

Feature article

Improving autonomous self healing via combined chemical/physical principles



Philipp Michael, Diana Döhler, Wolfgang H. Binder*

Chair of Macromolecular Chemistry, Institute of Chemistry, Division of Technical and Macromolecular Chemistry, Faculty of Natural Science II (Chemistry, Physics and Mathematics), Martin-Luther-University Halle-Wittenberg, von-Danckelmann-Platz 4, Halle D-06120, Germany

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ABSTRACT

Chemical and physical principles to achieve self healing (SH) polymers with shape-persistent and multiple healing properties are reviewed, focusing on recent literature of the past ~10 years. The interplay of different healing principles in one and the same material, together with principles to achieve shape-persistent SH polymers (microphase segregation, cluster formation, nanofillers/nanocomposites, shape-memory effect) is discussed citing ~80 references.

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Since 2001 the first self healing (SH) polymer has been realized [1], a large body of principles, materials and functional applications of SH polymers in technology has been generated [2]. With the advent of SH materials not only a new vision of material science had been accomplished, but also the exploitation of highly sophisticated chemical and physical principles had entered the field of commodity polymers. Thus e.g. encapsulation techniques [2d] have been optimized to enable the controlled embedding of potentially reactive components [3] allowing sufficient fast crosslinking and consequently crack-repair after mechanochemical damage [4]. Besides the application of supramolecular bonds [5] which can act as reversible crosslinking systems and thus enable multiple SH principles [6], the optimization of reversible and irreversible covalent bonding systems as a responsive concept towards stress has been realized and forms the basis for a stress-dependent reactivity [7]. Chemically weak bonds (such as e.g. thiol-bonds [8]; reversible Diels–Alder systems [9], nitroxides [10], disulfides [8,11] and acylhydrazones [11a,12]) can now be used to tune the conditions, under which SH is taking place, including all stimuli-driven polymers. Thus, most of all the time scale required to achieve restoring of the initial materials properties, the required temperature at which SH takes place together with the initial materials properties can be adjusted. This in turn has allowed to generate a

vast multitude of polymers with SH properties, among them rubbers [13], coatings [2d,14], anti-corrosion systems [14c,15], thermal and light driven repair-approaches [11c,16], all exploiting different principles of repair.

Still there are three main issues of SH concepts which remain intensive areas of research (see Fig. 1): a) shape persistency and multiple SH in the same material, b) stress-sensing and SH and c) void-filling in SH processes.

As for the first issue, a major obstacle concerns the question: how can multiple SH materials with shape persistent properties be achieved? As supramolecular approaches contain dynamic bonds able to reorganize and remend themselves permanently, shape persistence of such materials requires additional structuring principles together with the SH ability on the correct time scale. Cluster formation [17], partial crosslinking [11b,18], microphase separation [19] or the introduction of nanocomposite-principles [20] are feasible solutions to the generation of SH materials bearing both properties, multiple healing and shape-persistence.

A second main issue concerns stress-sensing and site-directed SH at the damaged position. Stress-induced chemical reactions [21] together with other healing principles can present a viable strategy to detect and repair damage site-specific. Important for a successful design of SH materials is the careful adjustment of stress, required to break or activate the desirable bond useful for SH in relation to other bonds (e.g. supramolecular bonds [5,6] or other chemically labile bonds [8–12,22]). Only the presence of a careful interplay with other material properties such as the presence of

* Corresponding author. Tel.: +49 (0) 345 55 25930.

E-mail address: wolfgang.binder@chemie.uni-halle.de (W.H. Binder).

