Self-Healing Polymers: From Biological Systems to Highly Functional Polymers

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Contents

Abstract

The self-healing phenomenon is well-known from nature. Since the last 15 years, several approaches were developed in order to transfer this behavior into synthetic materials and to enable the preparation of multifunctional polymers. The following chapter summarizes the different polymers and their corresponding healing mechanism and provides an overview of the current state of the art. Additionally, the healing of functions as well as the characterization of the self-healing behavior is provided. Furthermore, a short comparison between polymers and other material classes is presented. Finally, the first commercial available systems are summarized showing the way for future developments in this area.

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Abbreviations

Cp	Cyclopentadiene
DA	Diels-Alder
DCPD	Dicyclopentadiene
EHM	Eisenberg-Hird-Moore model
ENB	5-Ethylidene-2-norbornene
hDA	Hetero Diels-Alder
IR	Infrared spectroscopy
Mebip	2,6-*Bis*(methylbenzimidazolyl)pyridine
NMR	Nuclear magnetic resonance spectroscopy
PEG	Poly(ethylene glycol)
PIB	Poly(isobutylene)
PPG	Poly(propylene glycol)
RAFT	Reversible addition-fragmentation chain transfer
ROMP	Ring-opening metathesis polymerization
SAXS	Small angle X-ray scattering
TDCB	Tapered double cantilever beam
TEMPO	2,2,6,6-Tetramethylpiperidinyl-1-oxy

1 From Nature to Synthetic Materials

In the early human history, the usage of materials was limited to natural materials (e.g., stone, wood, fur, etc.). Later on, humans became capable of fabricating synthetic materials resulting in a large variety of different materials utilized nowadays. In recent years, the design of novel materials is increasingly based on natural archetypes. Despite our capability to synthesize and prepare almost every imaginable material, some natural examples are still outstanding and unrivalled, to name just a few examples, gecko feet, which are capable to “stick” to almost every material allowing the reptile to run on the ceiling, [1] spider silk outperforming almost every synthetic fiber [2], as well as natural composites (e.g., nacre) featuring mechanical properties far beyond those properties from the single components [3]. Consequently, a biomimetic material research is ongoing providing a novel blueprint for material design. Important lessons from nature are the hierarchical structuring of materials (e.g., up to seven levels in bone) as well as their ability for repair – some materials are even continuously remodeled (e.g., bone) [4, 5]. In particular, the ability of nature to repair damage and to restore the original properties as well as functions is intriguing. This feature is generally not found in common synthetic materials: Damage will sooner or later lead to the complete failure of the material. In nature, a cut in the finger will be healed; typically 70% of the maximum load and maximum stiffness will be restored within several days [6]. Even a more severe damage/injury can be healed: a broken bone [7]. Depending on the fracture, even full recovery is achieved within a few weeks [8]. Additionally, self-healing is also present at the

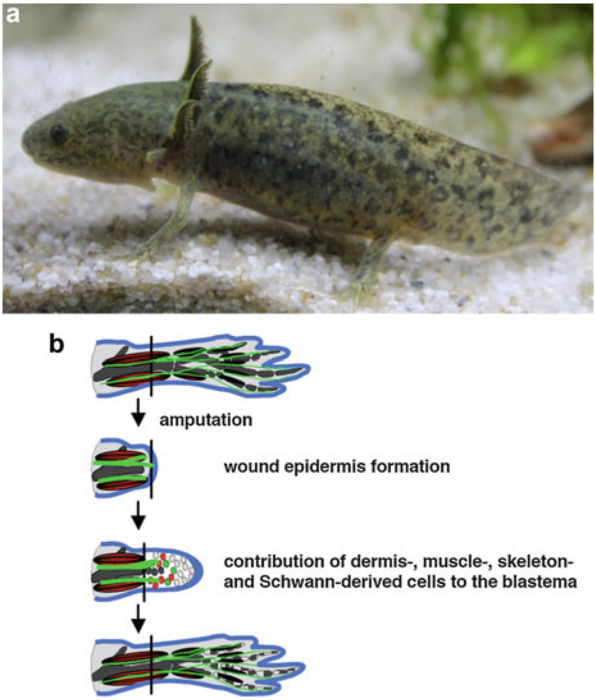

Fig. 1 (**a**) Photograph of an axolotl and (**b**) schematic representation of the regeneration of a limb. (Reprinted with permission from Ref. [11])

molecular level, for instance, the healing of DNA [9] and the repair cycle of the photosystem II [10]. A masterly performance is the regeneration of whole limbs by the axolotl (*Ambystoma mexicanum*) (see Fig. 1) [11, 12].

These examples provide the basis for the bioinspired design of self-healing materials [13–15]. Important lessons from nature include bleeding (i.e., transport of material to the damage location, mobility for closure of the damage), vascular networks corresponding to our vascular blood system providing transport also after damage, hierarchical structures enabling outstanding material properties, and reversibility (e.g., the constant remodeling of bones or the reversible interaction of molecular building blocks).

2 General Mechanism and Classification

The biological systems described above are very complex, and nature is the expert for the design of materials with self-healing properties. However, the question of what we can learn from nature arises at this point. In general, the strategy of self-healing can partly be adapted from nature [16]. An injury at our finger will subsequently lead to bleeding, which represents the generation of a mobile phase resulting in a filling of the wound. However, the blood would stream out and no real closure, and, thus, self-healing could take place without an immobilization of the mobile

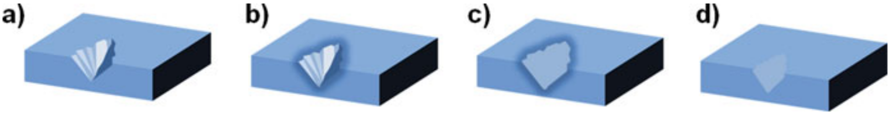

Fig. 2 Schematic representation of the healing of mechanical damage: A scratch occurs and results in a damage of the material (**a**). The generation of a mobile phase (**b**) leads to a closure of the crack (**c**) and to a regeneration of the original mechanical properties (**d**). (Adapted with permission from Ref. [17])

phase, which is in that case the coagulation. This basic mechanism results in a crack closure and partial restoration of the function. However, nature goes further and substitutes the healing materials (the coagulated blood) with the original material (the skin). This general healing mechanism can also be found in synthetic polymeric materials and consists of the crack propagation, the generation of a mobile phase, and the immobilization (see Fig. 2) [17].

Nevertheless, this general healing mechanism can be achieved in many different ways. Since polymers and polymer composites are easy to functionalize, many different healing strategies were already developed. These approaches can be divided by two different classifications [17]. The first differentiation divides the strategies according to the requirement of an external stimulus. Thus, on the one hand autonomous healing takes place without the utilization of an external trigger like light or heat. Nonautonomous self-healing materials must be activated in order to obtain the mobile phase, which can be obtained in the simplest case by heating to a certain temperature (i.e., the healing temperature). This classification is quite controversially discussed in literature since the final application and the conditions in which the material is used define the final influences [18]. Thus, a material can be an autonomous self-healing material in temperate climate zones, whereas it will be nonautonomous in the Arctic Circle.

A more useful classification divides the self-healing materials into extrinsic and intrinsic [17]. Extrinsic healing requires the presence of an additional self-healing agent. This healing agent is embedded into the polymer matrix (by encapsulation into capsules or the utilization of vascular networks) and is released when the scratch occurs resulting in the formation of the mobile phase [19, 20]. Intrinsic self-healing materials, on the other hand, can heal mechanical damage by itself without any further additives/embedded healing agents. This behavior is realized by the utilization of a specific polymer design and by the incorporation of functional groups, which can provide a certain kind of reversibility in order to later activate the formation of the mobile phase [21]. A general overview of the already used polymeric self-healing materials and the resulting properties as well as the corresponding healing conditions is provided in Table 1. Furthermore, selected examples of intrinsic self-healing polymers are depicted in Fig. 3. Additionally, it can be mentioned that the mechanical properties for extrinsic self-healing systems strongly depend on the matrix. In the case of intrinsic systems, the molecular design and the functional moieties are crucial for the mechanical properties.

Table 1 Summary of selected self-healing polymers and their properties with a comparison to biological systems

Classification	Self-healing mechanism	Chemical compounds	Polymer class	Mechanical data (E-modulus,etc.)	Healing conditions and efficiencies	References
Extrinsic self-healing	The healing is based on the release of healing agent when a crack occurs. The healing agent is encapsulated into capsules or vascular networks	DCPD/ENB[a]	Epoxy	Fracture load up to 200 N	Bulk healing; autonomous healing at RT, 100% efficiency	[22]
			Polystyrene-*block*-polybutadiene-*block*-polystyrene	Tensile strength 4 MPa	Bulk healing; healing at RT for 24 h, 80% efficiency	[23]
		Siloxanes[a]	Epoxy	No values provided[b]	Bulk healing; healing at RT for 24 h, 50% efficiency	[24]
			Epoxy-vinyl ester	Fracture load up to 37 N	Bulk healing; autonomous healing at RT, 50% efficiency	[25]
			Poly(dimethyl siloxane)	No values provided[b]	Bulk healing; autonomous healing at RT, 100% efficiency	[26, 27]
		Epoxy[a]	Epoxy	Young's modulus up to 15 GPa	Bulk healing; healing at 130 °C, up to 50% efficiency	[28]
				Failure load 68 N	Bulk healing; healing at 80 °C for 48 h, up to 80% efficiency	[29]
		Amine-epoxy[a]	Epoxy	Critical load 130 N	Bulk healing; healing at 30 °C for 48 h, up to 100% efficiency	[30–32]
		Thiol-epoxy[a]	Epoxy	Young's modulus 3.7 GPa	Bulk healing; healing above 150 °C within minutes; 100% efficiency	[33–36]

(*continued*)

Table 1 (continued)

Classification	Self-healing mechanism	Chemical compounds	Polymer class	Mechanical data (E-modulus,etc.)	Healing conditions and efficiencies	References
		Thiol-ene[a]	Epoxy	No values provided	Bulk healing; healing at RT for 3 to 5 days, 100% efficiency	[37]
		Thiol-isocyanate[a]	Epoxy	Peak load 84 N	Bulk healing; healing at RT for 1 to 5 days, 100% efficiency	[38]
		Azide-alkyne[a]	Poly(isobutylene)	Storage modulus 2 MPa	Bulk healing; healing at 60 °C for 5 days, 100% efficiency	[39]
		Acylhydrazine/ methacrylate[a]	Epoxy	Elastic modulus 1.8 GPa	Bulk healing; autonomous healing at RT; up to 100% efficiency	[40]
		Glycidyl methacrylate[a]	Epoxy	Fracture toughness 0.68 MPa $m^{1/2}$	Bulk healing; healing at 25 °C for 72 h, 100% efficiency	[41]
		Maleinimide[a]	Epoxy	Flexural strength 3.3 GPa	Bulk healing; healing at RT for 1 to 20 days, up to 80% efficiency	[42–44]
		Isocyanate[a]	Epoxy	Young's modulus 3.3 GPa	Bulk healing; autonomous healing at RT	[45]
			Polyurethane	Fracture toughness 0.02 MPa $m^{1/2}$	Bulk healing; healing RT for 24 h, 100% efficiency	[46]

		Cyanoacrylates[a]	Epoxy	Compression strength 180 MPa	Bulk healing; autonomous healing at RT	[47]
			Polyester	Stiffness 0.87 Nm^2	Bulk healing; autonomous healing at RT, 97% efficiency	[48]
		Vinyl ester[a]	Epoxy and vinyl esters	No values provided[b]	Bulk healing; autonomous healing at RT	[49]
		Unsaturated polyester[a]	Epoxy	No values provided[b]	Bulk healing; autonomous healing at RT	[50]
Intrinsic based on covalent bonds	(Retro-) Diels-Alder	Furan-maleimide	Network based on DA-units	Compression modulus: 3.1 GPa	150 °C for 24 h; up to 57% efficiency	[51, 52]
			Epoxy	No values provided	Scratch healing; healing at 140 °C for 30 min	[53]
			Polyurethane	No values provided[b]	Scratch and bulk healing; healing at 120 °C for 5 min, up to 80% efficiency	[54, 55]
			Block copolymer	Indentation modulus 1.8 GPa	Scratch healing; healing at 155 °C for 4 h; up to 100% efficiency	[56]
			Methacrylate	Indentation modulus 1.5 GPa	Scratch healing; healing at 120 °C for 1 h; 100% efficiency	[57–59]
		Anthracene-maleimide	Poly(ethylene adipate)	Tensile modulus: 26 MPa	100 °C for several days; up to 55% efficiency	[60]

(*continued*)

Table 1 (continued)

