in the material. It can be superficial, such as scratches, (micro) cracks, or cuts; it can be deep, such as the propagation of surface damage, fiber debonding or delamination, ending up in catastrophic damage; or it can be molecular scale damage, *e.g.* breakage of the material network.[5] The localization and scale of these types of damage play an essential role when considering the self-healing capability of the material. The aim is to reach one single protocol that assures achieving healing at all scales; however, specific protocols can be designed for particular types of damage according to the intended application of the material.

The second factor, temporality, is given by the time gap between the damage event and its repair. Even in nature, self-healing is time-dependent, not instantaneous. The target is to minimize the time for healing to occur. One way to reduce this time is by conferring mobility to the material, the third key concept. Mobility promotes the diffusion of the healing agent to the damage area, as well as the reformation of the broken bonds. This concept is key to optimize others, *e.g.* if the mobility of the agent is not adequate, it will not flow towards the damage or it will do so slowly.



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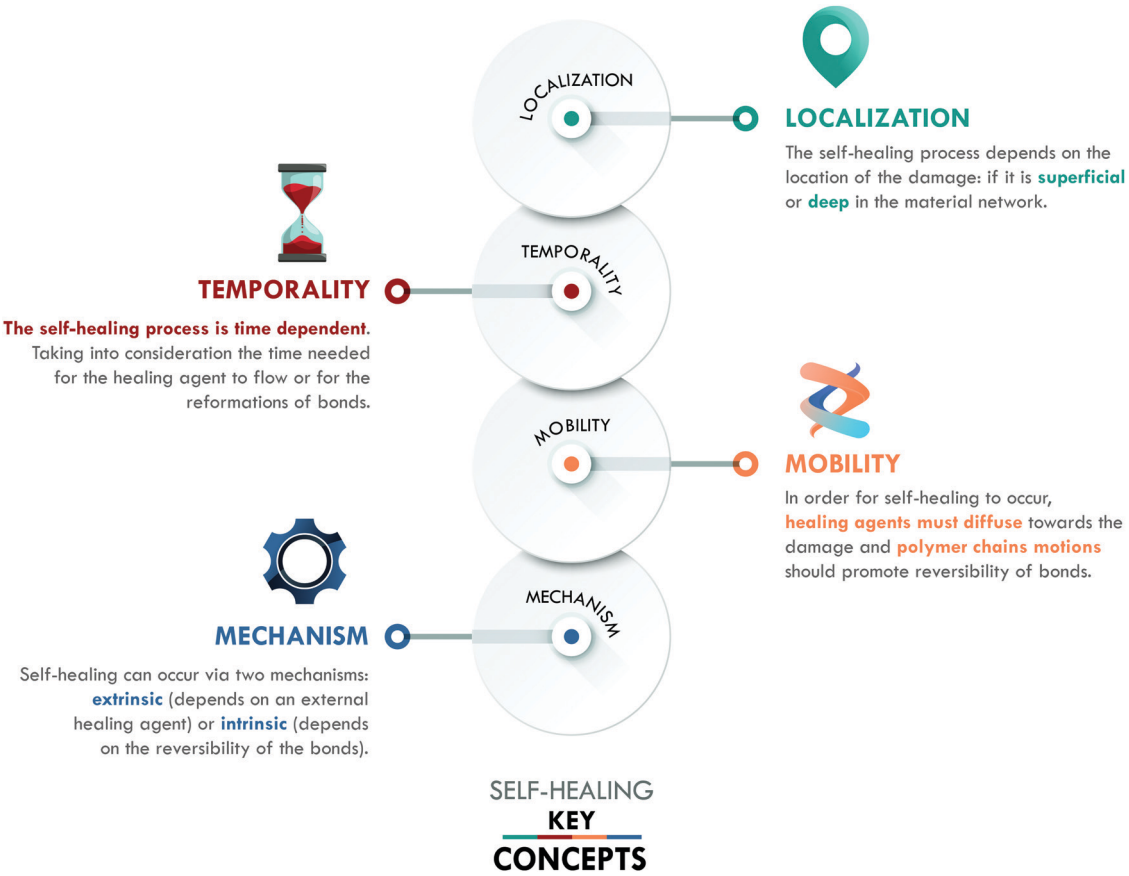


Fig. 1 Self-healing key concepts.

The last key concept in self-healing is the mechanism. This concept enables the classification of self-healing materials into two families: extrinsic and intrinsic. Extrinsic self-healing materials are those in which the process depends on an external agent, normally dispersed in the form of capsules or vascular systems. These agents are released to seal the damage and do not specifically interact with the matrix. On the other hand, intrinsic self-healing materials are those in which the reversible bonds present in the material can be restored after a damage event.[5] In the case of polymers, extrinsic systems have widely been used in thermosets, mainly in epoxy resins,[13–15] while intrinsic mechanisms have widely been considered in elastomers, such as silicones,[16] polyurethanes,[17] and general purpose rubbers.[18–20] At this point, it is important to clarify that the current use of the terms intrinsic and extrinsic in the field of self-healing, to classify materials according to the type of mechanism involved, differs from their traditional use to designate physical quantities. In chemistry, intrinsic describes properties independent of size, shape, and quantity (*e.g.* density and refractive index, among others); meanwhile, extrinsic refers to dependent properties (such as weight and volume). The authors recognize that the use of these terms has some limitations, despite their extensive validation and widespread use in the self-healing field.[6,7,10,11,21] All of the above has motivated us to propose a new classification, based on the self-healing mechanism and historical development, which enables organizing self-healing materials into four generations (Fig. 2).

Although it was not the first published mechanism (as we will later explain), the first generation of self-healing materials was based on extrinsic mechanisms and employed encapsulated external healing agents. This generation had the disadvantage of only supporting a single cycle of self-healing.[6] To overcome this limitation, the second generation of self-healing polymeric materials emerged, based on intrinsic mechanisms, using the chemistry of reversible bonds; however, the self-healing capability and mechanical performance of the materials were in compromise: the increase of one meant the decrease of the other. The intrinsic approach has been studied in all kinds of polymers, with special emphasis in the field of elastomers.[7,10] Later, further development of extrinsic systems was initiated through healing agents confined in vascular networks, giving way to the third generation of self-healing polymeric materials, with strong inspiration from nature. These systems have been extensively studied in thermosets, but their application in elastomers remains limited except for a few reports on silicones.[22]

Finally, the fourth generation is currently growing fast and aims to overcome the different drawbacks of the previous generations. Hence, its objective is to develop a polymer with excellent mechanical properties, and high healing efficiency

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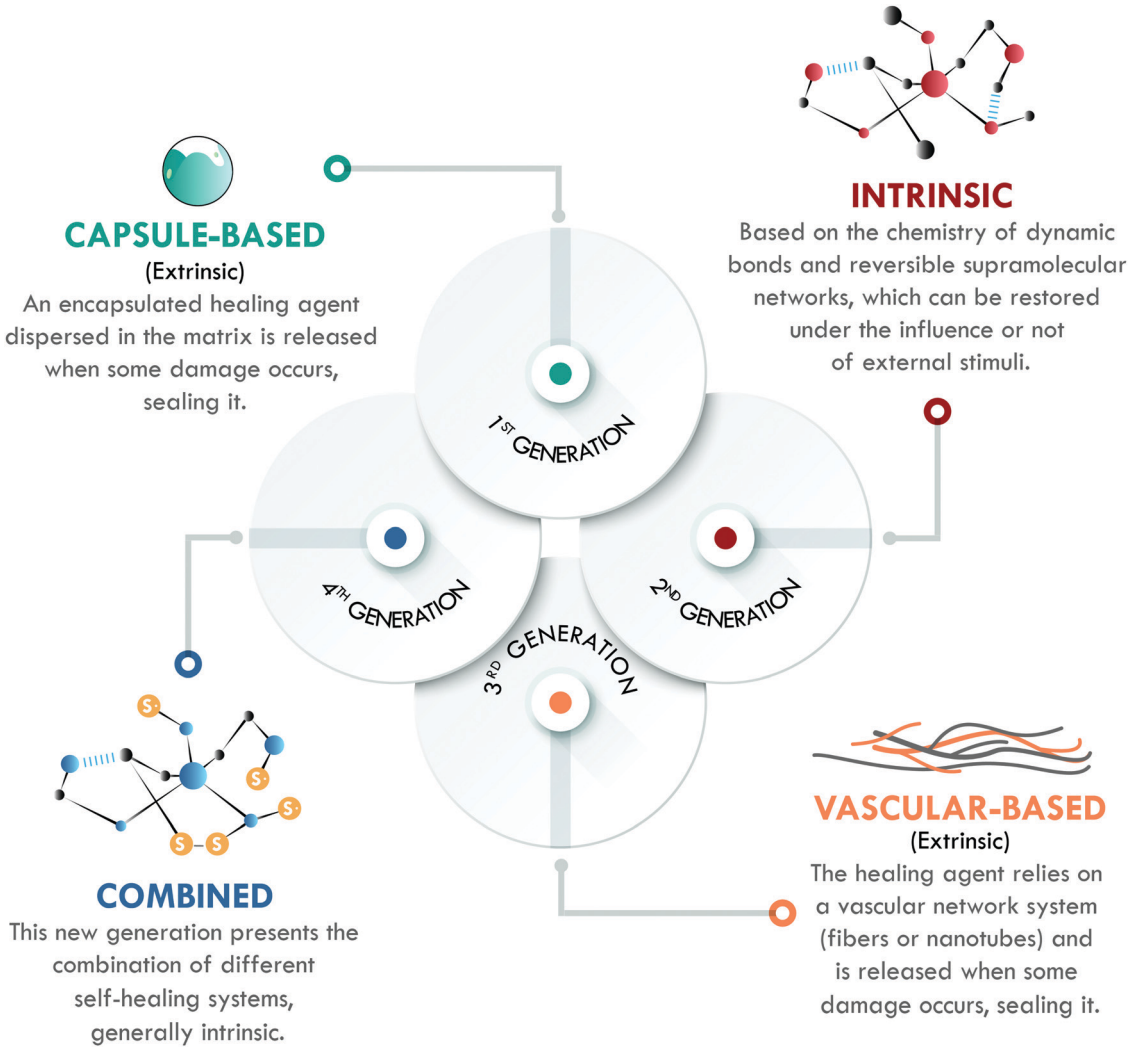


Fig. 2 Generations of self-healing materials according to the healing mechanism involved.

and resistance to multiple damage cycles through the combination of different healing mechanisms. However, the road to this point has been long and there are still some challenges to overcome.