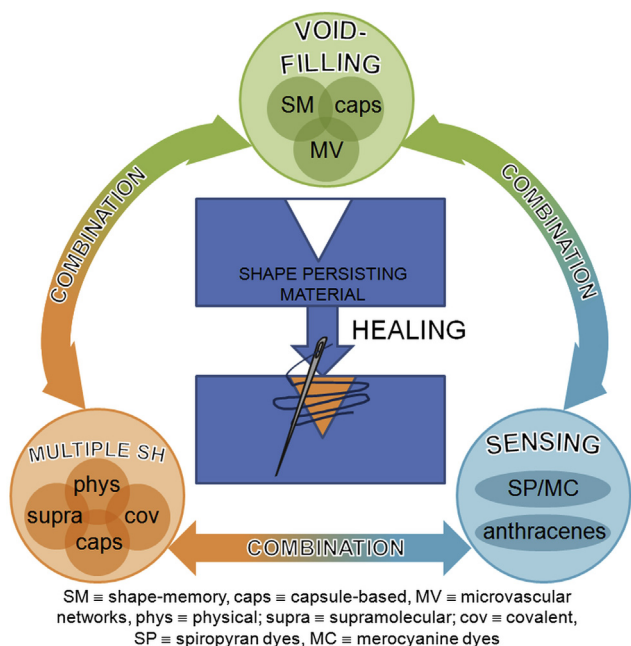


Fig. 1. Combinations of healing principles addressing improved void-filling of cracks via shape-memory (SM) assisted SH, capsule-based (caps) SH, or via microvascular networks (MV) to enable faster and more efficient healing; stress sensing in combination with void-filling or multiple healing concepts combined with either itself or covalent (cov) healing principles.

stiff (e.g. crystalline) domains, able to introduce additional network-points for a successful transmittance of force will enable the design of such SH-materials.

Finally, damage-induced voids need to be filled during SH processes in order to enable physical contact between the two ruptured sites, in turn leading to healing via network-formation. Basically void-filling is difficult, as additional material needs to be transported to the void during/before the healing is taking place. Besides relatively simple approaches (e.g. the use of continuous channel structures filled with liquid ingredients [23]) or the use of principles of shape-memory (SM) polymers [24] in combination with conventional healing principles are an important concept to enable a faster and more efficient SH. Together with site-specific stress-sensing [25], these methods can truly enable both – healing and identification of a damage site thus improving material safety significantly.

The current review is focusing on combinations of healing principles addressing three issues (see Fig. 1): improved void-filling of cracks, to enable faster and more efficient healing; stress-sensing in combination with healing, and multiple healing concepts combined with either itself or covalent healing principles. Important is the rationale that the combination of two or more SH principles yields an advantage in terms of initial physical properties and chemomechanical response. Furthermore, issues like the restoration of large damage volumes as well as the creation of shape-persistent but highly dynamic and sufficient SH materials are addressed.

1. Void-filling

SH polymers are defined as responsive polymeric materials which can repair upcoming mechanical damages such as cracks in an autonomous fashion. In order to enable an effective healing

without manual intervention by man or machine, the gap created by the rupture event must be closed autonomously. Therefore, the polymer chains need sufficient mobility for diffusion in order to bring reactive groups on the crack plane in close spatial proximity, in turn facilitating SH [16d].

At least in theory, void-filling can be achieved by relatively simple methods using microcapsules [1] or microvascular networks [26]. Accordingly, the created void volume is refilled by adding liquid material out of a reservoir to the crack plane, followed by subsequent triggering of network formation in turn restoring the material properties. Other approaches close the gap by more complex mechanisms, especially by so called SM [27] effects (see Table 1). SM polymers can be deformed by applying external stress and fixed in a second temporary shape [28], which persists until an appropriate stimulus induces the recovery of the initial shape. This behavior can be used for enabling physical contact between ruptured surfaces thus closing the gap. In order to fully restore the material properties it is important to combine those SH concepts with other principles which generate crosslinked networks (see Fig. 2).

One of the first true SH approaches filling cracks by insertion of additional material was developed by White et al. based on the ring opening metathesis polymerization (ROMP) of embedded dicyclopentadiene filled microcapsules [1]. Due to the autonomous release of the mobile healing agent into the crack plane by the damage event itself, the gap was physically closed and the subsequent network formation and re-bonding to the epoxy matrix enabled the restoration of material properties. Besides the limited amount of healing agent, the long healing time of 48 h complicated the healing of larger damage due to the weakening of the material by the damage event resulting in loss of strength and finally in loss of shape. One solution was to combine different SH concepts in a two-stage restoration strategy based on vascular networks [26c] (see Fig. 3). Two independent vascular systems are filled with reactive low-viscosity fluids. In the first step a dynamic gel is generated ensuring the fast closing of the gap (gel chemistry) and thus retaining the shape of the sample matrix. In the second, slower step a polymerization takes place, forming a stable covalently linked network in turn restoring the mechanical properties of the matrix material. The fast dichloroacetic acid catalyzed gel formation between Gelator type A (bis-acylhydrazine telechelic PEG) and Gelator type B (tris[(4-formylphenoxy) methyl]ethane) took place within a few minutes under formation of a semisolid, covalently cross-linked network based on dynamic acylhydrazone bonds. Subsequent polymerization of 2-hydroxyethyl methacrylate using cobalt naphthenate and methyl ethyl ketone peroxide as radical redox initiators restored the permanent network properties. The vascular nature of the embedded networks allowed the transportation of larger amounts of the healing agents to the damaged region compared to the microcapsule based approaches. Thus mm-sized impact regions were filled within 20 minutes while restoring the materials function within several hours, combined with an approximately 62% recovery of material properties.