Classification	Self-healing mechanism	Chemical compounds	Polymer class	Mechanical data (E-modulus,etc.)	Healing conditions and efficiencies	References
		Cyclopentadiene-cyclopentadiene	Network based on Cp-units	Compression modulus: 1560 to 1759 MPa; E-modulus >3 GPa	120 °C for 20 h; up to 110% efficiency	[61]
		Fulvene-cyanoolefine	Network based on DA-units with small PEG spacers	No values provided	10 s at room temperature; no efficiency provided	[62]
	(Retro-) Hetero-Diels-Alder	Dithioesters-cyclopentadiene	Network based on hDA-units	No values provided^{b}	Heat press for 10 min. at 120 °C; over 100% efficiency	[63]
	[2 + 2]-Cycloaddition	Coumarin based	Polyurethane	No values provided^{b}	Scratch healing; lighting for 1 min. with 254 nm + 90 min. with 350 nm	[64, 65]
		Cinnamate based	Network based on cinnamate groups	Flexural strength: 42 to 50 MPa	Lighting for 10 min. with λ > 280 nm; ca. 20% efficiency	[66]
	[4 + 4]-Cycloaddition	Anthracene based	Polyglycerol	No values provided	Scratch healing; lighting for 15 min. with 254 nm + 24 h at RT	[67]
	Acylhydrazones	Acylhydrazones crosslinker	Methacrylate	No values provided	Scratch healing; heating for 24 h at 100 °C; 100% scratch closure	[68]
	Imines	Dialdehyde and multivalent imine	Network based on imine units	Tensile strength 4 MPa	Scratch healing; heating at 35 °C	[69]

	Disulfides	Disulfide crosslinkers	Epoxy based on PEG and PPG	No values provided[b]	Bulk healing; heating for 1 h at 60 °C; 65% efficiency	[70–72]
				Tensile strength 0.23 MPa	Bulk healing; healing for 24 h at RT; 90% efficiency	[73]
			Polyurethane	Tensile strength 0.81 MPa	Bulk healing; healing for 24 h at RT; 95% efficiency	[74, 75]
			Acrylate	Young's modulus 20 kPa	Scratch healing; applying force using an AFM tip at RT	[76]
		Thiuram-disulfide crosslinkers	Polyurethane	Young's modulus 12 MPa	Bulk healing; visible light irradiation at RT for 24 h; 100% efficiency	[77]
	Polysulfides	Tetrathiol and tetrasulfide as crosslinkers	Organic and inorganic network based on silicone	No values provided[b]	Scratch healing: heating for 10 min at 70 °C; 100% efficiency	[78]
	Urea	Urea crosslinks	Poly(urethane-*co*-urea)	Young's modulus 1.22 MPa	Bulk healing; healing for 24 h at 37 °C; 87% efficiency	[79]
	Alkoxyamine	Alkoxyamine crosslinker	Polystyrene	No values provided[b]	Scratch healing; heating for 30 min at 125 °C	[80, 81]
			Polyurethane based on PEG	No values provided[b]	Healing for 150 min at 80 °C; 70% efficiency	[82]
	Diarylbibenzofuranone	Diarylbibenzofuranone crosslinker	Poly(propylene glycol)	No values provided[b]	Healing for 24 h at RT; 98% efficiency	[83]
	Transesterification	Carbonic acids	Epoxy-*co*-polyesters	Force at break 15 N	Healing for several hours at RT; up to 80% efficiency	[84, 85]
		Boronic acids	Network based on boronic esters and thiol-ene adducts	No values provided[b]	Healing for 3 days at RT and 85% humidity; up to 90% efficiency	[86]
			Polycyclooctene	No values provided[b]	Healing for 16 h at 50 °C; up to 90% efficiency	[87]

(*continued*)

Table 1 (continued)

Classification	Self-healing mechanism	Chemical compounds	Polymer class	Mechanical data (E-modulus,etc.)	Healing conditions and efficiencies	References
Supramolecular intrinsic healing	Hydrogen bonds	Thymine	Poly(isobutylene)	No values provided (for rheology see Ref.)	Bulk healing; healing at 20 °C for 72 h	[88]
		Hamilton wedge	Poly(isobutylene)	No values provided (for rheology see ref.)	Bulk healing; healing at RT for 48 h	[89]
			Poly(styrene-*block*-butyl acrylate)	Young's modulus 12 MPa	Bulk healing; healing at 30 °C for 24 h; 95% efficiency	[90]
		Amide	Poly(methyl methacrylate) brush polymer	Young's modulus 32 MPa	Bulk healing; healing at RT for 24 h; 80% efficiency	[91]
			Methacrylate	No values provided	Scratch healing; healing at 50 °C for 30 min	[92]
			Polystyrene brush polymer	Young's modulus 35 MPa	Bulk healing; healing at RT for 24 h; 90% efficiency	[93]
		Ureas	Poly (dimethylsiloxane)	No values provided[b]	Bulk healing; healing at RT for few hours	[94]
			Network based on ureas	No values provided[b]	Bulk healing; healing at RT for 3 h	[95, 96]

		Ureidopyrimidone	Poly(butyl acrylate)	No values provided	Bulk healing; healing at RT for 50 h; 100% efficiency of adhesion recovery	[97]
			Poly(lactic acid)-*alt*-poly(ethylene-*co*-butylene)	Young's modulus from 4 to 150 MPa	Scratch healing; lighting for 20 min with UV light	[98]
			Poly(styrene-*block*-butyl acrylate)	Young's modulus up to 40 MPa	Bulk healing; healing at 45 °C for 18 h; 75% efficiency	[99]
	π-π- Interactions	Pyrene-naphthalene diimide	Polysiloxane	No values provided	Scratch healing; heating at 120 °C	[100]
			Poly(propylene oxide) and polybutadiene	Tensile modulus 3×10^5 pa	Healing for 240 min at 100 °C; up to 95% efficiency	[101, 102]
	Ionomers	Surlyn®	Poly(ethylene-*co*-methacrylic acid)	No values provided[b]	Healing induced by ballistic impact; healing at different temperatures possible	[103–107]
		Copolymers acrylate and acrylic acid	Acrylates	No values provided	Scratch healing; healing at temperatures between RT and 100 °C for some hours; up to 100% efficiency	[108, 109]
				Elastic moduli of 1 MPa	Bulk healing; healing with magnetic-induced heating for 15 min; 100% efficiency	[110]

(*continued*)

Table 1 (continued)

Classification	Self-healing mechanism	Chemical compounds	Polymer class	Mechanical data (E-modulus,etc.)	Healing conditions and efficiencies	References
	Metallopolymers	Terpyridine ligands	Methacrylates	Indentation modulus of 2 GPa	Scratch healing; heating for several hours at temperatures between 60 °C and 150 °C depending on metal salt	[111–113]
		Mebip ligands	Poly(ethylene-*co*-butylene)	No values provided[b]	Scratch healing; UV-light irradiation 60 s	[114, 115]
		Histidine ligands	Methacrylates	Indentation modulus of 2 GPa	Scratch healing; heating for several minutes to hours at temperatures between RT and 150 °C depending on metal salt	[116]
		Imidazole ligands	Graft copolymers out of styrene and butyl acrylate	No values provided[b]	Healing for 3 h at RT; 100% efficiency	[117]
	Host-guest interactions	Crown ether based	Acrylate	No values provided[b]	Scratch healing; healing for 3 min at RT	[118, 119]
			Methacrylate	No values provided[b]	Scratch healing; healing for 20 min at RT	[120]
		Cyclodextrin	Methacrylate	No values provided	Scratch healing; healing for 24 h using 1.5 V at RT	[121]
			Acrylate	Maximum stress at break 73 kPa	Bulk healing; healing for 24 h at RT; 84% efficiency	[122–124]
Selected biological systems						

Skin	Wound healing by bleeding		Protein	Elastic modulus 66 MPa	Bulk healing; autonomous healing at 37 °C; healing time depends on wound size; 100% efficiency	[125]
Bone	Transport of new minerals to the broken part	Calcium-phosphate	Mineral	Elastic modulus 20 GPa	Bulk healing; autonomous healing at 37 °C within 4 to 6 weeks; 100% efficiency	[126, 127]
Mussel byssus threads	Interaction between dopamine and iron(III) and zinc(II) and histidine	Zinc(II)-histidine and iron(III)-dopamine	Protein	Young's modulus 500–900 MPa	Bulk healing; healing at 37 °C within 168 h; up to 100% efficiency	[128]

General comment: Efficiencies for the scratch healing tests were not provided only if a 3D analysis of the scratches were performed; furthermore, hydrogel (organogel)-based systems are not listed due to their dependency of the water (or organic solvent) content; the maximum healing efficiency is 100%, and higher values (in particular in the case of extrinsic systems) are normalized to that value.

[a] These mentioned chemistries were adopted from reference [20], and a more detailed overview of the specific chemistry behind the healing is presented in this excellent review article.

[b] In these cases the exact values are not provided; however the graphs of the mechanical testing can be found in the publications.

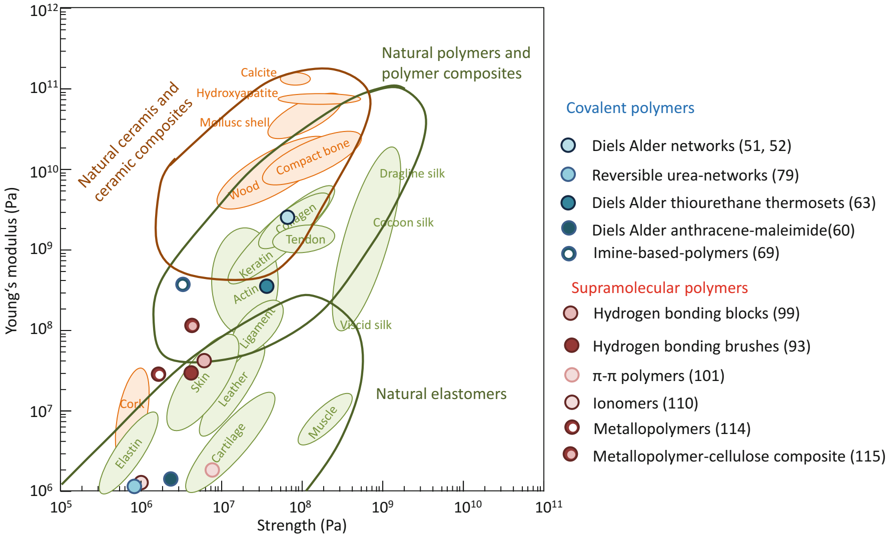

Fig. 3 Schematic representation of the mechanical properties of selected examples of intrinsic self-healing polymers and a comparison to biological materials. (The biological values are adopted from Ref. [3])

In the following paragraph, a more detailed description of each healing mechanism is provided. Firstly, extrinsic self-healing systems will be discussed. Most of the extrinsic self-healing polymers are based on the pioneering work of White and coworkers [22]. The authors incorporated microcapsules filled with dicyclopentadiene into an epoxy resin. When a crack occurs, the capsules are broken and the liquid monomer is released resulting in a filling of the crack. The mobile phase is immobilized by the ring-opening metathesis polymerization (ROMP) of the dicyclopentadiene induced by the contact with the embedded Grubbs catalyst (see Fig. 4).

The basic system could be further improved and different parameters were optimized. Thus, the healing agent, the catalyst (which is not always required), the polymeric matrix, as well as the capsules (composition as well as size) were varied in order to achieve a more robust and better healing system. A summary of the different systems is given in Table 1, and for a detailed overview of the underlying chemistry in capsule-based systems, the interested reader is referred to an excellent review of Du Prez and coworkers [20].