2.2. Timeline of self-healing polymers

According to the literature, in the 1970s, Malinskii *et al.*[23–25] presented one of the first studies on polymer self-healing, specifically in poly(vinyl acetate) (PVAc). Later, Jud *et al.*[26] and Wool *et al.*[27,28] deepened the study about healing of cracks in poly(methyl methacrylate) (PMMA), polystyrene (PS) and hydroxy-terminated polybutadiene (HTPB). Nevertheless, all these studies and those in the following years were based on chain interdiffusion,[29] a highly known concept in polymers, which only requires a temperature slightly higher than the glass transition temperature (T_g) of the material to occur. Ellul *et al.*[30] presented the concept of self-adhesion in butyl rubber (IIR), as an essential preliminary step to ensure good contact between the surfaces to be repaired. The concept of autonomic self-healing, as we know it today, was introduced by Dry *et al.*[31,32] in the early 1990s; mainly in cement and epoxy resins. However, it was not until the publication of White *et al.*[13] that the definitive impulse for the development of self-healing polymeric materials began. This work is considered as the starting point of self-healing polymers (Fig. 3). According to White *et al.*,[13] self-healing was given by the incorporation of a healing agent (dicyclopentadiene, DCPD) embedded in microcapsules and a platinum catalyst (Grubb's catalyst) dispersed in an epoxy resin. Upon the release of the agent and encountering the catalyst, polymerization of the DCPD would occur, sealing the crack. This method, in its initial stage, enabled efficiencies of up to 75% in the recovery of the maximum load in a fracture toughness test. The implementation of this methodology in elastomers, specifically in poly(dimethylsiloxane) (PDMS), was carried out by Keller *et al.*,[33] who used a chemistry based on two types of microcapsules. They introduced a high molecular weight resin of PDMS functionalized with vinyl groups and a platinum catalyst in one, while in another they encapsulated an initiator and a PDMS copolymer with active sites that would serve to link the vinyl groups of the functionalized resin by the platinum catalyst action. This chemical reaction, also

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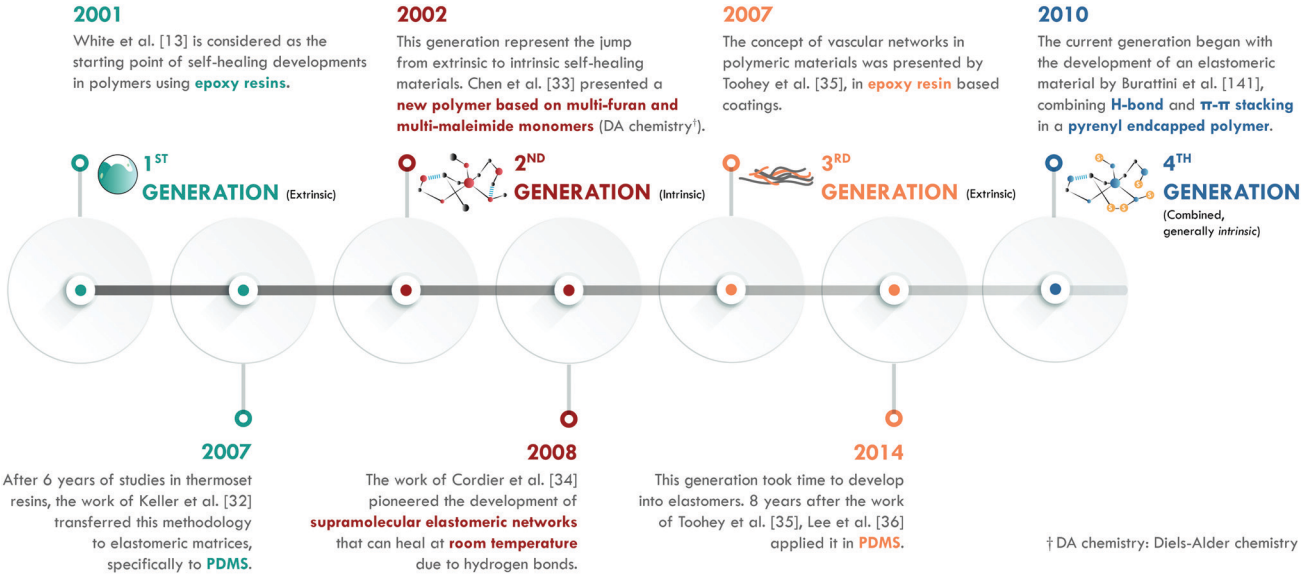


Fig. 3 Timeline of generations in self-healing polymers.

based on the polymerization of external agents, allowed efficiencies of up to 120% in the recovery of the tear strength. This first generation has been classified in several ways according to the arrangement of the healing agents and catalysts. The most widespread classification comprises five types: single-capsules, capsule/dispersed catalyst, phase-separated droplet/capsules, double-capsules, and all-in-one capsules. It is also possible to establish classifications according to encapsulation techniques (for example: *in situ* polymerization, sol–gel reaction, interface polymerization, and emulsion, among others).[34]

The second generation is based on the chemistry of the dynamic bonds. Any bond or interaction that is reversible under equilibrium conditions is considered dynamic and can be classified as: covalent and non-covalent. Although polymeric materials based on reversible chemistry had been developed in the past, Chen *et al.*[35] specifically designed the first self-healing polymer based on multi-furan and multi-maleimide monomers (Diels–Alder chemistry). In this work, fracture toughness tests were carried out after healing at temperatures between 120 and 150 °C, achieving an efficiency of 57% in the recovery of the maximum load. At the same time, the effect of pressure on the repair process was evaluated, concluding that it had a minimal influence on the healing efficiency of this material. This work represented an important development in the field because it showed a recovery of 80% after subjecting the material to a third healing cycle, thus proving the occurrence of multiple healing cycles.

Years later, Cordier *et al.*[36] first introduced the intrinsic self-healing methodology into an elastomer by designing and synthesizing molecules that could form chains and crosslinks through hydrogen bonds. Therefore, they had constructed a supramolecular network that was capable of restoring itself at room temperature. In this work, time dependence in the self-healing process was evidenced: longer times implied greater efficiencies. At the same time, they concluded that self-healing was not an instantaneous process.

The third generation of self-healing materials began with the work of Toohey *et al.*,[37] although the concept had been explored almost twenty years earlier by Dry *et al.*[31,32] The definitive stimulus for this generation took considerable time, due to the difficulties of incorporating vascular networks into a polymer matrix. This generation is usually classified according to the nature of the vascular network and its preparation technique. For example, electrospinning (coaxial electrospinning or emulsion spinning), solution blowing (coaxial solution blowing or emulsion blowing), and tubes and channel networks (micro/nano, such as hollow glass fibers and carbon nanotubes, among others).[22] Toohey *et al.*[37] used the previously described methodology by White *et al.*,[13] but the DCPD healing agent was confined in a net embedded in the epoxy resin coating. The healing efficiency was also measured as the retention of properties in fracture toughness tests, with efficiencies of over 40% and supporting up to 7 healing cycles.

The difficulty of incorporating vascular networks in the matrix has hindered this generation in elastomers. Only one group has reported the incorporation of electrospun vascular networks in PDMS.[38–41] Lee and coworkers[38,39] prepared two co-axial electrospun networks with polyacrylonitrile (PAN) as the shell, and with either dimethylvinyl-terminated dimethylsiloxane (resin monomer) or methylhydrogen dimethylsiloxane (curing agent) as the core. Thus, the two core materials only interacted upon cutting the PAN shell. The self-healing efficiency was qualitatively evaluated as an anti-corrosive barrier, showing good performance. Thus, the design of resistant vascular networks that do not break during high shear, conventional processes remains a challenge.

A fourth generation is currently emerging within this field. However, this new generation does not mean that further developments using the previous approaches have stopped. On the contrary, these strategies are largely under development and are under study for both traditional and advanced applications.