Other elegant SH concepts for closing the gap between the cracked planes deformation are based on SM assisted SH. One of the simplest approaches followed the so called close-then-heal (CTH) mechanism. For this purpose, shape memory polyurethanes (SMPUs) as well as thermoplastic particles were embedded within a matrix material [29a,b]. In order to heal a crack, the composite was heated above the T_g of the SMPU fiber resulting in the activation of the SM effect. The shrinkage of the crack bridging SMPU fibers led to gap closure while bringing the crack planes into contact. Further heating resulted in the melting of the incorporated thermoplastic particles, enabling flow into the crack plane. After cooling to ambient temperatures, the molten thermoplast solidified

Table 1

Overview on SM assisted SH via I) thermally-induced, II) thermally- and light-induced, III) light-induced and IV) ultrasound-induced methodologies.

SM polymer	SH principle	T _{SM} [°C]	Healing conditions	η _{SH} ^b [%]	Ref.
I) Gelation + network formation	Gelation with 1: radical polymerization or 2: thiol-ene click reaction	–	T _{SH} = RT	62	[26c]
SMPUs + thermoplastic particles	Melting of thermoplastic particles and physical crosslinking/entanglement	62	T _{SH} = 80 °C	61	[29]
Polymer blends of linear poly(ε-caprolactone) and crosslinked poly(ε-caprolactone) networks	Melting and physical crosslinking/entanglement	55	T _{SH} = 80 °C	95	[14b,30]
Diethylenetriamine cured epoxy resin + SM alloys	Encapsulation of DCPD, ROMP	80	T _{SH} = 80 °C	80	[27,31]
Poly(urethane)s	DA and rDA reactions between maleimide and furan moieties	100	T _{SH} = 70–90 °C	85	[32]
Graphene-poly(acrylamide-co-acrylic acid) hybrid materials	Hydrogen bonding and π-π-interactions	37	T _{SH} = 37 °C	Quant. ^a	[33]
II) Polydisulfide networks containing crystalline regions	Disulfide exchange reactions	80	UV light of 320–390 nm, intensity of 2000 mW/cm ²	Quant. ^a	[11c]
III) Methacryloxypropyl-terminated polydimethylsiloxane (MAT-PDMS)	Encapsulation of MAT-PDMS and photopolymerization	–	Sunlight	72	[16f]
Cinnamide moiety containing PDMS (CA-PDMS)	Encapsulation of CA-PDMS and photodimerization	–	Sunlight	36	[34]
2-Ureido-4-pyrimidinone side groups + benzophenone side groups	Hydrogen bonding and photocrosslinking	65	UV-light of 365 nm, intensity of 5 mW/cm ²	Quant. ^a	[35]
IV) Poly(ε-caprolactone) based poly(urethane)s	DA and rDA reactions between maleimide and furan moieties	65	High-intensity focused ultrasound of 3 W	92	[36]

^a Quant. ≡ quantitative healing of the material properties.^b Percentage of self-healing.

and thus healed the damage. In order to expand this concept to larger volume damage, the SMPU fiber was modified with a two-step acrylic coating which enhanced the shape fixity and workability of the fiber [29c], in turn enabling repeated healing of wide-opened cracks with a healing efficiency up to 61%.