However, the first developed synthetic self-healing systems featured same draw-backs. The most important one is the limited multiple healing behavior at the same position. If the capsules are empty due to a previous healing event, another crack at the same position cannot be healed anymore since no healing agent is present. In order to overcome this problem, several groups focused on the development of vascular networks, which are inspired by the human skin [129, 130]. The blood system in humans is responsible for the delivery of the "healing agent" to the wound. This basic principle was transferred into synthetic materials as depicted in Fig. 5

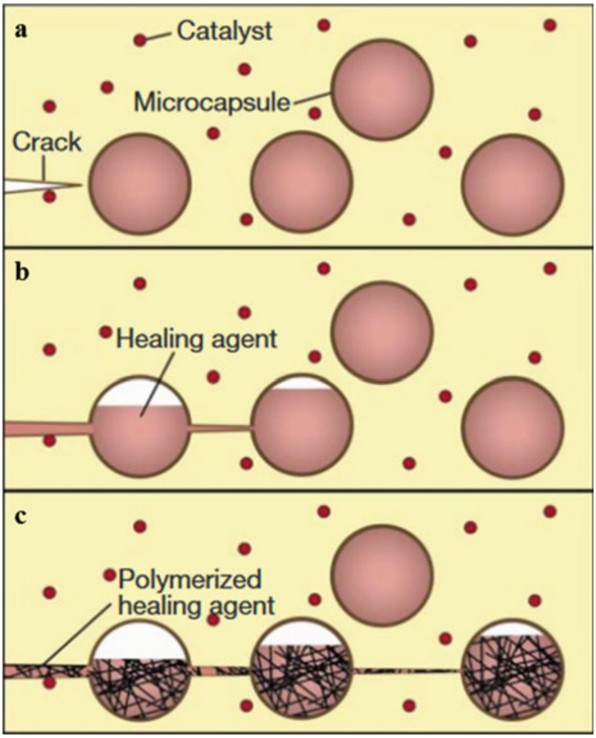

Fig. 4 Schematic representation of the self-healing principles of capsule-based materials: (**a**) A crack occurs; (**b**) the crack leads to the rupture of the capsules resulting in a release of the liquid monomer, which is subsequently polymerized (**c**) leading to a filling of the crack and the restoration of the original mechanical properties. (Reprinted with permission from Ref. [22])

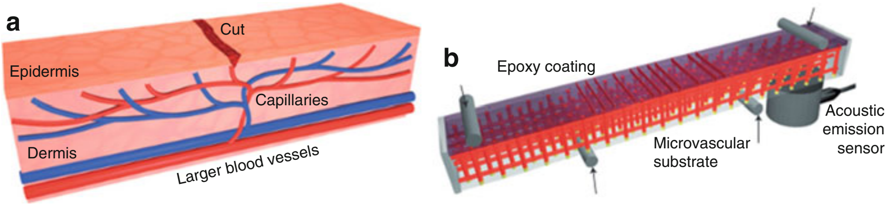

Fig. 5 Schematic presentation of the healing of the human skin (**a**) and the adopted synthetic material using hollow fibers as transport ways for the healing agent (**b**). (Reprinted with permission from Ref. [129])

[129]. For this purpose, hollow fibers were incorporated into a polymeric material, and these were utilized for the transport of healing agents [131]. This setup has two advantages compared to the capsule-based system. On the one hand, the transport of the healing agent to the crack is enhanced, and, furthermore, a healing at the same position can be obtained as shown by Toohey et al., who measured a healing efficiency of approximately 50% after seven healing cycles [129]. Furthermore, the microvascular system was further improved by varying the polymeric matrix, the healing agent, the catalyst, as well as the fibers [31, 32, 132–134]. One recent

development in the context of vascular network-based self-healing materials was the possibility to heal large volume damage [40]. For this purpose a two-stage mechanism was required since the healing agent itself is too less viscous and would flow out. Thus, a previous gel formation by the reaction of a *bis*-acylhydrazine and a trialdehyde was required increasing the viscosity of the healing agent. Afterward, the real immobilization by polymerization was obtained resulting in healing of a round crack with a diameter of 35 mm.

The extrinsic self-healing stills lacks in healing over a longer period of time. The vascular networks still lose their mechanical properties during time and a reduced self-healing efficiency after several healing cycles were observed [129]. Thus, further optimization of the flow of the healing agents is required in order to obtain long-term healing and to enable application.

Another concept, which is more promising in terms of healing of a long period of time, is intrinsic self-healing [21]. In this case, the healing is not based on an external healing agent. Instead the material itself has a special design, which offers the possibility to generate a mobile phase. The mussel byssus threads are the most prominent biological examples of such system, [128] which will be discussed in the section about self-healing metallopolymers.

In general, intrinsic self-healing polymers are based on a kind of reversible linkage. This reversible character offers the switching between the solid, non-healing, and the mobile phase. Thus, a smart design of such materials would offer both: high mechanical performance and excellent self-healing properties [21]. However, the realization of the perfect combination is quite difficult, and most intrinsic self-healing materials still lacks in mechanical stability or autonomic self-healing behavior without any external trigger. The reversible character of intrinsic polymeric systems can be generated in many different ways and requires a special molecular process, which can be triggered by an external stimulus and, furthermore, is reversible resulting in the original molecular state. The most useful classification of intrinsic self-healing polymers is the classification into covalent-based [135] and supramolecular-based systems [136].

Firstly, the dynamic covalent system will be discussed in detail. Most of the investigated systems belong to reversible covalent-based self-healing that describes the utilization of cycloadditions [135]. These processes are ring formation reactions, which are, under specific circumstances, reversible. In particular, three different cycloadditions have been utilized for the design of self-healing polymers: Diels-Alder reactions and [2 + 2]- and [4 + 4]-cycloadditions (see Fig. 6). In all three cases, the cycloaddition is reversible and can be switched between the closed state (cycloaddition adduct) and the open state, which is required for the generation of a mobile phase. Whereas the Diels-Alder reaction is thermally reversible, the other two cycloadditions can be switched by light irradiation. However, photo-switchable systems have not often been utilized so far for self-healing polymers, and the [4 + 4] was used, to the best of our knowledge, only once [67]. For the [2 + 2]-cycloaddition, two different structures were incorporated into polymers in order to realize self-healing materials. On the one hand, cinnamate derivates were utilized [66, 137–139], and the other possibility is the application of coumarin systems [64, 65].

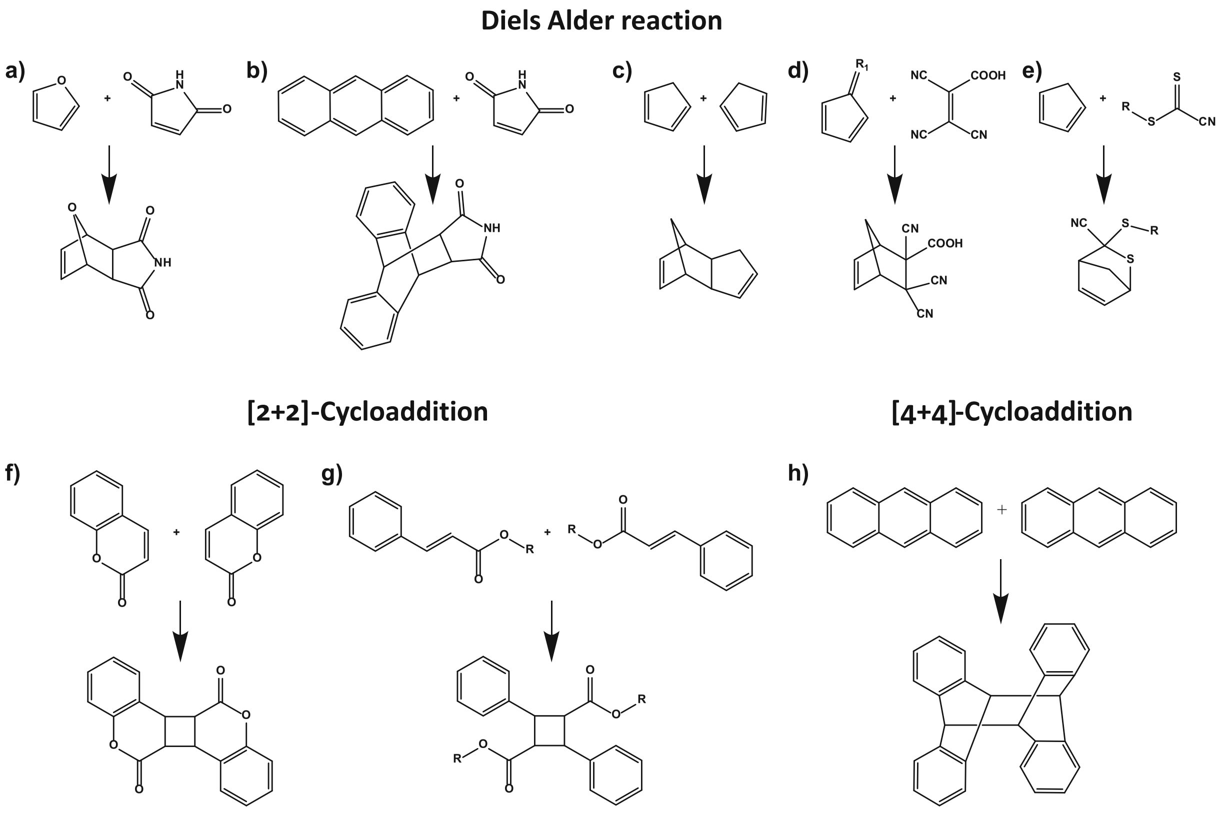

Fig. 6 Schematic representation of the utilized cycloadditions for the design of self-healing polymers: Diels-Alder reaction (**a**–**e**), [2 + 2]-cycloaddition (**f** and **g**), as well as [4 + 4]-cycloaddition (**h**)

The by far most investigated class of cycloadditions for self-healing polymers is the Diels-Alder reaction. In that case the reversible retro-Diels-Alder reaction proceeds under thermal treatment, and the temperature strongly depends on the chosen dienophile as well as diene and ranges from room temperature up to 200 °C [140]. The diversity of the utilized systems is depicted in Fig. 6. The most promising as well as the most investigated system is the maleimide-furan system. The cycloaddition between these two compounds proceeds even at room temperature, whereas the retro-Diels-Alder temperature happens at temperatures above 100 °C [141]. Furthermore, furan as well as maleimide can easily be functionalized in order to incorporate them into polymeric materials. The pioneering work on this system was performed by the group of Wudl, who were able to design a polymer network consisting of multifunctional furan and maleimide units [51, 52]. During thermal treatment the network opens due to the retro-Diels-Alder reaction enabling the generation of a mobile phase. This process leads to a healing, and during cooling the network is reformed again recovering the excellent mechanical properties (E-modulus of 3.1 GPa). Besides the network based only on furan and maleinimide units, also copolymers containing the Diels-Alder units were investigated like epoxy, [142] polyesters [143, 144], or methacrylates [57, 58, 145]. A recent development was the incorporation of this self-healing strategy into block copolymers. Thus, Barthel et al. were able to synthesize a diblock copolymer consisting of poly (ethylene glycol) as well as a furan-glycidyl ether (FGE) [56]. The crosslinking with a low molar mass bismaleimide was performed resulting in a polymer network, which was able to heal scratches within 3 h at 155 °C (see Fig. 7).

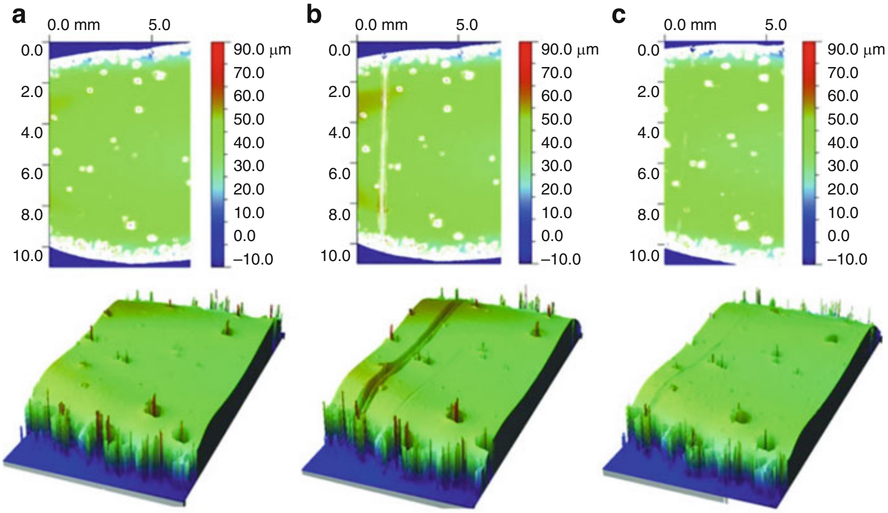

Fig. 7 Schematic representation of the self-healing behavior of a PEG-*b*-PFGE copolymer crosslinked by a low molar mass bismaleimide: (**a**) Film before scratching, (**b**) scratch, and (**c**) self-healing after 3 h at 155 °C. (Reprinted with permission from Ref. [56])

The reversible cycloadditions are not the only utilized reversible covalent interactions, which have been used for the design of self-healing polymers. Di- and polysulfides are other important substance classes in this context. However, the exact molecular mechanism is still not fully understood, and several explanations are provided [135]. Thus, the healing can be based on a reversible metathesis like reaction between two functional groups [70] or the homolytic cleavage of the S-S bond, [146] which can also be promoted by the addition/generation of radicals. Other possibilities are the exchange reaction between a free thiol [71] and the disulfide or the reduction of the S-S bond [147]. All mechanisms are described in literature and can potentially contribute to the overall healing mechanism of disulfide-based materials. Besides disulfides also polysulfides could be utilized for such an approach. For instance, the group of van der Zwaag presented a hybrid material containing inorganic as well as organic compounds [78]. Furthermore, tetrasulfides were incorporated in order to achieve healing. During thermal treatment, the concentration of S-S bonds in the network decreases, resulting in a (partial) decrosslinking and finally healing at 70 °C. This mechanism could be studied using several techniques like IR spectroscopy or rheological measurements.