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Table 1 Papers published on self-healing rubbers using the first three generations over the last five years

Healing mechanism	Rubber matrix	Ref.
First generation: capsular self-healing systems		
Single-capsule systems		
Capsule based	Polyurethane – PU	47
Double-capsule systems		
Capsule based	Polydimethylsiloxane – PDMS	48
Capsule based	Polyurethane – PU	42
Second generation: intrinsic self-healing systems		
Non-covalent systems		
Dipole–dipole interactions	Fluorinated elastomer	49
Hydrogen bonds	Epoxidized natural rubber – ENR	45 and 50–53
Hydrogen bonds	Butadiene rubber – BR	19
Hydrogen bonds	Polydimethylsiloxane – PDMS	54–60
Hydrogen bonds	Polyurea elastomer – PUE	61
Hydrogen bonds	*Eucommia ulmoides* ester elastomer	62
Hydrogen bonds	Lignin-based supramolecular elastomer	63
Hydrogen bonds	Supramolecular elastomer	64–68
Hydrogen bonds	Industrial acrylic elastomer	69
Hydrogen bonds	WSP[a] – photonic elastomer	70
Hydrogen bonds	Poly(AAm/ChCl-*co*-MA/ChCl)[b]	46
Hydrogen bonds	Hybrid polymer networks	71
Hydrogen bonds	Conductive elastomer	72
Ionic interactions	Natural rubber – NR	18 and 73–75
Ionic interactions	Epoxidized natural rubber – ENR	76
Ionic interactions	Brominated natural rubber – BNR	77
Ionic interactions	Brominated butyl rubber – BIIR	78–80
Ionic interactions	Ethylene propylene diene rubber – EPDM	81
Ionic interactions	Polydimethylsiloxane – PDMS	82 and 83
Ionic interactions	Polyampholyte-based elastomer	84
Ionic interactions	NR/BIIR	85
Ionic interactions	SBS/EMAA copolymer[c]	86
Ionic interactions	Poly(isobutylene-*co*-isoprene)	87 and 88
Metal–ligand coordination	Nitrile rubber – NBR	89
Metal–ligand coordination	Polydimethylsiloxane – PDMS	16 and 90–98
Metal–ligand coordination	Polyurethane – PU	99
Metal–ligand coordination	Aminopropyl methyl phenyl polysiloxanes – AMPS	100
Metal–ligand coordination	NBR/poly(vinyl chloride)	101
Host–guest interactions	Alkyl acrylate-based elastomer	102
Shape memory	ENR/poly(latic acid)	103
Covalent systems		
Diels–Alder chemistry	Natural rubber – NR	104
Diels–Alder chemistry	Styrene butadiene rubber – SBR	105
Diels–Alder chemistry	Ethylene propylene diene rubber – EPDM	106
Diels–Alder chemistry	Polydimethylsiloxane – PDMS	107–111
Diels–Alder chemistry	Polyurethane – PU	17 and 112–118
Diels–Alder chemistry	Silicon-based elastomer	119 and 120
Diels–Alder chemistry	Styrene butadiene styrene rubber – SBS	121–123
Diels–Alder chemistry	Polymer/graphene-based material	124
Diels–Alder chemistry	Elastomer coatings	125
Diels–Alder chemistry	Soft robotics – pneumatic actuator elastomers	126–130
Disulfide bonds	Natural rubber – NR	131–133
Disulfide bonds	Styrene butadiene rubber – SBR	20 and 134
Disulfide bonds	Butadiene rubber – BR	135 and 136
Disulfide bonds	Chloroprene rubber – CR	137
Disulfide bonds	Polydimethylsiloxane – PDMS	138 and 139
Disulfide bonds	Polyurethane – PU	140 and 141
Boron-based bonds	Styrene butadiene rubber – SBR	142
Boron-based bonds	Silicon elastomer	143
Boron-based bonds	Poly(*n*-butyl acrylate)	144
Boron-based bonds	Boronic ester-based polymer	145
Imine bonds	NR latex-based elastomer	44
Imine bonds	Polydimethylsiloxane – PDMS	146–148
Transesterification reactions	Epoxidized natural rubber – ENR	149–151
Transesterification reactions	Thiol-epoxy elastomer	152
Alcoxyamine bonds	Poly(butyl methanol methacrylate) – PBMM	153
Oxime-carbamate bonds	Poly(oxime-urethane) – POU	154
Urea bonds	Polyurethane – PU	155

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Table 1 (*continued*)

Healing mechanism	Rubber matrix	Ref.
Third generation: vascular self-healing systems		
Electrospinning (ES) based systems		
Vascular based – coaxial ES	Polydimethylsiloxane – PDMS	39–41, 43 and 156
Channel network systems		
Vascular based – micro	Polydimethylsiloxane – PDMS	157

[a] Water-soluble supramolecular polymer – WSP. [b] Polyacrylic amide (AAm)/choline chloride (ChCl)-*co*-maleic acid(MA)/ChCl – poly(AAm/ChCl-*co*-MA/ChCl). [c] Styrene butadiene styrene/ethylene-methacrylic acid copolymer elastomers – SBS/EMAA copolymer.

For example, the use of extrinsic mechanisms has shown a notable increase in coatings,[39] instrument panels,[42] and sponges,[43] while intrinsic ones have turned out to be more versatile for general purpose elastomers in innovative applications such as nanogenerators,[44] sensors,[45] conductive elastomers,[46] and even tires.[20] Table 1 summarizes some examples of the published work in the last five years in self-healing rubbers based on the first three generations.

Despite all this work, the dichotomy between mechanical properties and self-healing efficiency is still an unresolved challenge. The combination of healing mechanisms as a way of positively balancing these two parameters is the core of the fourth generation.

3. Fourth generation of self-healing rubbers

Since the work of Burattini *et al.*,[158] the literature on combined self-healing mechanisms is steadily growing (Fig. 4), and has focussed on intrinsic self-healing mechanisms, always searching for an optimal combination of dynamic bonds, either covalent (those that require a stimulus for reversibility) or non-covalent (those that are intrinsically reversible due to their lability).[159] Such a strategy has also been considered for different, but not distant, purposes in elastomers, such as recyclability;[160–163] however, this section concentrates on self-healing articles. Table 2 summarizes the publications of the fourth generation of self-healing rubbers, where σ_R refers to the tensile strength prior to healing, η is the healing efficiency, and T is the temperature at which the healing was performed. The discussion of this review is focused on these characteristics.

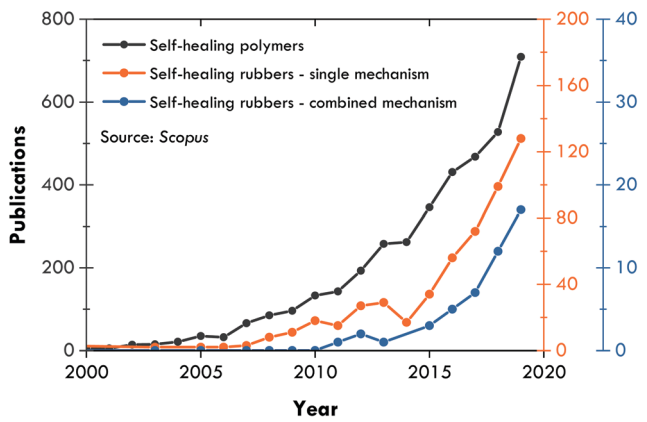


Fig. 4 Evolution in the number of publications on self-healing rubbers.

3.1. Combined non-covalent systems

Intrinsic self-healing mechanisms of non-covalent nature comprise all those weak interactions that can occur between different families of atoms, such as van der Waals interactions, π–π stacking, dipole–dipole interactions, hydrogen bonding, ionic interactions, metal–ligand coordination and host–guest interactions. Some authors[208,209] attribute self-healing capability to the existence of the shape memory effect (SM). It is not clear if SM can be considered as a self-healing mechanism itself. We have included it in this section because, without a doubt, it assists the self-healing process, especially in its initial stages, when the best possible contact between the surfaces is required, contributing to achieving high healing efficiencies. Fig. 5 summarizes all non-covalent interactions and their basic definition.

Non-covalent systems are characterized by having low bonding energy compared to pure covalent systems,[216] so they usually have higher healing efficiencies since this facilitates the restoration of the broken bonds even at room temperature. The non-covalent interaction most used in elastomers is based on hydrogen bonds, which have been combined with other interactions of the same nature to design self-healing materials with diverse performances. Burattini *et al.*[158] reported a combination of healing moieties (π–π stacking and hydrogen bonds) in an elastomeric network based on polyimide and polyurethane with pyrenyl end groups. The π–π stacking was due to the π–electron-deficient diimide groups and the π-electron-rich pyrenyl units. Meanwhile, the formation of hydrogen bonds occurred at the intermolecular level, between the terminal residues of the pyrenyl groups in polyurethane. This material reached a tensile strength of 0.2 MPa, with a healing efficiency higher than 80% with respect to the tensile strength. Following the same combination of intrinsic mechanisms, Zuo *et al.*[164] designed, for the first time, a fluorescent polysiloxane-based elastomer with 60% healing efficiency at room temperature and a tensile strength of 3.28 MPa. In this study, supramolecular interactions were confirmed through molecular simulation. The prepared materials presented interesting potential for bioimaging purposes.

The second most commonly used non-covalent mechanism employs ionic interactions. Xu *et al.*[165] successfully combined

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Table 2 Fourth generation of self-healing rubbers