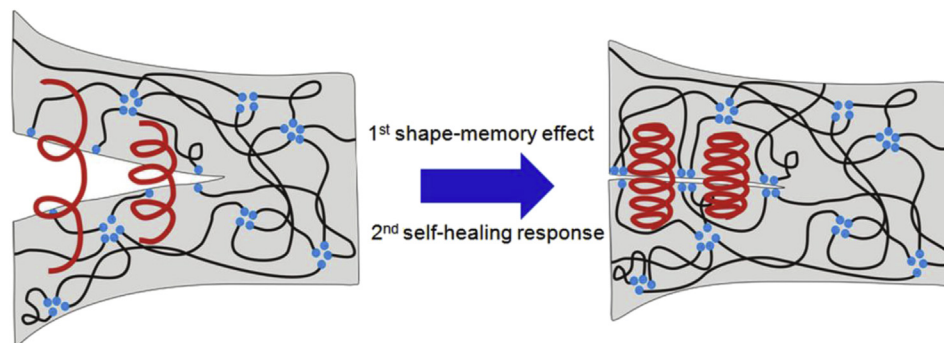
SM assisted SH can also be achieved by preparing polymer blends consisting of linear poly(ε-caprolactone) and crosslinked poly(ε-caprolactone) networks [14b,30]. Whereas the latter one is used to assist crack closure due to inherent SM properties, linear poly(ε-caprolactone) is applied as healing component activated by the same heating step used for the activation of the SM response.

Another smart example for the realization of SM assisted SH is the combination with microencapsulation concepts [27,31]. Thus, a SH system based on diethylenetriamine cured epoxy resin containing additional pretensioned shape memory alloy (SMA) wires was reported. The SH response was triggered by microencapsulation of the healing agent dicyclopentadiene (DCPD) which is released to the damaged area due to mechanical impact. The SM effect of the incorporated SMA wires was activated by inducing an electrical current heat within the material which induced the crack closure in turn supporting the microcapsule based SH behavior. Hence, the healing efficiencies increased from 49% up to 80% in case of combining the microencapsulation approach with SMA wires [27,31]. However, the SMA wires had to be arranged perpendicular

to the crack surfaces, thus hindering the realization of the concept for practical applications together with considerable processing complexity and increased material costs.

Besides heat also light can be used to trigger SM behavior. SH via photoinduced formation of new non-covalent or covalent chemical bonds across the generated crack surface thus enables to achieve an autonomous healing response outdoors [16d]. Light-triggered processes can be operated “on-demand” whereas remote activation as well as spatially controlled activation within a material are possible by irradiation. Optically controllable SM assisted SH materials based on a wide range of polymers can also be obtained by the addition of light-activatable nanoscale heaters like nanoparticles [16g], where localized heating effects trigger the healing response and activate the SM effect. Indeed, the crack then must be located on the surface or within a transparent material in order to achieve sufficient light-introduced healing.

A first example of an extrinsic, photo-induced SH matrix formulation based on the photopolymerization of methacryloxypropyl-terminated polydimethylsiloxane using encapsulated benzoin isobutyl ether as photoinitiator was reported [16f]. Upon 20 minutes of sunlight exposure a conversion of 72% was obtained, while the healing of a larger damage volume was achieved due to the applied encapsulation strategy. In contrast, a similar SH approach using a cinnamide moiety-containing PDMS

**Fig. 2.** Shape-memory (SM) assisted SH concept. Void-filling due to SM effects figured as contracted “spring” followed by SH (shown as a red spring) due to network formation.