As already shown with the previous examples, the reversibility or the dynamics of a system is crucial for the self-healing process of intrinsic healable polymers. These dynamic processes were summarized by Lehn and coworkers under the term "dynamers," which include several substance classes [148]. For instance, imines and acylhydrazones are named in this context since both are able to perform dynamic exchange reactions or cleavage of the covalent bond [149–152]. However, most of the investigations were performed in solution, and the transformation of this knowledge into the solid state is rather difficult. Nevertheless, it was possible to utilize polymers containing these dynamic groups for the preparation of self-healing materials. In particular, the acylhydrazone-based polymers featured self-healing properties, which can either be based on the cleavage of the bonds (at low pH values and in the presence of water) or the dynamic exchange between two functional units. For hydrogels, Deng et al. could report a self-healing process at very low pH values resulting in a depolymerization of the network [153]. However, the healing at high pH values was not possible, but the limitation can be overcome with a double network structure using disulfide bonds as a second reversible element [154]. Changing from hydrogels to solid materials, the healing mechanism changes as reported by Kuhl and coworkers [68]. Therefore, the authors designed a methacrylate-based polymer network crosslinked by acylhydrazone functions and could show the healing ability of these materials. However, a rather low tendency for healing was observed, and higher temperatures were required, which could be explained by the reduced flexibility in the solid state (i.e., bulk polymer) compared to the hydrogels (see Fig. 8). Furthermore, mechanistic investigations were performed using IR and solid-state NMR, revealing that the healing is presumably based on the exchange reaction between two functional groups. Besides the acylhydrazones, also imines were utilized for the design of self-healing polymers, but to a lesser extent [69]. Nevertheless, an impressive example was recently presented by Liu and coworkers [155]. The authors presented the healing of a protein-based hydrogel which was

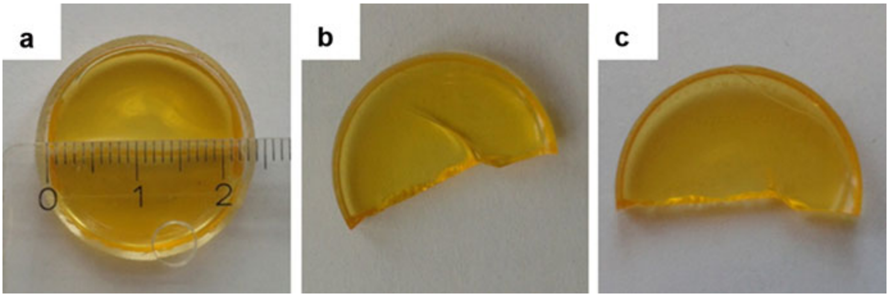

Fig. 8 Representation of the self-healing behavior of a methacrylate-based acylhydrazone network: (**a**) polymer film, (**b**) inflicted scratch, and (**c**) healing after the scratch after 64 h at 100 °C. (Reprinted with permission from Ref. [68])

obtained by the crosslinking of a protein with a dialdehyde. The formation of imine bonds introduced a reversible element, which was further opened by the generation of protons due to an enzymatic process. Thus, healing of the gel at room temperature was observed.

Comparable self-healing phenomena could be obtained for ester crosslinked polymers. Also in these materials a dynamic exchange between functional groups is responsible for the healing mechanism. This so-called transesterification could be found for carboxylic [84] as well as boronic esters [87]. The healing mechanism is based on the exchange between two ester functions, which can be enhanced by the addition of Lewis acids [84].

The last possibility to design self-healing polymers based on reversible interactions is the utilization of stable radicals as well as the corresponding adducts. A typical and well-known stable radical in polymer science is the 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), which is utilized in the nitroxide-mediated polymerization [156] or organic radical batteries [157]. This concept was also transferred into self-healing polymers. For this purpose, polymer networks crosslinked by a TEMPO unit were prepared, and the self-healing was studied in detail. Firstly, the group of Zhang studied polystyrene-based systems, and these systems revealed a self-healing behavior at 125 °C [80]. Furthermore, the molecular mechanism was studied using various techniques, in particular by ESR [81]. Thus, the authors could demonstrate that the healing is based on a crossover reaction between two functional groups. Additionally the basic principles could also be transferred into polyurethane systems revealing a lower healing temperature of 80 °C due to an increased flexibility of the polymer backbone [82].

Another radical-based concept is the utilization of diarylbibenzofuranon (Fig. 9). In this particular case, the healing is based on the dissociation of the adduct into two stable radicals [83]. The equilibrium between the two species is more dynamic than the TEMPO-based one, and, thus, a healing process at room temperature could be observed.

The class of covalently crosslinked system is investigated in detail, and a wide range of reactions are already applied for this purpose. Furthermore, there are also

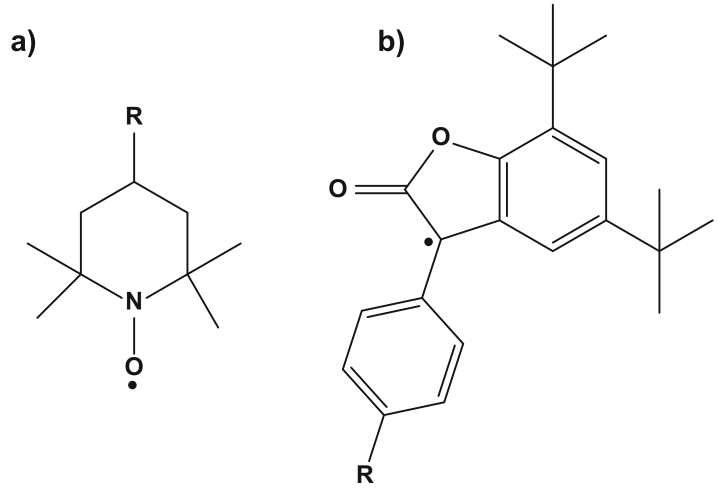

Fig. 9 Schematic representation of the utilized stable radicals for the production of self-healing materials: TEMPO (**a**) and diarylbibenzofuranon (**b**)

supramolecular interactions available, which feature also a kind of reversibility. The advantage of these secondary interaction is the simple tunability of the strength and, consequently, of the properties of the material [136]. However, this feature makes it somewhat challenging to design materials offering both self-healing abilities and distinguished mechanical properties [158]. Thus, a high degree of reversibility leads to excellent self-healing properties, but it goes hand in hand with poor mechanical performance. Despite this tightrope walk, it was possible to utilize several supramolecular motifs for the design of self-healing materials, which will be discussed in detail in the following paragraph: hydrogen bonds, ionic interactions, metal-ligand bonds, π-π interactions, as well as host-guest complexes [136].

Hydrogen bonds are by far the most investigated supramolecular interactions in terms of self-healing properties [159]. For this purpose, several structural motifs have been studied, e.g., ureas, ureidopyrimidone or nucleobases. An impressive example of hydrogen-based self-healing polymers was presented by Leibler and his group [95, 96]. The authors synthesized a polymer network containing urea functions, which were responsible for the crosslinking and, additionally, for the self-healing behavior. The authors claimed that the healing of the material is based on the formation of unbound hydrogen bond units at the crack due to the damage event and that these free moieties reform hydrogen bonds if the two parts are placed together. Thus, healing at room temperature could be obtained within minutes. However, if the material parts are kept away from each other and the healing process was started after several hours, an insufficient healing was obtained and the mechanical properties were not restored. This phenomenon was explained by the reassembly of the freshly formed hydrogen bonds, and, thus, no sticking of the polymer was possible anymore.

After the first development of hydrogen bond-based self-healing materials, several other systems were studied in detail. One important moiety is thymine, which is also a natural building block of the DNA. The utilization of thymine in polymeric materials mostly requires a complementary partner, which can be, e.g., diaminotriazine [160]. However, it is also possible to utilize thymine without any additional partner as shown by Binder and coworkers [88]. In that case, the authors functionalized poly(isobutylene) (PIB) with thymine functions and constructed another network by alkyne-azide click chemistry. The very polar thymine units lead to aggregates within the copolymer, and during a scratch free supramolecular moieties are obtained, which are reformed by the contact of two freshly cut surfaces resulting in a healing. However, the effect of phase separation seems to be more important for the self-healing than the contribution of the reversible hydrogen bonds itself.

One very similar moiety compared to thymine and one of the most frequently investigated molecular units in the context of self-healing materials is barbiturate. Mostly, this system is used with the corresponding Hamilton wedge as shown in Fig. 10 [161]. The rather strong hydrogen bonds as well as the simple functionalization procedure allow a broad range of potential polymer structure. Thus, Herbst et al. were able to end functionalize PIB with either one or two hydrogen bonding motifs [89]. A mixing of the corresponding polymers led to a network formation via clusters since the highly polar functional groups segregated from the unpolar polymer backbone. Furthermore, the healing ability at room temperature was studied, and a healing after 48 h could be obtained. An improvement was reported

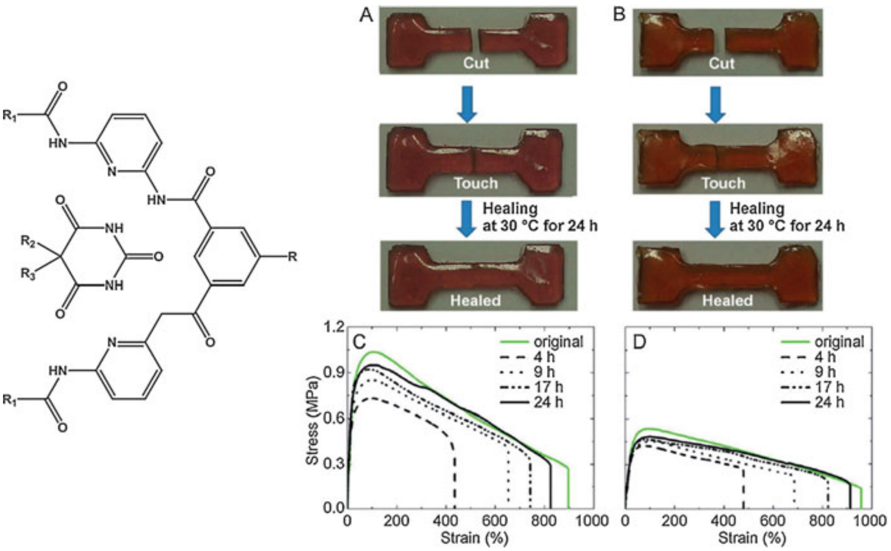

Fig. 10 Schematic representation of the supramolecular pair based on barbiturate and the corresponding Hamilton wedge (left) and the self-healing ability of block copolymers based on these interactions (right). Healing of the block copolymer containing only barbiturate (**A** and **C**) and the adduct of the block copolymer containing barbiturate as well as a Hamilton wedge containing polymer (**B** and **C**). (Reprinted with permission from Ref. [90])

3 years later by the same group. Therefore, the group prepared block copolymers with the hydrogen bonding (barbiturate) units localized in the hard block (polystyrene) [90]. These materials also featured a healing ability after 24 h at 30 °C as shown in Fig. 10. However, the utilization of α,ω-difunctionalized polyisoprene with two Hamilton wedges and the block copolymer resulted in weaker mechanical properties, but also cracks could be healed at room temperature.

However, the main disadvantage of all the investigated hydrogen bonding-based self-healing polymers is the weak mechanical performance. Thus, only very soft materials were obtained. In order to overcome this problem, Guan and coworkers developed a multiphase phase system offering both mechanical stability and self-healing properties [93]. For this purpose, the authors prepared a polystyrene-based copolymer which featured brushes containing a polyacrylate with an amide function. This function enables hydrogen bonds and, thus, crosslinking. Furthermore, a phase separation was obtained between the hard and the soft block. Although the introduction of non-flexible hard blocks, the copolymer still featured a self-healing ability at room temperature and good mechanical properties (E-modulus of up to 35 MPa).