First healing mechanism	Second healing mechanism	Rubber matrix	σ_R (MPa)	η (%)	T (°C)	Ref.
Combined non-covalent systems						
Hydrogen bonds	π–π stacking	Pyrenyl end-capped polymer	0.20	80	100	158
Hydrogen bonds	π–π stacking	Polysiloxane-based polymer	3.28	60	120	164
Hydrogen bonds	Ionic interactions	Carboxylated SBR – XSBR	1.30	92	RT	165
Hydrogen bonds	Ionic interactions	NR	18.50	79	50	166
Hydrogen bonds	Ionic interactions	Polymer complexes	27.00	92	RT	167
Hydrogen bonds	Ionic interactions	PDMS	0.08	115	80	168
Hydrogen bonds	Ionic interactions	PDMS	—	90	RT	169
Hydrogen bonds	Ionic interactions	BIIR	5.60	39	70	170
Hydrogen bonds	Ionic interactions	Self-healing elastomer	13.50	82	RT	171
Hydrogen bonds	Metal–ligand coordination	IR	21.00	73	80	172
Hydrogen bonds	Metal–ligand coordination	P-Cur[a]	1.80	98	RT	173
Hydrogen bonds	Metal–ligand coordination	PDMS	2.60	90	RT	174
Hydrogen bonds	Metal–ligand coordination	PU	14.80	92	RT	175
Hydrogen bonds	Metal–ligand coordination	Acrylic copolymer	3.85	89	80	176
Hydrogen bonds	Metal–ligand coordination	PDMS copolymer	—	[b]	80	177
Hydrogen bonds	Metal–ligand coordination	PU	7.13	71	RT	178
Hydrogen bonds	Host–guest interactions	Acrylic copolymer	8.60	75	RT	179
Hydrogen bonds	Host–guest interactions	PU	11.07	93	100	180
Hydrogen bonds	van der Waals forces	PU	0.35	100	50	181
Hydrogen bonds	Dative bonds B–O	PBS[c]/PDMS	0.18	86	RT	182
Hydrogen bonds	Dipole–dipole interactions	SBS	3.50	28	80	183
Metal–ligand coordination	π–π stacking	PDMS	0.30	100	RT	184
Ionic interactions	Ionic Interactions	NR	2.60	75	80	185
Combined covalent systems						
Disulfide bonds	Imine bonds	PDMS	0.15	95	RT	186
Disulfide bonds	Imine bonds	PU	34.60	[d]	—	187
Disulfide bonds	Imine bonds	hb-PAM[e]	4.00	91	RT	188
Combined non-covalent/covalent systems						
Hydrogen bonds	Disulfide bonds	Poly(urea-urethane)	0.84	97	RT	189
Hydrogen bonds	Disulfide bonds	PU	9.50	96	Sunlight	190
Hydrogen bonds	Disulfide bonds	Poly(urea-urethane)	7.70	97	60	191
Hydrogen bonds	Disulfide bonds	PU	5.01	100	60	192
Hydrogen bonds	Disulfide bonds	Polyurea	—	[d]	150	193
Hydrogen bonds	Disulfide bonds	ENR	9.30	98	120	194
Hydrogen bonds	Disulfide bonds	PU	25.00	90	100	195
Hydrogen bonds	Disulfide bonds	PU	3.39	95	80	196
Hydrogen bonds	Disulfide bonds	PU	0.34	88	RT	197
Hydrogen bonds	Disulfide bonds	PU	20.00	94	90	198
Hydrogen bonds	Disulfide bonds	PDMS	—	[f]	Various	199
Hydrogen bonds	Diels–Alder chemistry	PDMS/PU	1.10	99	140, 80	200
Hydrogen bonds	Diels–Alder chemistry	PU	37.11	92	120, 60	201
Hydrogen bonds	Boron-based bonds	ENR	1.86	99	RT	202
Hydrogen bonds	Imine bonds	PDMS	0.16	93	RT	203
Hydrogen bonds	Imine bonds	BR	1.52	>100	80	204
Hydrogen bonds	Imine bonds	PDMS	0.40	95	RT	205
Hydrogen bonds	Ditelluride bonds	WSP	19.00	86	RT	206
Hydrogen bonds	Diselenide bonds	WSP	15.34	84	RT	207
Shape memory	Disulfide bonds	PU	23.00	41	80	208
Shape memory	Disulfide bonds	PU	5.40	94	80	209
Shape memory	Disulfide bonds	PU	26.00	98	70	210
Ionic interactions	Diels–Alder chemistry	Acrylic copolymer	13.00	86	60	211
Metal–ligand coordination	Boron-based bonds	ENR	9.00	85	80	212
Metal–ligand coordination	Imine bonds	PDMS	0.05	88	RT	213
Metal–ligand coordination	Diels–Alder chemistry	PU	3.25	100	RT	214
Metal–ligand coordination	Disulfide bonds	Poly(urea-urethane)	9.40	100	80	215

[a] Curcumin polymer block – P-Cur. [b] The self-healing process was only qualitatively evaluated by profilometry. [c] Poly(butylene succinate) – PBS. [d] The self-healing process was evaluated by optical microscopy under different external stimuli. [e] Hyperbranched polyazomethine – hbPAM. [f] The self-healing efficiency was calculated for the elongation at break.

them with hydrogen bonds in a carboxylated styrene-butadiene rubber (XSBR) filled with chitosan nanoparticles. The formation of ionic clusters enabled the configuration of a crosslinked supramolecular network with reversible bonds at room temperature that reached healing efficiencies of up to 92% with a tensile strength of 1.3 MPa. Sattar *et al.*[166] used this same combination for the first time to prepare silica filled (SiO_2) natural rubber (NR) compounds. Their strategy involved the ionization of the natural proteins and lipids of the elastomer to produce the ionic crosslinks. The dynamic supramolecular network was

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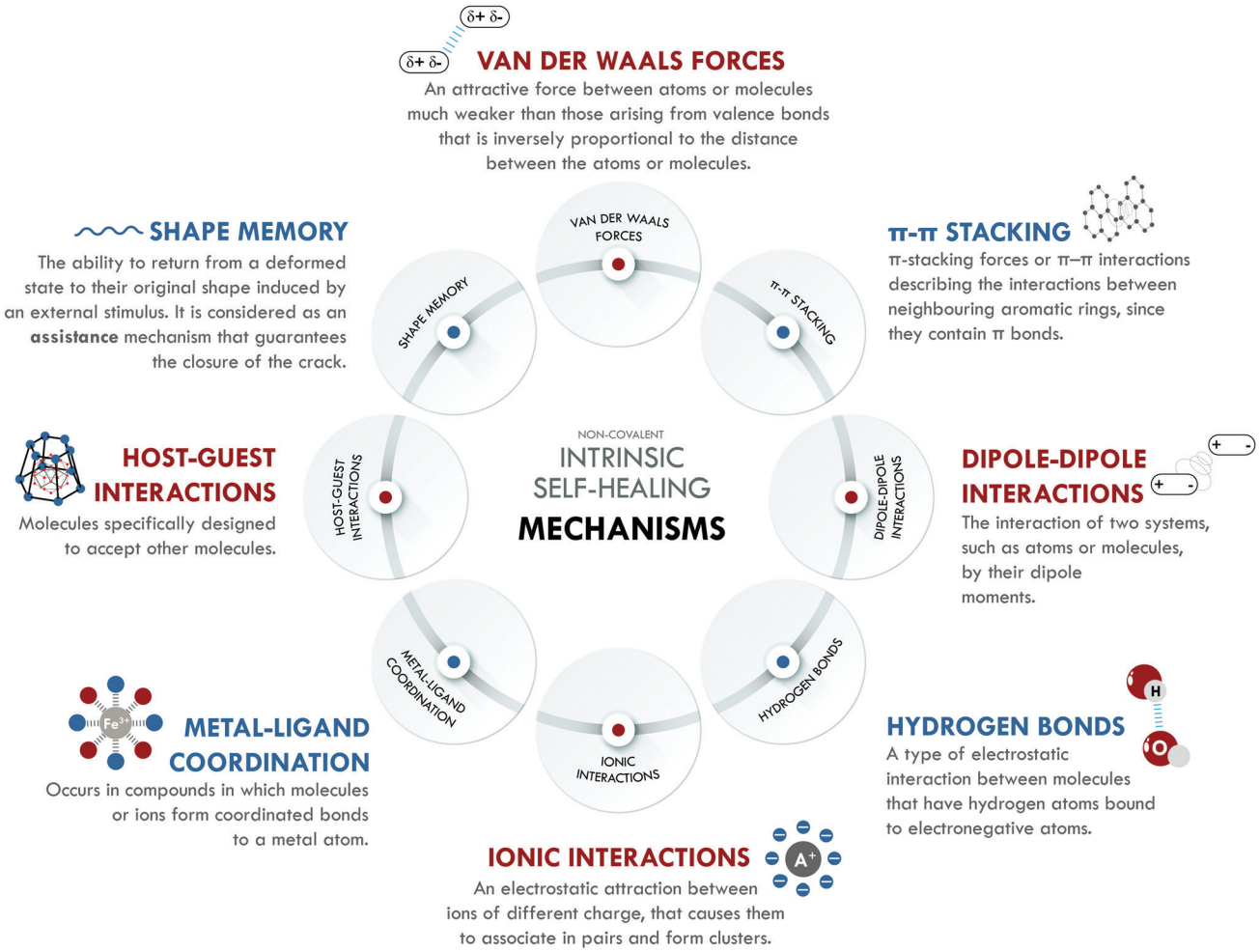


Fig. 5 Non-covalent intrinsic self-healing mechanisms.

formed by adding magnesium sulfate ($MgSO_4$), which provided Mg^{2+} ions, and formed electrostatic pairs with the negative charged lipids, arising from the acidic ionization. This procedure resulted in healing efficiencies of 79% at 50 °C with an excellent tensile strength of 18.5 MPa. The formation of the ionic network was confirmed by Fourier-transform infrared spectroscopy (FTIR) and by comparison with deproteinized NR, in which the repair efficiency was only 52%.

Combined hydrogen bonds and ionic bonds were also considered by Guo *et al.*,[167] giving rise to a non-covalent network with the highest tensile strength and the best resistance/efficiency ratio reported. They prepared ternary polymer complexes of branched poly(ethyleneimine) (bPEI), poly(acrylic acid) (PAA) and poly(ethylene oxide) (PEO) (bPEI/PAA/PEO). These ternary complexes facilitated the formation of electrostatic interactions, between the bPEI and PAA, and of hydrogen bonds, between PAA and PEO (Fig. 6). Thanks to a positive effect between both interactions, an elastomeric material was obtained with a tensile strength of 27.4 MPa and a healing efficiency of 92% at room temperature in a high humidity atmosphere. More recently, the same joint mechanisms were explored in a special purpose rubber, brominated butyl rubber (BIIR), with opposite results. Stein *et al.*[170] designed an elastomeric network of BIIR modified with one uracil and one imidazole moiety. The latter provided the ionic groups that associate in so-called ionic clusters, while the former, with a bifunctional structure containing two diamidopyridyl moieties, was responsible for the formation of hydrogen bonds. The incorporation of hydrogen bonds worsened the healing efficiency achieved with only ionic interactions, since they decreased the tensile strength to 5.7 MPa and the healing efficiency to 39% from a tensile strength of 10.7 MPa and a healing efficiency of 74% at 70 °C.

The metal–ligand coordination bond is another non-covalent option widely combined with hydrogen bonds. One of the most relevant studies was performed by Liu *et al.*[172] They reported poly(isoprene) (IR) with unprecedented mechanical properties, 21 MPa, and good healing efficiency, 72% at 80 °C. These results were attributed to three factors: first, to the dynamic nature of both mechanisms; second, to the mobility of the IR chains, which facilitated self-healing at the selected temperature and time; and third, to a positive effect thanks to the combined mechanisms (Fig. 7).