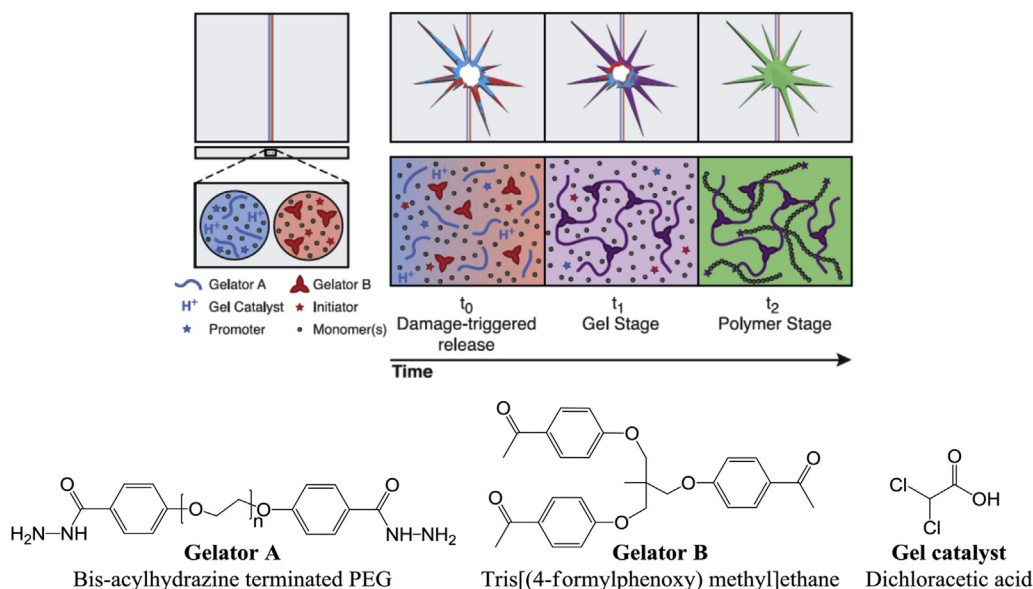


Fig. 3. Two-stage restoration strategy: Two independent vascular systems (red and blue channels) filled with low-viscosity fluids were ruptured at t_0 and release their content onto the crack plane. Subsequently a gel is generated (purple) ensuring the fast closing of the gap, followed by a slower polymerization stage (green) restoring the material properties. The chemical structures of the Gelators A and B as well as of the crosslinking catalyst are shown below. Reprinted from Ref. [26c] with permission from AAAS.

resulted in a photo-induced healing efficiency of 36%, although a prolonged sun-light exposure of 6 h was required [34] to effect this healing efficiency.

Another approach of a light-triggered SM assisted SH material is based on the dense incorporation of dynamic and reversible 2-ureido-4-pyrimidinone side groups together with benzophenone side groups, the latter acting as photoactive moieties, forming weakly crosslinked elastomers via a covalent network, additionally reinforced via the hydrogen bonding-moiety [35].

Indeed, the differentiation between thermal- and light-introduced SM assisted SH is not always trivial so that a combination of both stimuli can be useful in particular cases. Thus, covalently crosslinked but structurally dynamic polydisulfide networks containing crystalline regions as physical crosslinks were reported [11c]. Due to reversible disulfide exchange the so created material possessed thermally induced SM properties and a light-triggered SH response. Upon UV-exposure for 5 minutes correlating to a temperature increase up to 78 °C, a complete scratch recovery was observed, whereas no significant healing was accomplished after heating to 110 °C.

A third option to trigger SM assisted SH is the use of ultrasound prior to a precise damage localization. Thus, an ultrasound-induced directed and localized healing of a poly(ϵ -caprolactone)-based polyurethane, dynamically crosslinked by Diels–Alder chemistry of attached furan and maleimide groups, was reported [36] (see Fig. 4). Upon ultrasound treatment, equivalent to an temperature increase from 37 to 90 °C the so created polymer showed a repeatable SH ability within 60 minutes with a healing efficiency of 92% after the first, 84% after the second and 70% after the third healing cycle due to SM assisted crack-closure. In contrast, healing experiments at 90 °C resulted in decreasing healing efficiencies, thus emphasizing the importance of the mechanical vibration of the ultrasound wave facilitating SH via retro-Diels–Alder reactions.

Poly(urethane)s, bearing maleimide and furan moieties linking thermally induced SM, display assisted repeatable SH properties with healing efficiencies of around 85% [32].

In order to further enhance mechanical properties as well as SM properties graphene sheets were incorporated to obtain graphene-poly(acrylamide-co-acrylic acid) hybrid materials [33]. When

incorporating 10 – 30 wt% graphene, a self-healable hard-soft system, analogous to thermoplastic elastomers due to the “zipper effect” of a dynamic hydrogen-bonding network within the soft phase, was created. Thus, complete SH of a cut specimen as well as shape-recovery was observed after 30 minutes heating to 37 °C [33].