π-π Interactions represent another important class of supramolecular interactions utilized for self-healing materials. In order to obtain such an interaction, an electron-rich as well as an electron-poor aromatic compound is required [162]. As electron-accepting unit, only naphthalene diimide was utilized, and it was incorporated into polymers as end groups or as repeating units. Furthermore, electron-rich aromatic systems are required, and mostly two different systems were used up to now: perylene [163] and pyrene [100–102, 164]. If both polymers are combined, secondary interaction takes place (see Fig. 11) resulting in crosslinking of the polymer as well as a chain folding. The obtained polymeric materials feature the ability to close cracks during thermal treatment since the thermal activation of the π-π interaction leads to a disassembly and, finally, to mobility, which is required for closing the crack. During cooling, the π-π interactions are reformed, and the original properties of the polymer can be reobtained. Firstly described in 2009, the π-π interaction was already used several times for the preparation of self-healing materials [100]. In the first approach, a polysiloxane containing two pyrene units as end groups were mixed with a naphthalene diimide containing copolymer resulting in the formation of a supramolecular network. This material is able to heal cracks at temperatures above 90 °C. The basic principles could also be transferred into other systems, and, thus, other copolymers for the naphthalene diimide containing part were utilized such as poly(propylene oxide) [101, 102, 164]. Furthermore, polybutadiene was used as building block for the pyrene block [101]. Additionally, the mechanical performance could be enhanced by the utilization of cellulose nanocrystals [165]. Finally, also perylene was incorporated into a polymeric structure resulting in a π-π interaction [163]. In that case, healing after 40 min at 70 °C or after 14 min at 125 °C could be observed.

Ionomers are a very important class of supramolecular healable materials [136]. These copolymers reached already the industrial scale and are sold by DuPont under the trade name Nucrel® poly(ethylene-*co*-methacrylic acid) or Suryln®

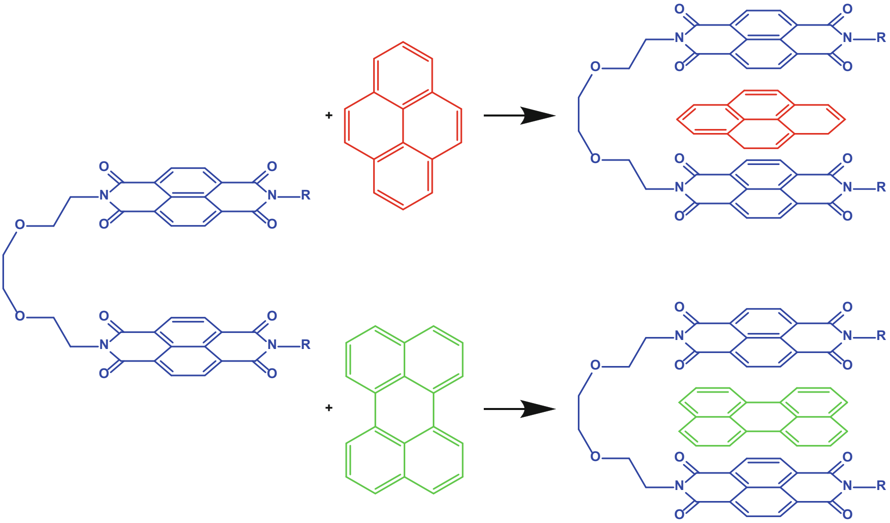

Fig. 11 Schematic representation of the formed complexes by π-π interaction starting from a naphthalene diimide derivates and pyrene (red) and perylene (green). (Adopted from Ref. [163])

(different salts of poly(ethylene-*co*-methacrylic acid)) [166, 167]. These copolymers feature excellent mechanical properties and are used as packing materials or top layers for, e.g., golf balls [167]. The commercial availability leads to several publications reporting the self-healing ability of Nucrel® and Suryln®. However, the self-healing effect of those polymers is up to now not used on an industrial scale. Nevertheless, the self-healing phenomenon is studied by several groups and will be described in the following paragraph.

Generally, ionomers are defined as polymers containing a certain amount of ionic groups (1% to 15%), which leads to a special behavior since a phase separation of the ionic groups within the nonpolar backbone is obtained [168]. These so-called multiplets aggregate further to ionic clusters according to the Eisenberg-Hird-Moore model (EHM) [169]. Furthermore, the ionic clusters lead to a crosslinking of the polymer and to a reduced mobility at room temperature. During thermal treatment the order of the ionic clusters itself is destroyed, which can increase the mobility of the polymer chains. In the case of Suryln®, further thermal treatment would lead to a melting of the polyethylene parts, which are crystalline at room temperature (Fig. 12) [170].

Most investigations on the self-healing behavior of ionomers is focused on the testing of the healing abilities after a ballistic impact [103, 105, 171]. For this purpose, a polymer film was penetrated with a bullet resulting in a hole within the polymer. Furthermore, this kind of damage leads to heating of the polymer, which surrounds the generated hole [171]. Thus, parts of the polymer become sufficiently mobile to close the crack and to heal the damage. Kalista and coworkers investigated this behavior further at different temperatures [104]. The authors could show that the temperature of the film has a crucial influence on the healing abilities. However, the

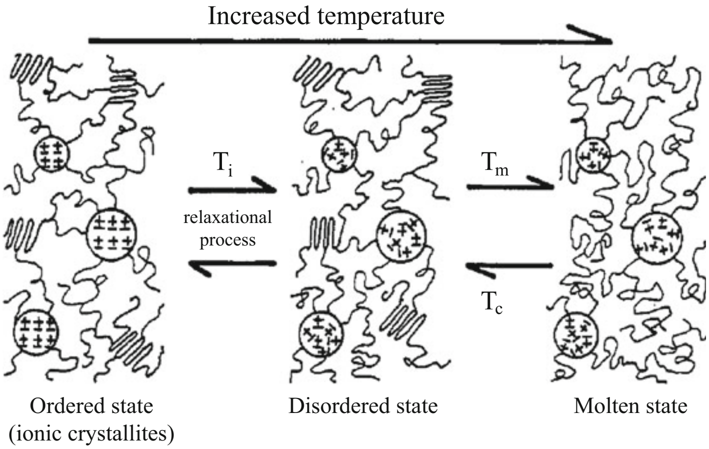

Fig. 12 Schematic representation of the thermal behavior of ionomers (in particular of Suryln®): The ordered state at room temperature with crystalline polyethylene as well as ionic cluster undergoes two thermal transitions; disorder of the ionic clusters and melting of the polyethylene. (Reprinted with permission from Ref. [170])

most important parameter is heating of the surrounding polymer, and, consequently, the heating has to be stronger if the polymer film is cooled before the penetration. Additionally, lower temperatures can cause a kind of brittleness of the film resulting in non-healing of the ionomer. This behavior can be in particular observed for low degrees of neutralization of Nucrel®. Despite all the ballistic tests, it still requires the access to a shooting place to perform these experiments, and in order to overcome this problem, Varley and van der Zwaag developed a similar method to test the same behavior without a gun [106]. For this purpose, they constructed a hydraulic tensile testing apparatus, which also resulted in hole formation.

The ballistic penetration is not the only method which was reported to test the self-healing capacity of ionomers. Exemplary, Bose et al. studied the scratch healing behavior of ionomers. Furthermore, the utilized copolymers were not based on Suryln or Nucrel. Instead they prepared a copolymer consisting out of *tert*-butyl acrylate and *n*-butyl acrylate [108, 109]. In a second step, the *tert*-butyl ester was cleaved off and the obtained acid was neutralized using different metal salts, i.e., zinc (II) and cobalt(II) acetate as well as sodium hydroxide. Furthermore, the ionic content was varied, and the synthesized materials were investigated using rheology as well as microscopy in order to follow the healing behavior of the scratches. The authors could show that these ionomers are also able to heal scratches, even if they were not generated by high impact damage. Furthermore, a correlation between the mechanical properties and the self-healing abilities was obtained since the crossover frequency of the storage and the elastic modulus obtained by rheology goes hand in hand with the mechanical and self-healing properties. Therefore, the authors could reveal the optimal design principle for having both mechanical stability and self-healing behavior [108, 109].

Metallopolymers are another important class of materials in terms of self-healing and are in some points comparable to the previous mentioned ionomers [172]. Metallopolymers are polymers featuring additionally a metal complex (i.e., a complex consisting of a metal ion and the corresponding ligands). This secondary interaction can influence the properties significantly, and interesting features can be obtained. Thus, metallopolymers were already utilized for special optical, shape memory, or certain biomedical applications [173]. However, the design of metallopolymers is rather challenging since the metal complex as well as the rest of the polymer influences the properties, respectively. The right combination can also lead to self-healing polymers. For this purpose, two basic mechanisms are described in literature: reversible opening of the metal complex or the formation of ionic clusters in analogy to ionomers [172]. The first one is already known in solution but strongly depends on the chosen metal ion-ligand combination. The second possibility requires a phase separation within the formed polymer of the metal complexes, which are mostly charged, from the rest of the polymer. Which contribution is the predominant one depends on the special design (the metal complex, the polymer backbone, the counterion, etc.).

The first self-healing metallopolymer film was described by the groups of Weder and Rowan in 2011 [114]. For this purpose, the authors synthesized a poly(ethylene-*co*-butylene) α,ω-end functionalized with 2,6-*bis*(methylbenzimidazolyl)pyridine (Mebip) ligand. Subsequently, the ligand-containing copolymers were mixed with either zinc(II) or lanthanum(III) bistriflimide resulting in metallopolymers. The healing was studied by inducing a scratch into the polymer film and irradiation with UV light. The lighting leads to a decomplexation resulting in flexibility. However, a secondary effect of the high-power UV light was the heating of the polymer film up to 220 °C, which further enhances the mobility. Thus, a healing was obtained within seconds. The mechanical properties could be enhanced by the utilization of cellulose nanocrystals, and the obtained composite materials featured E-modulus values up to 100 MPa [115]. Another optical healable metallopolymer was reported by Wang and Urban [174]. The authors used a poly(ethylene imine) and incorporated copper(II) complexes. These complexes undergo a geometry change during lighting, resulting in a volume change and, finally, in self-healing properties.

Metallopolymers are multi-stimuli-responsive materials, and, therefore, these polymers can be addressed by several external triggers [173]. The most frequently utilized one in terms of self-healing is temperature. The first thermal-induced self-healing of metallopolymers was reported by the Schubert group in 2013 [112]. The authors synthesized different methacrylate copolymers containing terpyridine moieties in the side chain via RAFT polymerization (see Fig. 13). Crosslinking with iron (II) sulfate resulted in metallopolymers which featured self-healing depending on the chosen copolymers. Whereas copolymers based on methyl methacrylate have a too high glass transition temperature, copolymers with lauryl methacrylate show self-healing abilities at 100 °C. Furthermore, the healing mechanism was investigated using Raman spectroscopy as well as theoretical calculations revealing that the healing process is presumably based on the partial decomplexation [175].

However, the required temperatures were rather high, and a follow-up study of the same group could show that it is possible to reduce the required energy input. For

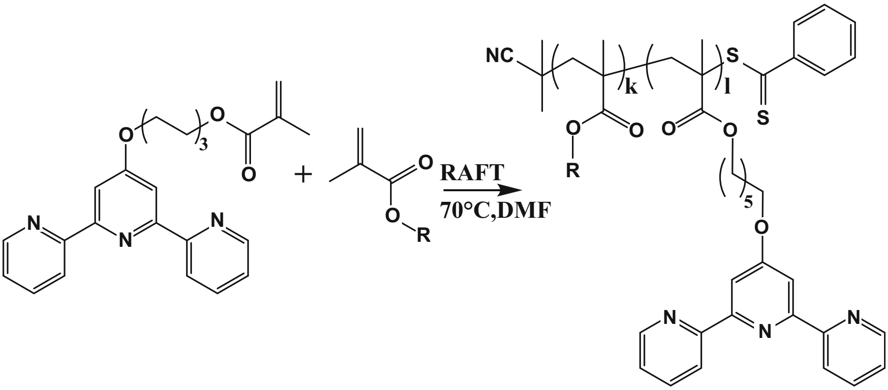

Fig. 13 Schematic representation of the synthesis of a terpyridine-containing copolymer, which can later be utilized for the complexation of different metal ions resulting in metallopolymer networks (Adapted from Ref. [113])

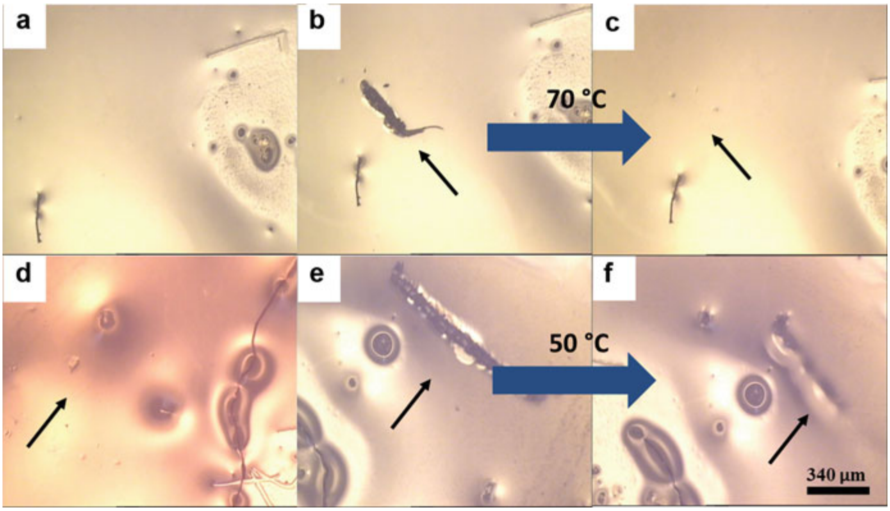

Fig. 14 Self-healing behavior of a metallopolymer network crosslinked by terpyridine-manganese (II) chloride complexes. Self-healing at 70 °C (**a**–**c**) and partial healing at 50 °C (**d**–**f**). (Reprinted with permission from Ref. [113])

this purpose, cadmium(II) acetate was used resulting in a weaker crosslinking since acetate-bridged complexes were formed [111]. Thus, healing at 70 °C within minutes was possible. Additionally, the required temperature could be further reduced to 60 °C by the utilization of manganese(II) chloride (Fig. 14) [113]. Finally, the Schubert group also presented a general predication of the healing ability of metallopolymers showing that rheology can be utilized as a prediction tool. If a crossover of the storage and the elastic modulus at a certain temperature is found, the material reveals self-healing. However, the film-forming properties are also important for the healing process, and thus, in the case of brittle films, the general correlation is not useful anymore.