These dual mechanisms were also reported in polyurethane (PU). PU and its variants are the most studied materials from

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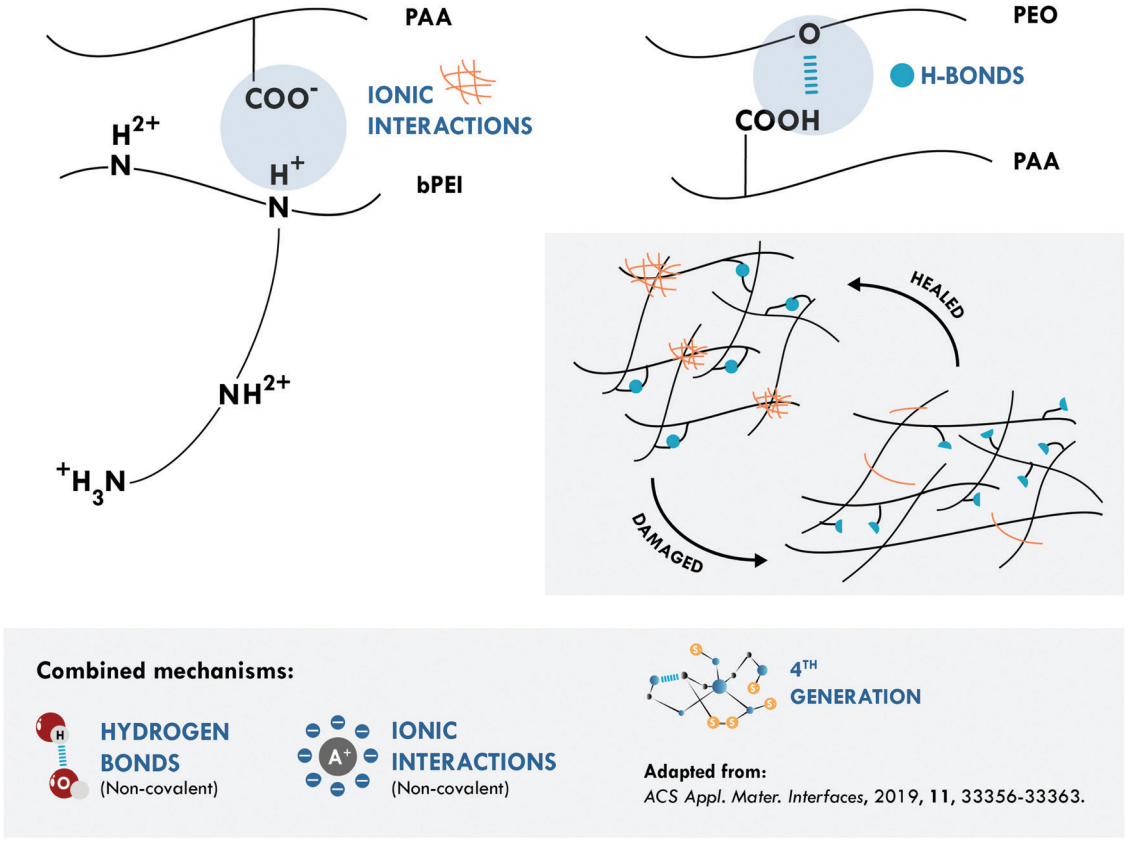


Fig. 6 Combination between hydrogen bonds and ionic interactions in bPEI/PAA/PEO.[167] ©2019. Adapted with permission from the American Chemical Society.

the point of view of intrinsic mechanisms, so it is not surprising that it is one of the first materials in which a network with three types of dynamic bonds has been reported: one covalent and two non-covalent, the latter being responsible for self-healing at room temperature. Zhang *et al.*[175] prepared a Cu(II)-dimethylglyoxime-urethane-complex-based polyurethane elastomer. Here, the metal–ligand coordination was given by the copper ions and the hydrogen bonds were between amino groups and esters of the main chain. A tensile strength of 14.8 MPa and an efficiency of 92% were achieved, with potential applications in wires.

In PU, two other mechanisms together with hydrogen bonds have also been reported: host–guest interactions and van der Waals forces, with very different results. Xiao *et al.*[180] designed a network based on the combination of host–guest interactions and multiple hydrogen bonds in waterborne PU (WBPU), an environmentally friendly option that decreases the effect of the release of volatile organic components into the atmosphere. They reported a tensile strength of 11.07 MPa and efficiency of 93%, close to the work described above with metal–ligand coordination, but at a temperature of 100 °C. On the other hand, Chen *et al.*[181] combined hydrogen bonds with van der Waals forces in poly(urethane urea) (PUU) in which a branched poly(propylene carbonate) (PPC) diol was used as the soft segment, obtaining a tensile strength of 0.35 MPa, with 100% healing efficiency at 50 °C. The origin of these results was ascribed to the bond energy of the van der Waals force, which is considerably low compared to other non-covalent mechanisms.

In summary, there is no clear tendency in the effect of combined non-covalent systems on healing and mechanical performance. Both properties seem to be strongly influenced by the energy of the selected bonds, the chemical structure of the matrix and the effect generated when combining different mechanisms. Moreover, not all the combinations are *a priori* useful; the positive combination effect clearly depends on the matrix and the competition between the interactions.

3.2. Combined covalent systems

Intrinsic covalent mechanisms are related to all those chemical bonds that can be formed between different atoms and can be dynamic under an external stimulus. Fig. 8 schematically summarizes some of these bonds and their basic definition. Clear examples are disulfides, which can undergo metathesis reactions, or Diels–Alder chemistry, where Diels–Alder and retro-Diels–Alder reactions occur at different temperatures. These bonds are of higher energy compared to non-covalent bonds,[216] so their contribution is usually associated with the mechanical performance of the material. However, their reversibility is a key factor in achieving high healing efficiencies.

The combination of covalent systems has been mildly reported with only two articles in recent years, using the same dual system with disulfide and imine bonds. Lv *et al.*[186] applied

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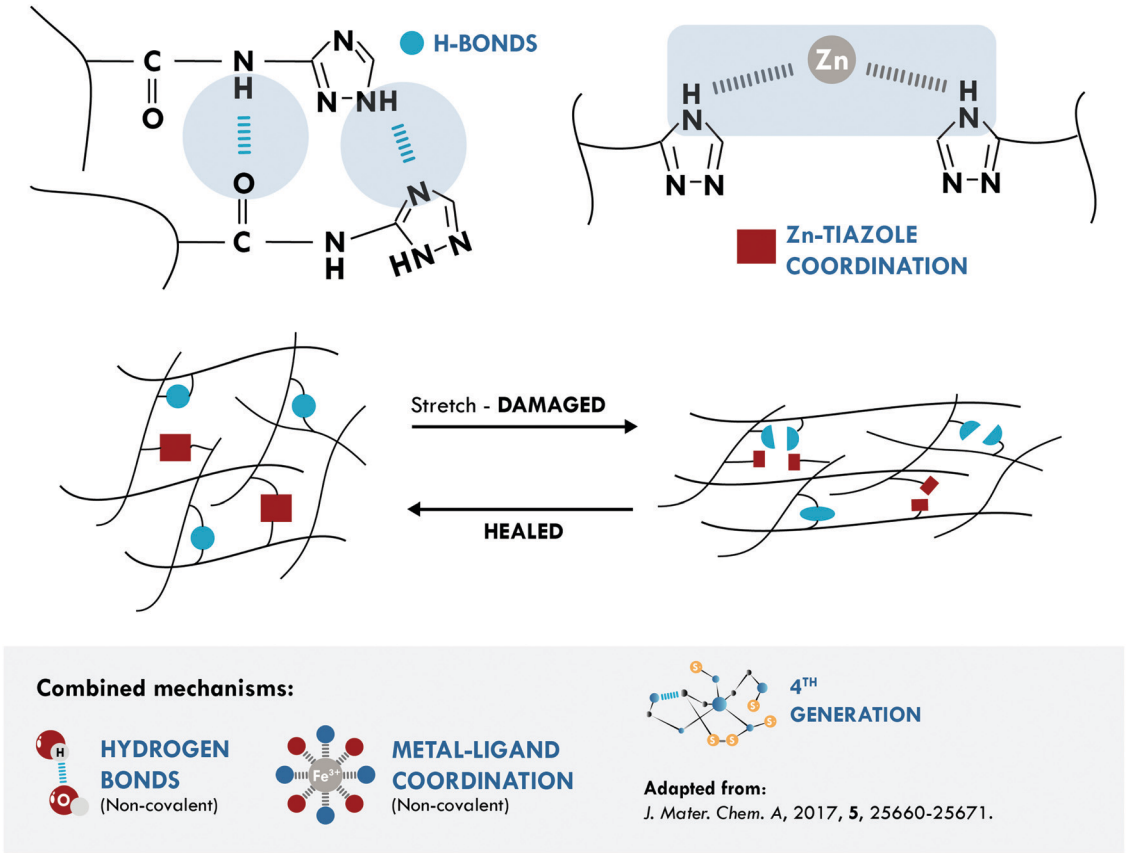


Fig. 7 Combination between hydrogen bonds and metal–ligand coordination in IR.[172] ©2017. Adapted with permission from the Royal Society of Chemistry.

aromatic disulfides, whose metathesis can occur at room temperature, contrary to aliphatic disulfides, which require an external stimulus. They obtained PDMS that could be repaired in just 4 h; however, its mechanical properties, typical of siloxane-based systems, were merely 0.15 MPa. Self-healing is mainly ascribed to the disulfide bond, which acted as a sacrificial bond, while the imine bond would mostly act as semi-permanent crosslink points for the elasticity and maintaining the original shape. Although the mechanical strength is low, this work serves as a proof of concept for certain applications (*e.g.* adhesives), in which high mechanical performance is not necessary. Lee *et al.*[187] used the same approach in PU, studying the metathesis of both dynamic bonds (Fig. 9). The elastomer preparation was carried out in two stages; first, they prepared a Schiff base from biomaterials such as cystine and vanillin, responsible for providing disulfide and imine bonds. Subsequently, the base was mixed with 1,4-butanediol (to ensure miscibility) and added to the precursors of PU (isophorone diisocyanate, IPDI, and poly(propylene glycol)-based thiol, PPG). They monitored the healing process through optical microscopy and reported complete healing of cracks in 120 min with the use of heat (65 °C) and UV irradiation. The material also exhibited a recyclability efficiency of 97% but the healing efficiency was not reported as a measure of the retention of tensile properties.