2. Multiple SH concepts

Multiple SH concepts require dynamic bonding/debonding strategies when embedded into a shape-persistent material. Often the lifetime of the used dynamic bonds [5,17,37], together with clustering effects [17] and substructure formation [5] can define the actual time scale and number of repetition cycles and thus the repeatability of SH. However, up to now no clear connection between the individual dynamics of a supramolecular bond and the SH property of the final materials has been accomplished, as not only the dynamics of the supramolecular bond alone determines the overall dynamics of the final network [38].

Basically, three different principles can be used to effect the generation and maintaining of shape-persistent materials with still SH properties: in the first one (a, see 2.1) two interwoven networks (irreversible/reversible [39]; reversible/reversible [11a,b,11d,12,16e,18b,40], see Table 2 and Fig. 5) can act together, one generating shape, the other SH properties. In this case usually the rigidity of one network can influence the dynamic properties of the second (usually SH) network, thus requiring a delicate balance between the dynamics of both networks.

Prominent examples are based on either the combination of two supramolecular bonding principles (e.g. hydrogen bonds/metal-coordination [40f,g], hydrogen bonds/ π -interactions [40j]), the combination of a supramolecular network with a covalent bonding strategy [11b,11d,12,16e,40h,i] (e.g. (photo-)crosslinked supramolecular networks [16e,39a–c,40i]), two covalent networks [39a] or on networks based on hydrogel formation [18b,40a–e].

The second strategy (b, see 2.2) is based on multiphase polymer systems [9,19,20,41] composed of a hard and a soft polymer block while taking advantage of phase-separation effects providing both

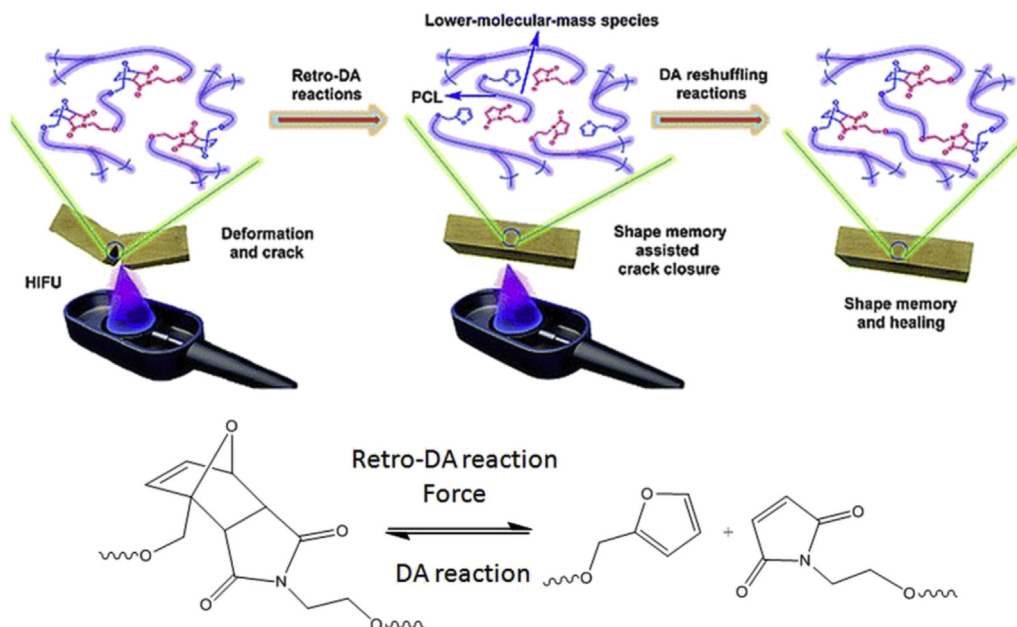


Fig. 4. Schematic illustration of ultrasound-induced SM assisted SH of poly(ϵ -caprolactone)-based polyurethanes reversible crosslinked via Diels–Alder reactions of furan and maleimide moieties. Reprinted and adopted from Ref. [36] with permission from The Royal Society of Chemistry.

mechanical stability and thus a shape-persistent material with still sufficient dynamics required to achieve a SH response.