The results in the field of synthetic self-healing metallopolymers are promising. However, these are far away from that what nature can do. Mussel byssus threads are also able to heal mechanical damage [176]. This behavior is found under living (harsh) conditions in an ocean at low temperatures [128]. Responsible for that behavior are iron(III)-dopamine as well as zinc(II)-histidine interactions [177, 178]. These interactions lead on one hand to mechanical stiffness and furthermore to the possibility to stick on the surfaces of rocks (mostly the iron(III)-dopamine interaction is responsible for this behavior) [179, 180]. Additionally, the partly opening and the reorganization of the metal complex can lead to a self-healing in mussel byssus threads (Fig. 15) [181]. This impressive behavior was tried to mimic also with synthetic materials. However, no approach comes close to nature so far. Nevertheless, more insights in the behavior of the mussel can be obtained, which can lead to novel materials with outstanding properties in the future.

Thus, iron(III)-dopamine or zinc(II)-histidine units were incorporated into polymeric materials or hydrogels revealing in self-healing abilities [116, 182, 183]. The weak interaction between those moieties led to a healing behavior at room temperature or slightly increased temperature. Furthermore, in the case of iron(III)-dopamine, it was also possible to utilize the pH value as trigger for the self-healing since a lower pH value led to a protonation of the dopamine [183]. Similar to the zinc(II)-histidine interaction, also zinc(II)-imidazole can be utilized for such an effect [117].

Host-guest interactions are the last important class of supramolecular self-healing materials. For the preparation of such polymers, a host (typical for self-healing polymers: cyclodextrin or crown ethers) interacts with a guest, e.g., ferrocene or ammonium salts. The non-covalent interactions are reversible and can be triggered by temperature or, in the case of ferrocene, by oxidation. The reversibility is the crucial aspect for the design of self-healing materials. The pioneering work in this field was performed by Harada and coworkers [122]. The authors could successfully synthesize a cyclodextrin- and ferrocene-containing polyacrylate, which crosslinks due to the host-guest interactions. The oxidation of the obtained gel led to an opening of the interactions resulting in mobility and the ability to self-heal (Fig. 16). Besides the interaction with ferrocene, cyclodextrin can also interact with, e.g., adamantane or azobenzene [123, 184]. Additionally, the host molecule can be changed toward crown ethers, which are more responsible for ammonium salts. This interaction can be triggered by several stimuli like temperature, pH value, or chemicals (e.g., other competing ions) [118]. These special features could already be utilized for the design of self-healing materials, and further development in this area is expected.

3 Functional Polymeric Materials

Most research on self-healing materials was and is still focused on the healing/restoration of mechanical properties. In this context, several mechanisms have been developed, which provide a regeneration of the mechanical properties under specific

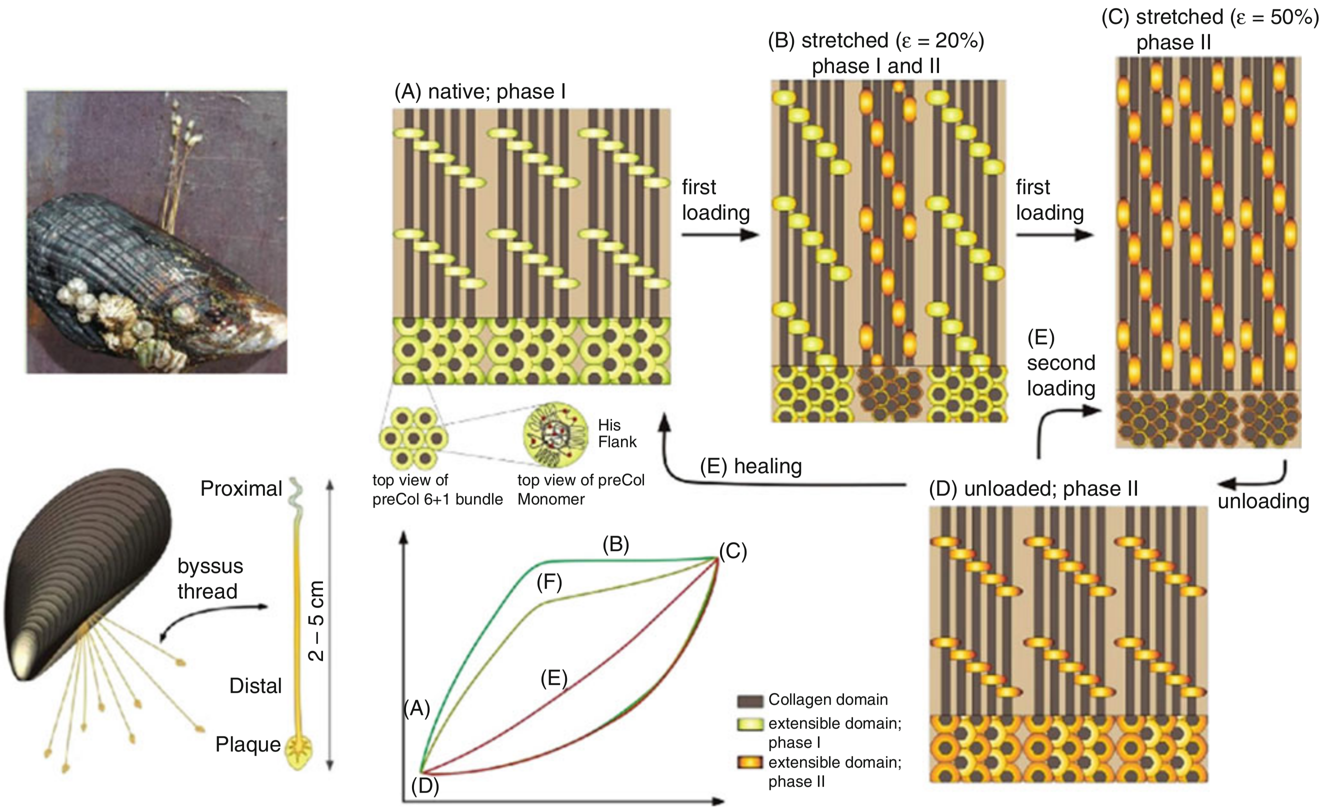

Fig. 15 Schematic representation of the healing mechanism of mussel byssus threads. (Reprinted with permission from Ref. [181])

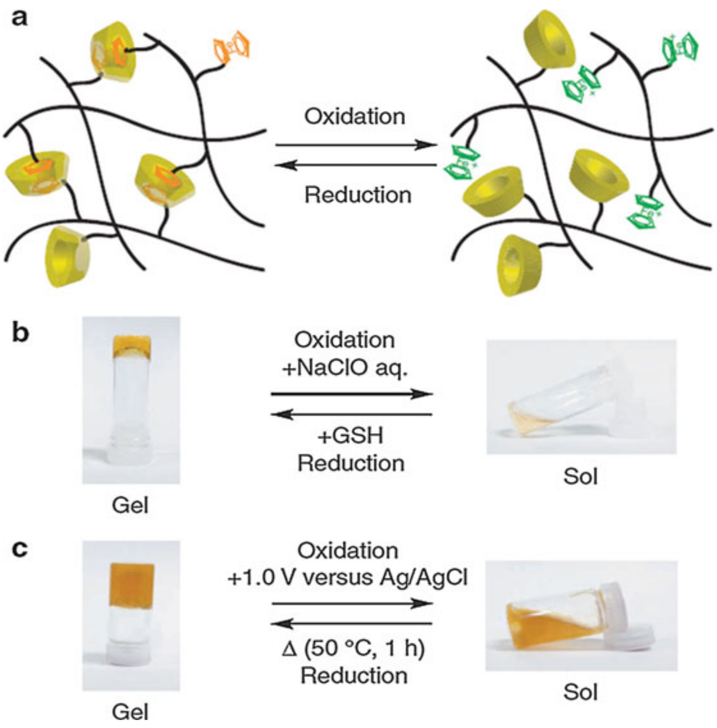

Fig. 16 Schematic representation of the self-healing healing process of polymer networks crosslinked by ferrocene-cyclodextrin interactions and the reversible opening induced by the oxidation of the ferrocene. (Reprinted with permission from Ref. [122])

conditions. Compared to nature, synthetic polymeric materials are still at the beginning of the development to multifunctional materials. Thus, nature can repair the mechanical performance as well as the function. For instance, a scratch in the human skin leads to a loss in both mechanical stability and function (e.g., as barrier against substances from the outside). After the scratch occurs, bleeding starts resulting in a closure of the crack. Up to this point, this behavior can also be found in synthetic materials. However, nature goes further and initiates a second healing step in which new skin is reformed having the same properties as before. Thus, the barrier function or the ability to sweat is reformed. This complex behavior is still influencing the research efforts in developing new materials, which feature both reparation of the mechanical performance and the regeneration of additional functions. The following paragraph will shortly demonstrate which functions can already be healed/restored in functional materials. For a more detailed description, the interested reader is referred to the literature [185].

The two most frequently investigated functions are conductivity as well as optical properties. Furthermore, it is also possible to restore special functions of coatings like superhydrophobicity.

Conductivity can be repaired in different ways, and several strategies have been developed in the past. First of all, it is possible to introduce reversible bonds into a conjugated polymer backbone. In this context, Williams et al. reported a conjugated polymer containing carbene metal complexes, which are able to be reversibly opened at higher temperatures in the presence of DMSO vapor [186]. Furthermore, the polymer featured electric conductivity comparable to silicon. However, the authors only studied the scratch healing behavior, which could be observed at higher temperature, and not the restoration of the conductivity, which has to be improved first.

Another possibility for the generation of self-healing conductors is the embedding of conductive material into a self-healing polymer. Thus, the group of Bao explored several combinations and could show the healing of the function as well as the mechanical stability by utilizing the polymer which was investigated by Leibler [95]. Firstly, the incorporation of nickel microparticles into that polymer matrix led to a material featuring a conductivity of 40 S cm^{-1}, which is a rather high value [187]. After a mechanical damage, 90% of the conductivity could be regenerated within seconds, and the complete recovery of the mechanical properties was obtained after 10 min. However, this basic principle could also be transferred into batteries. In lithium ion batteries, the main challenge is to increase the capacity. One possibility to increase the capacity of the anode is the utilization of silicon anodes. However, these electrodes are mechanically not stable due to a large volume change during charging/discharging, resulting in crack formation (see Fig. 17). However, Bao and coworkers could overcome this problem by the utilization of self-healing polymer, which holds the anode material together and enables the fabrication of a lithium ion battery with a capacity of nearly 3000 mAh g^{-1} over 20 cycles.