The limited literature of combined covalent-based mechanisms is a clear indication that these dual systems are not the preferred option in elastomeric matrices, nor in any other type of polymer. We can speculate and attribute such low development to two facts. On one side, the imperative need for an external stimulus (in most cases) for assuring the reversibility of the covalent bonds. On the other side, the high bond energy that limits molecular dynamics and, thus, partially restricts reversibility and healing.

3.3. Combined non-covalent/covalent systems

The combination of covalent and non-covalent bonds is one of the most explored systems among the fourth generation, obtaining materials with good mechanical performance and high healing efficiencies. For these dual systems, we can observe a prevalence of PU as a material, and hydrogen bonds/disulfide bonds as a designated combination. Rekondo *et al.*[189] were the first to apply this strategy and used aromatic disulfide metathesis to design a self-healing network of PUU. They reached 97% healing efficiency thanks to the aromatic disulfides, which are in constant exchange at room temperature, and to the urea groups, which can form quadruple hydrogen bonds. However, the mechanical properties were limited for high-performance applications. Xu *et al.*[190] solved this limitation by developing an interesting system where healing was promoted by sunlight, with potential application in the manufacture of smart photosensitive

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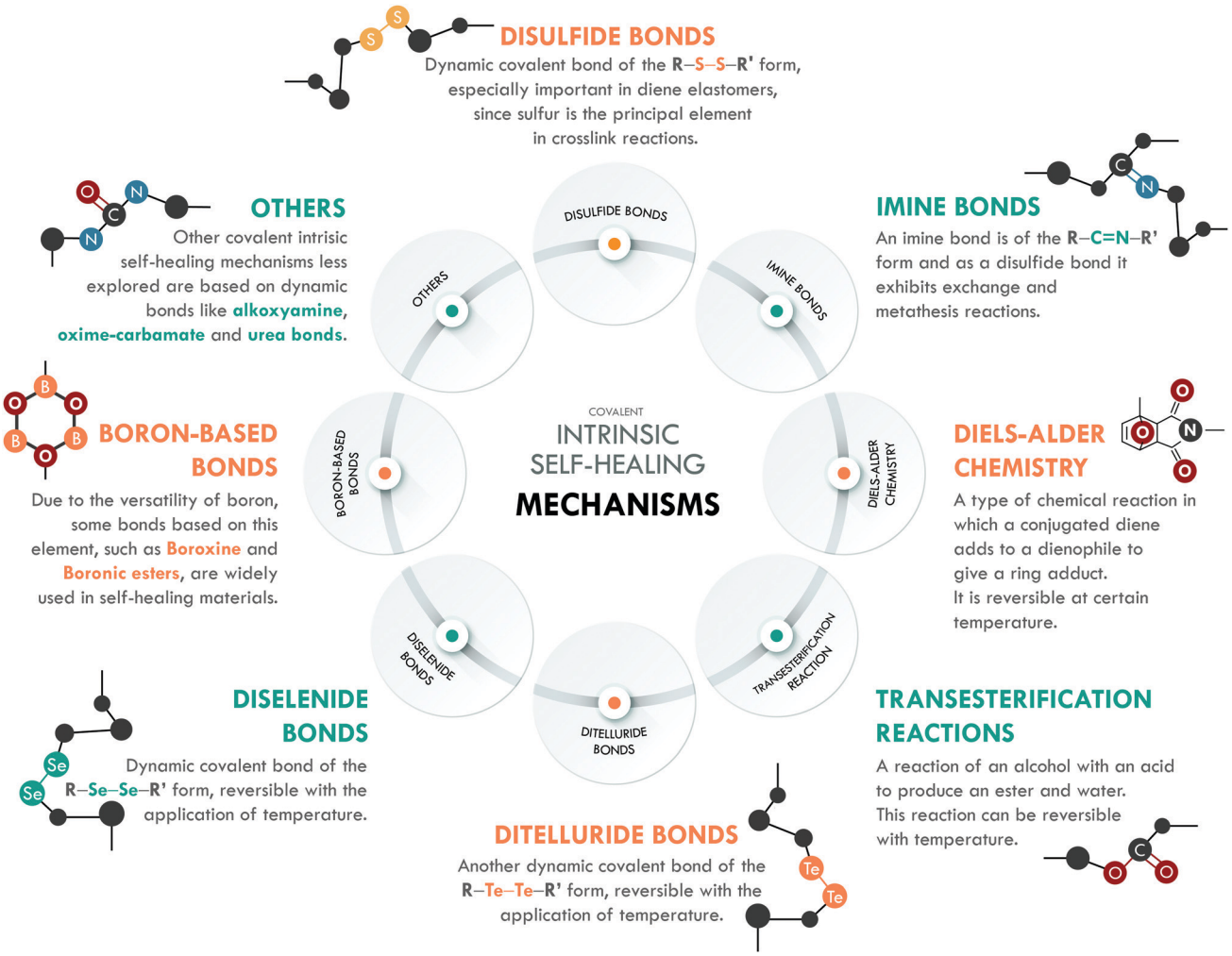


Fig. 8 Covalent intrinsic self-healing mechanisms.

polymers with high tensile strength. Although pure UV light was known to generate disulfide exchange, it was unknown if the low UV content in sunlight (between 3% and 5%) would be able to generate the same effect. They demonstrated, by mass spectroscopy and liquid chromatography (HPLC), that the UV component of sunlight was capable of generating a photochemical exchange reaction of disulfides in small molecules. Here, this exchange was favored by the formation of hydrogen bonds between amino groups adjacent to the disulfide groups of the main chain. They reported healing efficiencies of up to 96% with a tensile strength of 9.5 MPa. The development of PU with enough mechanical robustness continued to grow. Hu *et al.*[195] introduced 2-ureido-4[1*H*]-pyrimidione (UPy)-functionalized side groups in the hard segment of thermoplastic polyurethane (TPU). The introduction of these functional groups formed quadruple hydrogen bonds and generated a supramolecular network that increased the crosslink density of the hard domains. The result of this combination was a material with a tensile strength of 25 MPa and a healing efficiency of 90% at a temperature of 100 °C.

All these advances in PU have enabled its use in innovative applications, such as 3D printing, which seems quite distant for other elastomeric materials. Li *et al.*[196] reported one of the first examples of self-healing PU manufactured using digital light 3D printing (DLP), with potential application in the manufacture of sensors and flexible electronics. Their elastomer reached a tensile strength of 3.39 MPa with a healing efficiency of 95% after 12 h at 80 °C. At the same time, they proved that the material supports multiple healing cycles. The healing protocol was applied directly on a piece produced with a honeycomb structure, which corroborated the applicability and success of the designed system, being able to bend freely and withstand high deformation without failing.

More recently, Liu *et al.*[198] continued exploring different options on PU under this combination of healing mechanisms. They incorporated poly(vinyl alcohol)-*graft*-(ε-caprolactone) (PVA-PCL) into isocyanate terminated PU with disulfide bonds. The incorporation of PVA-PCL increased the formation of hydrogen bonds, which acted as physical crosslink points. They reported an improved tensile strength, of 20 MPa, and a positive effect of the hydrogen and disulfide bonds on the healing efficiency, reaching 94% at 90 °C. All the work done with PU highlights the good balance that can be reached

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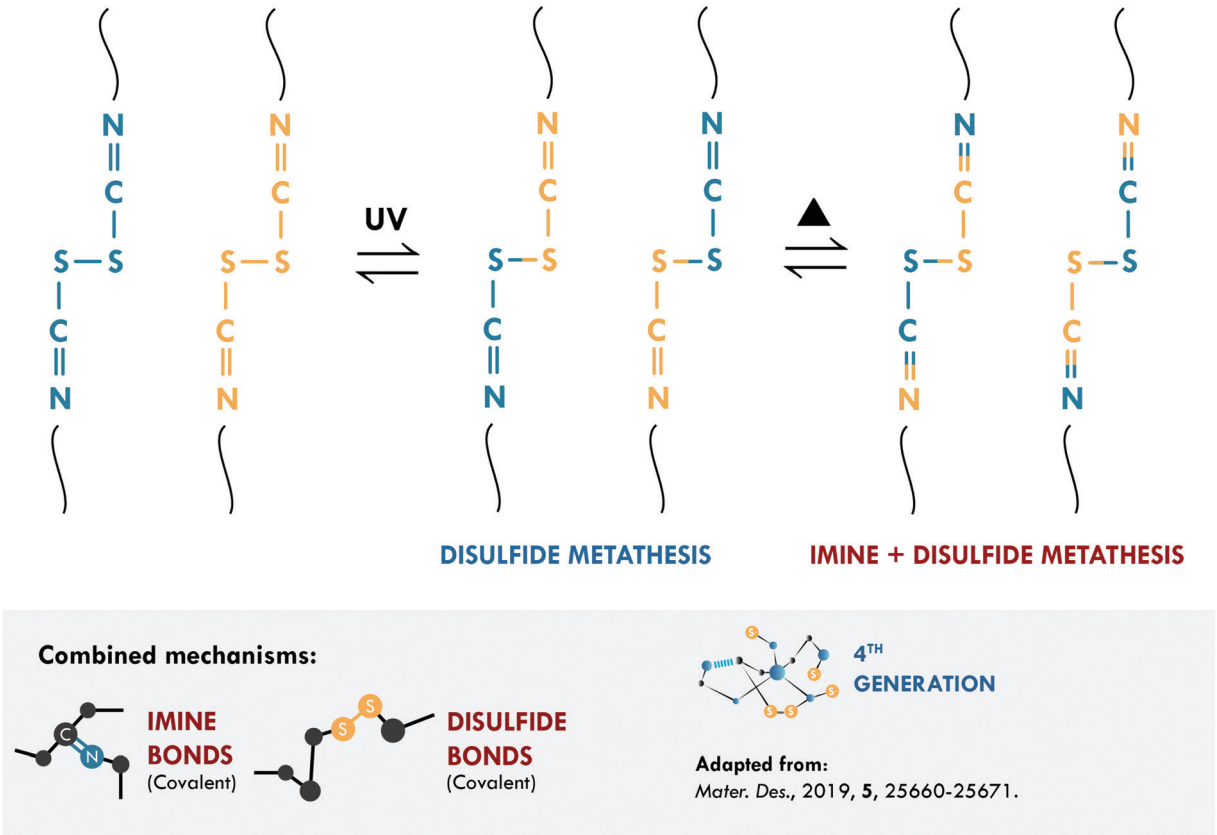


Fig. 9 Imine and disulfide metathesis in PU.[187] ©2019. Adapted with permission from Elsevier.

between mechanical performance and healing capability. However, in most cases the healing procedure applies high temperatures (>60 °C). Thus, room temperature self-healing is still a milestone to overcome in the development of high performance PU.