The third strategy effecting the generation of shape-persistent SH materials (c, see 2.3) involves a (usually nanoscaled) filler (such as nanocellulose [20,42], graphene oxide [43], metal nanoparticles [44]) which act as the shape-generating principle, together with a SH material, resulting in SH nanocomposites [20,42–44]. Again, the polymer/filler interaction will drastically change the SH properties and time scales, thus requiring a careful design of competitive material properties.

2.1. Multiple SH concepts based on two interwoven networks

2.1.1. Irreversible – reversible SH

A simple and efficient competing network design based on two covalent networks is generated via a bio-inspired photo-curable polymer network by incorporation of dopamine acrylamines into an irreversible thiol-ene network [39a]. Whereas an increase in the

dopamine acrylamide content resulted in improved mechanical properties and improved macroscopic adhesion due to hydrogen bonding interactions, a decrease in the crosslinking density of the thiol-ene network was observed at the same time.

Light-induced scratch healing in less than 1 h was reported for poly(urethane) networks containing oxetane-substituted chitosan precursors [39b,c]. During UV irradiation chitosan chain scission occurred, resulting in the formation of two reactive radicals which can further react with the oxetane ends resulting in an irreversible crosslinked material, in turn leading to the restoration of the material properties. The process is highly sensitive to the stoichiometry of the individual components as well as to their acidity. Furthermore, repeated healing at the same position was limited due to a lack of oxetane rings during healing used up in the previous healing cycles.

Room temperature SH concepts can also be realized by efficiently catalyzed covalent cross-linking reactions. Thus, the copper-catalyzed azide-alkyne “click” cycloaddition (CuAAC) [45] reaction

Table 2
Multiple SH concepts based on two interwoven networks to effect SH materials with shape-persistent properties: I) irreversible/reversible SH, II) reversible/reversible SH.

	SH concept	1 st SH principle	2 nd SH principle	Healing conditions	η_{SH} [%]	Ref.
I)	Thiol-ene polymer networks	Thiol-ene “click” reaction	Hydrogen bonding	UV light (16 mW/cm ²)	–	[39a]
	Oxetane-substituted chitosan	Chitosan chain scission and radical recombination	Hydrogen bonding	UV light (302 nm, 120 W)	–	[39b,c]
	poly(urethane) networks					
	CuAAC-based networks	CuAAC	Ionic interactions	T_{SH} = RT	–	[39d]
II)	Polybenzoxazine precursor-based network formation	Friedel–Crafts reaction	Hydrogen bonding	T_{SH} = 160 °C	Quant. ^a 55	[39e]
	Catechol-based healing of hydrogels	Metal ligand interaction	Hydrogen bonding	T_{SH} = RT	–	[40c,d]
				–	70	[40e]
				T_{SH} = RT	99	[18b]
	Host-guest polymer networks	Metal ligand interaction	Host-guest interaction: crown ether based molecular recognition	T_{SH} = RT	Quant. ^a	[40f,g]
	PDMS-based networks via dynamic exchange reactions	Acylhydrazone exchange	Hydrogen bonding	T_{SH} = RT	90	[12]
	Urea-urethane-based networks	Reversible urea bond formation	Hydrogen bonding	T_{SH} = 37 °C	87	[40h]
		Disulfide exchange	Hydrogen bonding	T_{SH} = RT	Quant. ^a	[11b,11d]
		π - π stacking	Hydrogen bonding	T_{SH} = 100 °C	95	[40j]

^a Quant. \equiv quantitative healing of the material properties.

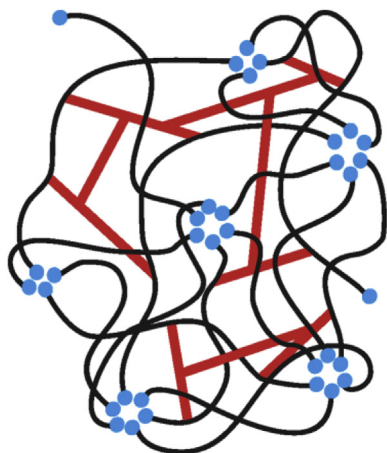


Fig. 5. Schematic illustration of an interwoven network structure consisting of two different networks, crosslinked via covalent bonds and/or supramolecular interactions. blue spheres: network with SH properties, red lines: shape generating (covalent) network.