The third possibility to enable healing of conductivity is the utilization of the extrinsic healing concept, i.e., the encapsulation a conductive material in capsules. The first approach toward this healing strategy was presented by the

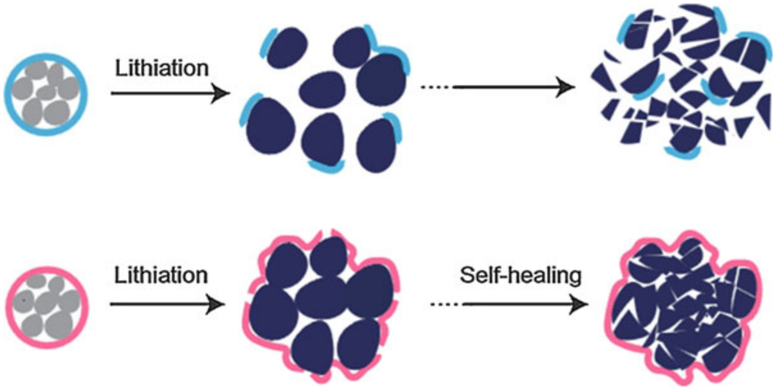

Fig. 17 Schematic representation of the self-healing property of a silicon anode compared to a normal one: Charging of the battery leads to a lithiation and to a volume change of the battery resulting in crack formation and to a total failure of the anode (above) or by the utilization of a self-healing binder (red) to a stable electrode. (Reprinted from Ref. [188])

Moore group in 2009 [189]. The authors were able to encapsulate carbon nanotubes. However, an addition of a nonpolar solvent is required in order to enhance the release. This basic principle could later be used for the reparation of silicon anodes [190]. For this purpose, carbon black as well as *o*-dichlorobenzene was incorporated into microcapsules. However, the addition of a core thickener was required leading to the restoration of the conductivity. Furthermore, it is also possible to utilize liquid metals (alloys) for this process like eutectic gallium indium [191, 192].

The healing of optical properties is still in its infancy, and only very few publications focus on the healing of optical active polymeric systems [185]. However, these properties can range from absorption to emission or in the simplest case to transparency. The latter one is a typical phenomenon known in the daily life. A clear top coating is scratched resulting in worse aesthetics due to the visible scratch. Healing of the scratch requires for certain applications (e.g., as clear top coating in cars) not only the disappearing of the scratch. Furthermore, it is required to obtain afterward again a clear coating, which has the same optical properties as before. One approach toward the solution of that problem was presented in 2011 by Braun and coworkers [193]. The authors tried to overcome scattering phenomena from the encapsulated capsules as well as from the healed polymer. For this purpose, dibutyl phthalate was encapsulated into a PMMA matrix. During crack propagation the capsules are ruptured resulting in a release of the dibutyl phthalate. Thus, a swelling is observed, which leads to healing of the crack and a regeneration of the transparency.

Furthermore, it can be possible to heal also other functions of optical active polymers like absorption or emission, which would be interesting, e.g., for solar cell applications. However, a self-healing polymer featuring this property does not exist so far. Nevertheless, first attempts were created like the utilization of a transport of fluorescent dyes through a polydimethylsiloxane matrix [194].

The last discussed function to be self-healed is the reparation of the surface properties of a polymer coating. One very impressive approach was presented from Esteves and coworkers [195–197]. The authors utilized the so-called self-replenishing of a coating. For this purpose, poly(ε-caprolactone) was prepared containing perfluoro-chains as well. These chains phase separate from the rest of the polymers and are moved to the top of the coating, leading to very hydrophobic properties. After the top layer of the coating is removed, the hydrophobicity is lost but is regenerated during time due to a subsequent phase separation process. This effect is schematically shown in Fig. 18.

4 Characterization of Self-Healing Polymers

The characterization of self-healing polymers represents a crucial part of the investigation of such materials. The major task is the investigation of the self-healing phenomenon itself and to quantify or at least to visualize the self-healing effect [198]. Furthermore, the material properties are of significant interest, which allow a

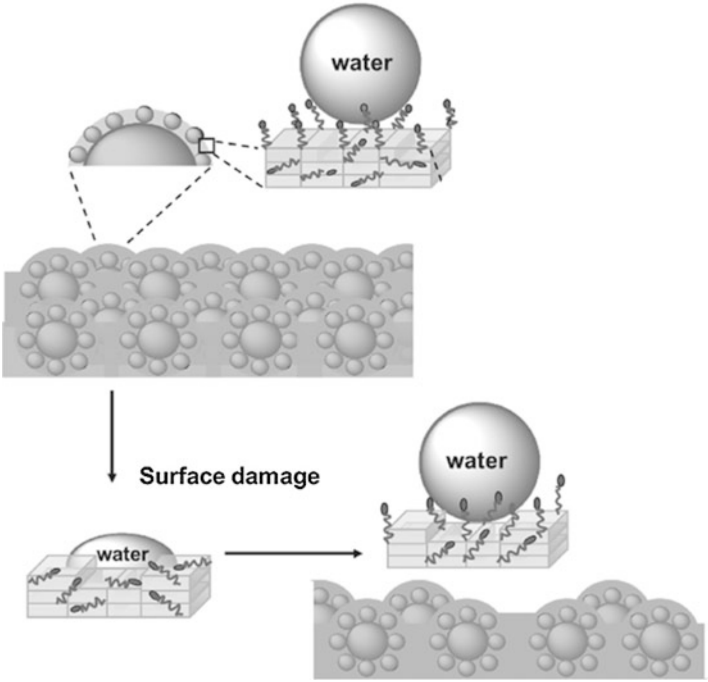

Fig. 18 Schematic representation of the self-replenishing effect of polymer coatings utilizing perfluoro-chains. (Reprinted with permission from Ref. [197])

comparison of the properties to materials without any healing ability. For this purpose, mostly standard mechanical tests are utilized. Additionally, the healing mechanism, in particular for intrinsic systems, should be studied in detail in order to analyze the molecular changes and to understand the basic principles of the self-healing process. Finally, the healing of functional materials, in which specific functions besides the mechanical properties are healed, requires the investigation of the corresponding property like conductivity (see Sect. 3). In the following part, the different methods of the investigation for self-healing processes as well as for the study of the molecular processes will be presented in detail.

The investigation of the self-healing properties can be realized by different tests. Tensile testing, tapered double cantilever beam, and scratch healing are the most common methods to analyze the healing ability. Furthermore, the healing after ballistic impact or the determination of the fracture mechanics was also utilized for this purpose [198]. However, a standardized testing of the self-healing properties is not available at the moment and has still to be developed. The problem behind the standardization of healing quantification is that the testing method strongly depends on the later application. Thus, materials, which will be utilized as coatings, should be studied via scratch healing analysis, whereas bulk material applications require the determination of the mechanical properties before and after the healing event [198].

The tensile test is the one of the most frequently utilized methods in terms of self-healing materials. The method allows the determination of the mechanical properties of the material, like E-modulus, tensile strength, or elongation at break. Furthermore, these properties can also be studied temperature-dependent. Finally, virgin and healed samples can be compared, and the healing efficiency can easily be determined. However, several parameters were utilized in the literature for the calculation of the healing efficiency. Some examples are elongation at break [199], the maximum load at failure [42, 52], or the recovery of the yield point stress [200]. The limitation of this method is the exact determination of the healing efficiency. During the healing event, the surface of the broken tensile specimen has to have contact. However, depending on the hardness of the material, this requirement is difficult to fulfill, and nonoptimal healing events take place resulting in a lower healing efficiency [198, 201]. Nevertheless, the method is widely utilized since it is easy to perform and both the healing process and the mechanical properties of the healed material can be analyzed. The method can also be applied for biological samples since threads can also be investigated by this technique. Thus, Harrington et al. studied the healing of mussel byssus threads using such testing equipment (Fig. 19) [128].

The tapered double cantilever beam (TDCB) represents another possibility to test the mechanical properties as well as the healing efficiency [202]. During the testing a load-displacement curve is generated which can also be utilized for the

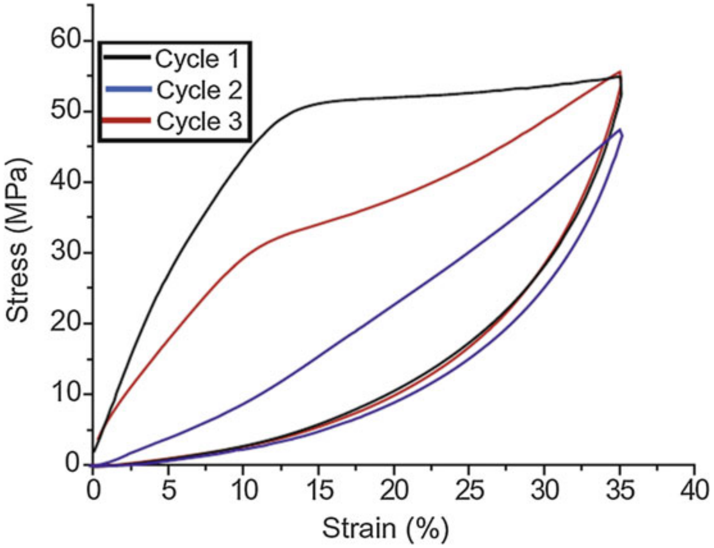

Fig. 19 Schematic representation of the healing within mussel byssus threads within three cycles of tensile testing. Cycle 1 describes the original mechanical properties, and cycle 2 was directly measured after the first cycle with no rest in between. The third cycle represents the healing of the mechanical properties of such a thread after 1 h at ambient conditions. (Reprinted with permission from Ref. [128])

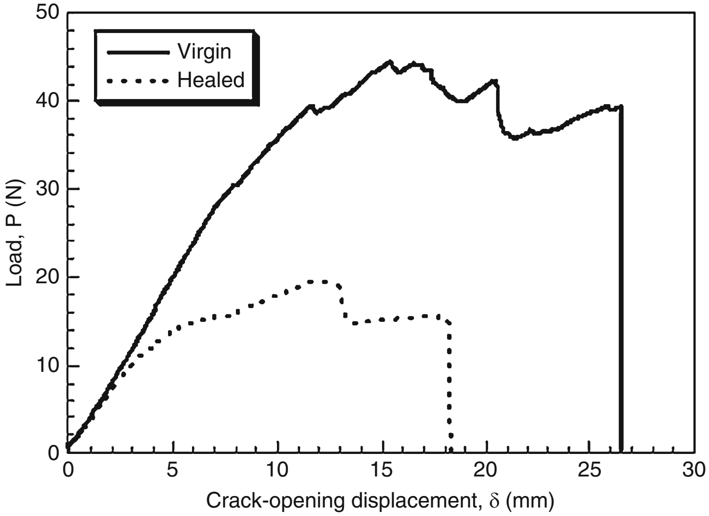

Fig. 20 Schematic representation of the data obtained by a TDCB for capsule-based healing system (dicyclopentadiene encapsulated into capsules in an epoxy resin with a Grubbs catalyst). The original material (solid black line) as well as the healed sample (dotted black line). (Reprinted with permission from Ref. [204])

determination of the healing efficiency. The fraction toughness is a useful parameter for this purpose [203]. The TDCB is mostly utilized for extrinsic self-healing systems. Thus, the capsule-based healing system (dicyclopentadiene encapsulated into capsules in an epoxy resin with a Grubbs catalyst) could be studied using this method, and typical curves revealed from this measurement are depicted in Fig. 20 [204].

A relatively similar approach compared with the TDCB is the testing of the fracture mechanics [198]. Also within this method, the crack propagation is analyzed, and healing efficiency as well as mechanical data can be obtained. However, this kind of testing is not often utilized for the determination of the healing ability of polymers although it seems to be quite promising for the investigation of soft materials [201, 205].