The second most studied system is a general purpose elastomer, in particular epoxidized natural rubber (ENR). Cheng *et al.*[194] considered two known principles: the vulcanization of the double bond of the main chain of *cis*-1,4 poly(isoprene) and the opening reaction of the epoxy ring. They performed a typical vulcanization reaction, to create multiple sulfur bonds in the main chain, together with the addition of aromatic disulfides, to couple to the radical generated during the ring-opening reaction (Fig. 10). Simultaneously, the ring-opening reaction generated multiple hydroxyl groups forming hydrogen bonds that assist the self-healing process. This combination resulted in a tensile strength of 9.30 MPa and 98% healing efficiency at 120 °C, compared to only 22% of an equivalent disulfide-free sample.

The metathesis reaction can also occur in other bonds formed by chalcogens (elements of group 16 of the periodic table, like sulfur). Fan *et al.* studied the exchange of ditelluride[206] and diselenide.[207] In both cases, water-dispersed supramolecular polymers (WSP) were prepared with aliphatic molecules with exchangeable bonds and pendant UPy groups. The latter, as shown in other studies, are capable of forming quadruple hydrogen bonds, with an important contribution to the mechanical properties and healing efficiency. This system resembled that of hydrogen and disulfide bonds, but with an interesting contribution: the exchange reaction occurred thanks to visible light. Both studies reported tensile strengths between 15 and 19 MPa with healing efficiencies around 85% at room temperature.

In 1950, Otto Diels and Kurt Alder received the Nobel Prize in Chemistry for their work on diene reactions.[217] More than half a century later, Diels–Alder (DA) chemistry has widely been used in the design of dynamic networks to overcome the irreversibility of most crosslink reactions.[218] Hence, it is not surprising that this chemistry represents one of the main mechanisms used in the design of self-healing materials. The DA reaction has been combined with hydrogen bonds for the design of two self-healing materials. Zhao *et al.*[200] applied it in poly(siloxane-urethane). In one case, they used isocyanate terminated PDMS combined with a DA diol (PDMS-DA-PU), while in a second case, they employed mixtures of the isocyanate terminated PDMS with a PCL diol and a DA diol (PDMS/PCL-DA-PU) (Fig. 11). Following the evolution of a crack, they concluded that the PCL system hindered the repair; however, it increased the stiffness of the soft segments. Meanwhile, the sample without PCL allowed total healing of the crack, recovering 96% of their initial tensile stress (1.1 MPa) compared to 83% efficiency of the PDMS/PCL-DA-PU samples (tensile strength of 3.25 MPa). The low mobility of PCL hindered the approach of the furan and maleimide groups to reform the DA adduct, but the hydrogen

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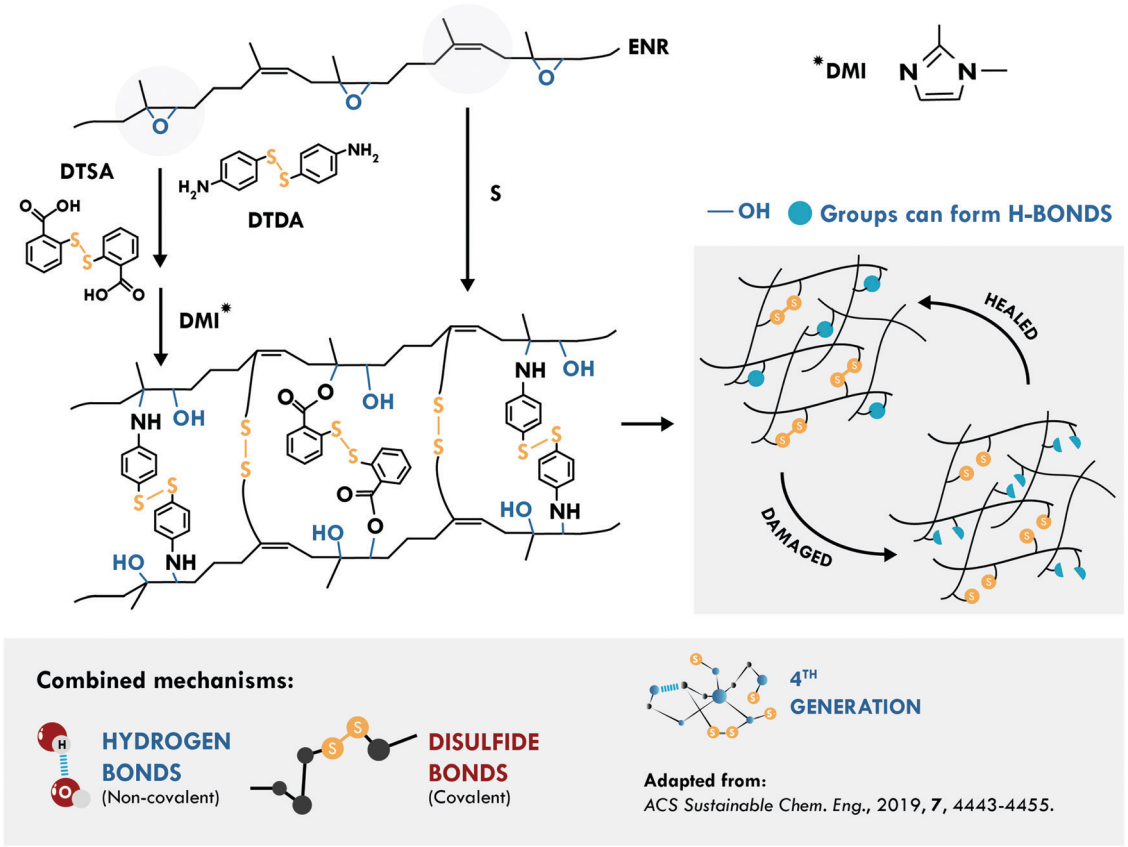


Fig. 10 Combination between disulfide and hydrogen bonds in ENR.[194] ©2019. Adapted with permission from the American Chemical Society.

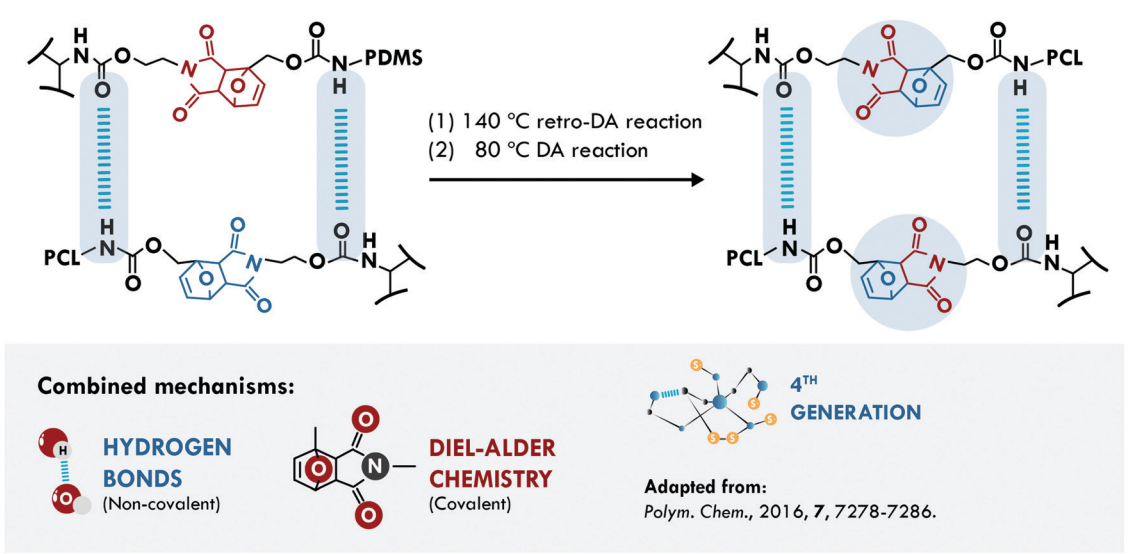


Fig. 11 Combination between DA chemistry and hydrogen bonds in PDMS-DA-PU.[200] ©2016. Adapted with permission from the Royal Society of Chemistry.

bonds could compensate and maintain a good healing efficiency with a considerable increase in the mechanical properties. Besides, the biocompatibility of the material was proved by cytotoxicity evaluation and animal wound healing experiments, making it a good candidate for applications of smart self-healing artificial skin.