A completely different method for the analysis of the self-healing behavior is the utilization of the scratch healing tests. In this case, no mechanical properties will be analyzed and will also not be utilized for the determination of any kind of efficiency. This testing method focuses more on the ability of the material to close scratches on a surface and is of particular interest for materials utilized later as coating [198]. However, most of the publications simply utilize the optical imaging of the scratch as well as analyze the presence and disappearance of a scratch during healing. This method can just be utilized to show the general healing ability of newly developed system; quantification is not possible. For this purpose, a 3D imaging of the crack is required, which allow the determination of the crack volume, the healing speed, as well as the percentage of healed volume (corresponding to a kind of healing efficiency). Thus,

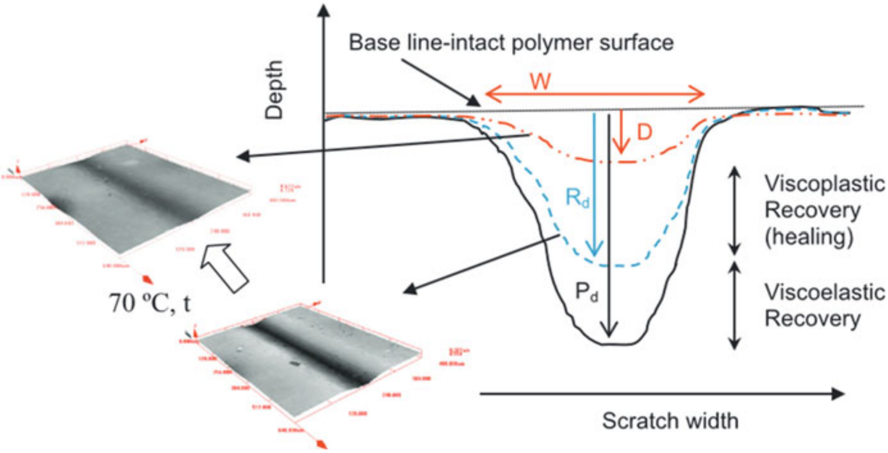

Fig. 21 Schematic representation of the quantification of the scratch healing behavior by the analysis of the residual volume of the scratch. (Reprinted with permission from Ref. [206])

also kinetic studies of the healing process itself would be possible. Such a system was developed by Garcia and coworkers [206]. This procedure requires the utilization of an indenter in order to induce defined cracks, which can later be utilized for the healing studies. Furthermore, the volume is measured using a confocal microscope, and the sample is placed on a heating stage, which enables the simulation of the required healing circumstances (Fig. 21). During the time the scratch is closed as well as the residual volume can be measured and be utilized for the analysis of the healing kinetics and the determination of the healing efficiency. This method was already used for different polymeric systems like ionomer [206], Diels-Alder crosslinked copolymers [57], tetrasulfide [78], or acylhydrazone-based networks [68].

Besides the investigation of the self-healing behavior itself, the characterization of the molecular processes, which enables this phenomenon, is a general important topic [198]. In particular, the behavior in the solid state is of great interest and cannot be simply transferred from solution investigations. Therefore, certain techniques are available which allow the analysis of the materials under healing conditions. The most efficient testing methods seem to be spectroscopic analysis like IR and Raman spectroscopy [198]. Both techniques were already utilized for such investigations, e.g., Raman spectroscopy was used for the analysis of the self-healing mechanism of metallopolymers [175]. The advantage with this kind of analysis is the specific study of molecular fragments which are responsible for the healing process. Thus, Bose et al. were able to follow the Diels-Alder units during thermal treatment and could show the opening of the Diels-Alder adduct at higher temperature [57]. This process is responsible for the generation of a mobile phase and finally for the healing process itself.

Both techniques are the most utilized methods for the understanding of the molecular dynamics. Furthermore, solid-state NMR [111] or scattering techniques like small angle X-ray scattering (SAXS) can be utilized to determine the behavior in the solid state [112]. Recently, a new method for the investigation of the self-healing phenomenon was presented by Garcia and coworkers [207]. The authors utilized broad dielectric spectroscopy in order to evaluate the flow behavior of the material.

5 Comparison with Other Material Classes

Self-healing materials are by far not limited to polymeric materials. Also other material classes have been investigated within this context. However, polymers are still the by far most studied self-healing material class. This fact can be related to the wide variety of different polymers available as well as the “easier” access to self-healing properties for polymeric materials compared to other systems. Considering the general mechanism, a mobile phase has to be generated. Within a typical polymeric material, the mobility can be provided by (liquid) healing agents as well as by elevated temperatures (ca. 100 °C). Metals as well as ceramics require much higher temperatures (close to 1000 °C) [17]. Particularly the former material class features another intrinsic drawback: The mobile species will be atoms compared to large polymer chains or segments.

Nevertheless, comparable approaches have been investigated for the other material classes. Self-healing metals are still the least studied material class [208]. One approach utilizes the precipitation of hard materials in growing voids (e.g., boron nitride). Similar to metals, most of the approaches for the healing of self-healing ceramics are based on high temperature processes [209]. Comparable to the above described encapsulation of healing agents, also oxidizable compounds (e.g., SiC, TiC) have been encapsulated within ceramics [210, 211]. A crack can be closed by heating resulting in the oxidation of the healing filler material resulting in the formation of an oxide, which closes finally the crack. Moreover, a special ceramic material, MAX phases, has been investigated. These materials can also form oxides upon heating resulting in a healing process [212–214]. Interestingly, concrete materials feature a similarly broad spectrum of different approaches for self-healing properties like polymers. The applied mechanisms range from the encapsulation, the design of damage-tolerant concretes combined with the “natural” ability of concrete for healing, to the encapsulation of bacteria, which can close the crack by precipitation of minerals [215–218].

6 Commercial Systems

The previous illustration of the wide variety of different self-healing polymeric materials sets expectations for further industrial/commercial applications of these materials. The field of smart polymers, particularly self-healing polymers, will strongly grow in the next years resulting in a market volume of 2.7 billion $ in 2020 [219].

However, not only the offered possibilities as well as the large versatility will determine the success of self-healing polymers, the “real” demands considering the corresponding applications will decide on the success. There are still some challenges to be solved to enable a commercial application of self-healing polymers:

- **Costs** – Many approaches are not based on the common commercial monomers as well as basic chemicals, resulting in higher costs of the resulting polymers. There is still a debate how much more expensive a self-healing material can be compared to the financial benefit which arises from the healing ability. For instance, the double lifetime of a self-healing polymer does not necessarily mean that the double price will be accepted. In fact, in certain application areas, the self-healing ability would be considered as additional asset of the next generation, which should come to the same (or even) lower price. Therefore it is not surprising that the current research on self-healing materials was mainly focused on areas which are not prize sensitive, i.e., aerospace and military.
- **Long-term stability/lifetime** – Many research studies show that the healing is possible multiple times. However, the calendrical lifetime is mostly neglected. Will the material still heal after 5 years?
- **Real-life applications** – The section on the characterization of self-healing polymers illustrated the importance for the selection of the right test/characterization method. Within the scientific community, there is a quest for more standardized test in order to enable a comparison of the performance of different materials. However, real-life applications would require a testing under the specific parameters.
- **Acceptance** – Interestingly, the field of self-healing polymers is easily comprehensible to the general public, e.g., terminology inspired by science fiction: terminator polymers [220]. Nevertheless, the fact that a (totally) new material was developed might hamper the application in more conservative industrial sectors.
- **Material properties** – Admittedly, many of the above described examples do not feature material properties relevant to typical applications. Future developments are required to achieve self-healing polymers with usable properties. Particularly, the supramolecular systems (as well as the highly reversible polymers) might feature an inherent disadvantage. The materials will show creep under load.
- **Need** – In the last years, polymeric materials have developed from *plastics* – sometimes synonymous used for material inferior quality – to high performance materials challenging other material class. For instance, the new generations of airplanes consist of >50% polymer composites as structural parts. Polymers have superseded metals. Considering the possibilities already offered by polymers as well as polymer composites, self-healing might currently be degenerated to a nice add-on instead of being a real asset. However, with a broadened view, self-healing is one aspect of smart materials. Different other properties as well as abilities (e.g., stimuli-responsiveness, shape memory, adaptive materials) will be inherent in the next generation of the materials we use.

Several of the above described general principles have been already utilized in commercial systems – extrinsic as well as intrinsic self-healing polymers have been utilized. The prime example, i.e., the capsule-based approach, has been commercialized by a company providing solutions for thermosets, coatings, as well as elastomers [221]. Hydrogen bonding self-healing polymers are offered by two companies: Arkema [222] as well as Suprapolix [223]. Another commercial supramolecular polymer is the ionomer Surlyn. The healing capability after ballistic impact is utilized in self-healing targets at shooting grounds [224].

The most common approach for commercial systems is self-healing polyurethane coatings, which are based on a network with a relatively low glass transition temperature. A scratch in the coating can be healed at elevated temperatures (e.g., warming by sunlight) due to the reflow of the material (see Fig. 22). These systems have been commercialized by several companies, including Covestro (formerly Bayer Material Science), Nissan, as well as Rühl. Besides the application as car coating, also the interior of cars (e.g., wooden steering wheel) is covered with this self-healing coating [225].

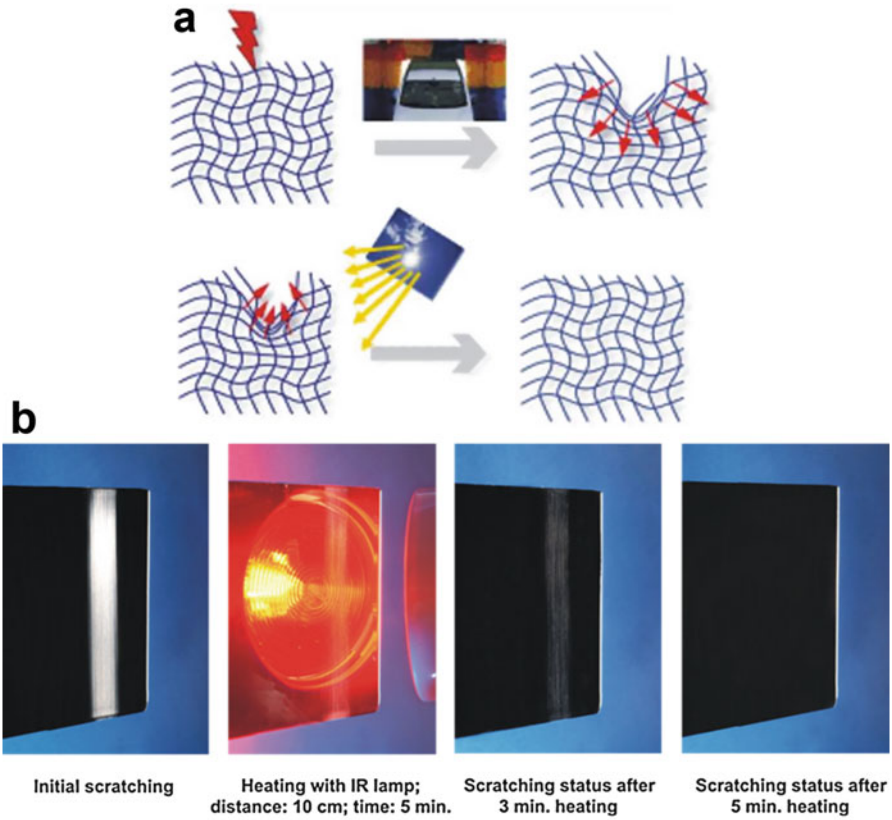

Fig. 22 Schematic representation of self-healing polyurethane coating. (**a**) Damage of the polymer network leads to deformation and gentle heating the restoration of the network. (**b**) Initial scratch is vanishing within few minutes. (Reprinted with permission of Covestro)

7 Conclusion and Outlook

Fifteen years ago, self-healing was introduced as a bioinspired research theme. Since this time, researchers aimed for the design of novel materials which feature this outstanding property. However, the comparison between natural and synthetic polymeric materials still is in strong favor for the biological systems; nature had several million years to perfect these materials. Nevertheless several new approaches have been studied in the last decade, and one can expect that the development will continue on a high level.

However, still some important challenges have to be solved. First of all the typical problems of both approaches (extrinsic and intrinsic) are in the main focus. Thus, the extrinsic systems will be developed toward longer stability against cracks enabling more healing cycles. For this purpose, the vascular networks will be of particular interest. However, a continuous flow of the healing agents even after several cracks has to be obtained. On the other hand, the intrinsic systems must be improved toward better mechanical properties. As it can be seen in Table 1, the most intrinsic self-healable materials feature poor mechanical properties with very low E-modulus values. Only the covalent systems based on the Diels-Alder reaction reported by Wudl and coworkers resulted in high moduli [51, 52]. Thus, the intrinsic systems and, in particular, the supramolecular materials have to focus on the combination of high mechanical stability and excellent self-healing properties.

Furthermore, the development toward multifunctional self-healing systems will be a major trend in the next years. Thus, the healing of functions and not only of the mechanical properties will be advanced. Additionally, the combination of both seems to be very promising, and some first results show the high potential of this research topic [185]. Nevertheless, the healing of specific functions is still in its beginning, and new general approaches will be studied in order to go the next steps to self-healing materials.

The development of new materials goes hand in hand with their characterization. However, a standard technique for the investigation of the self-healing phenomenon is still not available, and each material is tested differently [198]. Thus, it is hard to compare different types of polymers in terms of their ability to heal, but also regarding their mechanical properties. Nevertheless, the characterization has to be also suitable for the later application. For instance, the utilization as coating requires scratch healing, whereas bulk healing must be tested by tensile measurements. Therefore, the standardization of the characterization is required and further techniques must be developed.

The next years will provide more self-healing materials, which are based on their natural archetypes. Nature can still provide plenty of inspiration [226].

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