Yang *et al.*[201] also explored the combination of DA chemistry with hydrogen bonds. They prepared a reversible dual network

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by combining tri(2-furyl) phosphoramide (TFP) with a maleimide end-capped PU elastomer (MPU). With a precise stoichiometric relationship, these systems enabled the crosslinking of PU with TFP *via* DA chemistry. The healing mechanism comprised three stages: the rupture of the DA adduct through the rDA reaction at high temperature; then, the diffusion of the TFP and PU chains along the damaged surface; and, finally, the reformation of the DA bonds and hydrogen bonds between the hard segments of MPU and between MPU and TFP at 60 °C. This results in a self-healing elastomer with unprecedented mechanical properties (37.11 MPa) and a healing efficiency of 92%.

Another dynamic covalent link combined with hydrogen bonds is the boroxine bond. Guo *et al.*[202] modified an ENR matrix with 3-aminophenylboronic acid (APB). This introduced a functionality with pendant secondary amines and boron-hydroxyl groups thanks to the ring-opening reaction of the epoxy ring. The formation of boroxine bonds between the boron and hydroxyl groups, through the dehydration reaction, and the formation of hydrogen bonds between the secondary amines, gave the material a reversible character. This rubber exhibited a healing efficiency of 91% at room temperature (based on toughness) and, even after 10 healing cycles, continued to reach high efficiencies (71%), this reduction being attributed to the irreversible rupture of covalent bonds after each test. This material not only exhibited great self-healing performance, but also generated a fluorescent response under deformation and showed sensitivity to external stimuli such as strain and humidity. They also tested the material in the throat of a volunteer and observed the strain-dependent sensing of different sounds and expressions, proving its potential application to identify human actions.

The imine bond has also been used repeatedly for the development of dual elastomeric networks with hydrogen bonds, mainly in PDMS. Yan *et al.*[203] developed a network with high elongation and healing efficiency, 93% at room temperature, capable of being repaired at low temperatures, such as −20 °C. This study is one of the few cases that considered freezing temperatures in self-healing. Meanwhile Yang *et al.*[205] reported the creation of a PDMS sensor with a healing efficiency of more than 70% at room temperature and in different media such as air, water and artificial sweat. These sensors were capable of detecting human movements. Hence, the use of self-healing silicones as soft electronics and sensors and in other applications that do not require high mechanical properties is a very promising field.

All the studies described above involved the use of hydrogen bonds as the non-covalent contribution; however, they are not the only system used. Shape memory has also been shown to facilitate self-healing. Xu *et al.*[208] and Chang *et al.*[209] used it in combination with disulfide bonds to develop PU. In both cases, shape memory eliminated the gap between the two areas of the damaged surface, guaranteeing good contact and ensuring high healing efficiency. Other non-covalent systems were used as ionic interactions combined with DA chemistry in an acrylic copolymer.[211] In the last year, metal–ligand coordination has also been combined with different covalent systems and matrices such as ENR (with boron-based bonds[212]), PDMS (with imine bonds[213]), PU (with DA chemistry[214]) and PUU (with disulfide bonds[215]), but with very different results that limit establishing yet a clear trend for these combinations.

4. Outlook and perspectives

This minireview has defined what we dubbed "generations of self-healing materials", providing a short overview of their evolution and focusing on the latest advances in the field. Thus, it has been shown that over the last twenty years self-healing materials have evolved from simple systems that only supported a single healing cycle to systems capable of: supporting multiple cycles; being activated through sunlight, UV light or temperature; being repaired in different media than air; or being healed at room temperature within a few minutes. Remarkably, all these systems can be processed using conventional techniques and with more innovative methods such as 3D printing.

These improvements have mostly arisen over a short period of time with the development of the fourth generation of self-healing materials. These systems have evolved from the knowledge gained over previous generations, which are still under study. They are based on the combination of different healing mechanisms and could represent the path for making the definitive jump to commercial applications. One plausible explanation for the success of this approach is that covalent and non-covalent mechanisms complement each other: dynamic covalent bonds bring considerable improvements in mechanical properties and partially contribute to the self-healing capability, while non-covalent interactions act as the main sacrificial bonds providing substantial progress to the healing efficiency. In the near future, combinations will surely not be limited to two mechanisms, but it is likely that multiple combinations will be explored (three or more), seeking further positive effects.[219] The use of fillers or other additives as carriers of additional healing mechanisms could also be a promising option,[220,221] while molecular dynamics studies seem mandatory for simulating interactions between combined mechanisms and for predicting their effect on the self-healing capability.[181,222–224]

Fig. 12 shows the evolution between generations with a general and not-material specific trend towards self-healing elastomers with excellent mechanical performance (tensile strength higher than 10 MPa) and healing efficiencies higher than 80% in the absence of external stimuli. Special attention should be paid to general-purpose elastomers, such as natural rubber, or styrene-butadiene rubber, since most of the developments reported in the fourth generation concern rubbers for specific applications, such as polyurethanes or silicones. However, and despite great efforts, self-healing rubbers, and self-healing materials in general, continue to present serious limitations that should be resolved in the near future.

One of the main limitations is the absence of a unified protocol that permits quantifying the healing capability and, thus, establishing comparisons between systems or families of materials. This limitation becomes more important when trying to compare

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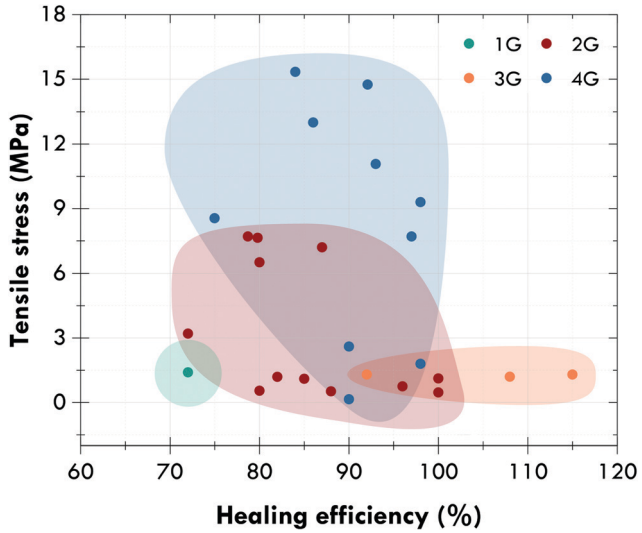


Fig. 12 Ashby diagram of the four generations of self-healing elastomers.

generations, where measuring protocols are different. As an illustrative example, healing within the first generation (encapsulated extrinsic systems) is usually measured through fracture toughness (K_{IC}) tests, while in the second and fourth (essentially intrinsic systems), healing is predominantly measured by tensile tests. This difference in criteria, even within the same generation, makes it difficult to establish fair comparisons between materials. The second limitation is related to the type of damage; it is urgent to think about their real scalability. Evaluating the tensile behavior and fracture toughness or monitoring superficial cracks is insufficient to ensure the behavior in service of self-healing materials. This scalability also refers to the evaluation of self-healing not only from the point of view of structural properties, but also regarding key limitations and properties defined for specific applications. Fatigue resistance, thermal and electrical conductivity, aging and the dichotomy itself between the dynamic nature of the reversible bonds and the stability of the materials (for example, chemical and thermal), among others, should be considered as soon as possible, to make the practical applicability of these strategies a reality.

Finally, according to World Bank estimates, global waste will grow 70% by 2050, increasing from 2.1 billion tons registered in 2016 to 3.4 billion tons.[225] More than 12% of this waste will be of polymeric origin. This review has presented the latest advances related to an effective alternative for reducing waste, extending the lifetime, and contributing to the evolution of smart materials. We hope that it will serve as an inspiration to researchers around the world to join efforts and make progress towards a more sustainable society. The world needs it.

List of abbreviations

AAm	Acrylic amide
AMPS	Aminopropyl methyl phenyl polysiloxanes
APB	3-Aminophenylboronic acid
BIIR	Brominated butyl rubber
BNR	Brominated natural rubber
bPEI	Branched poly(ethyleneimine)
BR	Butadiene rubber
ChCl	Choline chloride
CR	Chloroprene rubber
DA	Diels–Alder
DCPD	Dicyclopentadiene
DTDA	4,4-Dithiodianiline
DTSA	2,2-Dithiodibenzoic acid
EMAA	Ethylene-methacrylic acid
ENR	Epoxidized natural rubber
EPDM	Ethylene propylene diene rubber
ES	Electrospinning
FTIR	Fourier-transform infrared spectroscopy
hbPAM	Hyperbranched polyazomethine
HPLC	High-performance liquid chromatography
HTPB	Hydroxy-terminated polybutadiene
IPDI	Isophorone diisocyanate
IR	Poly(isoprene)
IIR	Butyl rubber
MA	Maleic acid
MPU	Maleimide end-capped polyurethane elastomer
NBR	Nitrile rubber
NR	Natural rubber
PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile
PBMM	Poly(butyl methanol methacrylate)
PBS	Poly(butylene succinate)
PCL	ε-Caprolactone
P-Cur	Curcumin polymer block
PDMS	Poly(dimethylsiloxane)
PEO	Poly(ethylene oxide)
PMMA	Poly(methyl methacrylate)
POU	Poly(oxime-urethane)
PPC	Poly(propylene carbonate)
PPG	Poly(propylene glycol)-based thiol
PS	Polystyrene
PU	Polyurethane
PUE	Polyurea elastomer
PUU	Poly(urea-urethane)
PVA	Poly(vinyl alcohol)
PVAc	Poly(vinyl acetate)
SBR	Styrene butadiene rubber
SBS	Styrene butadiene styrene rubber
SEM	Scanning electron microscopy
SM	Shape memory
TFP	Tri(2-furyl) phosphoramide
TPU	Thermoplastic polyurethane
UPy	2-Ureido-4[1*H*]-pyrimidione
UV	Ultraviolet
WBPU	Waterborne polyurethane
WSP	Water-soluble supramolecular polymer
XSBR	Carboxylated styrene butadiene rubber

Conflicts of interest

There are no conflicts to declare.

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