enabled fast crosslinking kinetics resulting in irreversibly linked rubbery materials [3,46]. Hyperbranched azide- and alkyne-functionalized poly(isobutylene)s chosen due to their high molecular mobility linked to fast gelation times below 1 h, resulting in high network densities [39d]. Four-arm star poly(isobutylene)s with azide endgroups and thymine hydrogen bonding moieties, applicable for a “click” crosslinking process were investigated, taking advantage of reversible supramolecular cluster formation and thus supramolecular network formation [18a]. Following this approach a weakly crosslinked covalent network strengthened by thymine interactions was obtained. SH studies of the double network structure revealed multiple SH at 20 °C within 24 h.

A single-time SH concept for high-temperature applications was accomplished by incorporating poly(bisphenol-hexamine benzoxazine) into a polysulfone matrix providing good stability as well as toughness at even elevated temperatures [39e]. After keeping a cut material for 4 h at 160 °C a toughness recovery of 55% mainly via hydrogen bonding interactions of the sulfone and hydroxyl groups, was reported. Furthermore, the thermally induced ring-opening reaction of the polybenzoxazine precursor resulted in additional irreversible network formation during the progressing Friedel–Crafts reaction [39e].

2.1.2. Reversible – reversible SH

Many recent SH hybrid hydrogels [18b,40a–e] and adhesives with bonding/debonding properties working under harsh environmental impact are inspired by mussel adhesive proteins. A high content of 3,4-dihydroxyphenylalanine (DOPA) is required resulting in the formation of reversible metal ligand interactions with Fe^{3+} and thus in a SH response [40a,b]. While undergoing a typical mussel-mimetic acidic-to-alkaline pH change the covalent Fe^{3+} -catechol network – present at acidic pH – was reinforced by

the increasing introduction of Fe^{3+} -catechol coordination bonds, which reversibly rupture during a damage event [40c].

SH within minutes was reported for dynamically reversible and stimuli-responsive host-guest polymer network gels [40f]. Thus, transparent polymer gels, moldable into shape-persistent objects with good mechanical properties were created by orthogonal self-assembly of a bis(dialkylammonium salt)-based monomer and a bis(benzo-21-crown-7)-based monomer. The SH properties were additionally supported by the formation of metal-ligand interactions between the triazole rings and $[\text{PdCl}_2(\text{PhCN})_2]$ [40f].

Stimuli-responsive supramolecular polymer networks with tunable topology and a SH response were created on the basis of host-guest interactions between a dibenzylammonium salt and dibenzo-24-crown-8 together with additional metal-ligand interactions between triazole rings/ $[\text{PdCl}_2(\text{PhCN})_2]$ or terpyridine ligands/ $\text{Zn}(\text{OTf})_2$ [40g].

SH resulted in 90% recovery of strain within a couple of hours [12] for double dynamic polymer networks prepared by a polycondensation reaction between carbohydrazide and a soft siloxane-based dialdehyde (see Fig. 6). Bis-iminourea-type subunits provided hydrogen bonding interactions and exchangeable acylhydrazone units allowing repeatable SH with mechanical integrity. It was found that the healing response was mainly attributed to hydrogen bonding interactions as the addition of an acid catalyst designed to accelerate acylhydrazone exchange did not improve healing efficiencies [12].

Poly(urea)s (PUs) and poly(urethane)s are an important class of polymers, where the introduction of SH properties is an important perspective for materials science due to their broad application range. In order to obtain autonomous repair of PU at low temperatures urea groups with bulky substituents like 1-(*tert*-butyl)-1-ethylurea were applied [40h]. Due to the reversible dissociation into amine and isocyanate-groups, the materials (containing approximately 15% DMF as swelling agent) form a multiple healing system able to heal within several hours, restoring mechanical properties due to the network reinforced by stiff hydrogen bonding interactions.

The inherent reversibility of disulfide bonds, such as bis(4-aminophenyl) disulfide, have found application as dynamic crosslinkers within poly(urea-urethane)s aiming at the design of an elastomeric network which can be easily (re-)processed in a hot press within 20 minutes while applying a pressure of 30 bar at 150 °C [11b,11d]. Quantitative healing was obtained after 24 h at room temperature due to a constant aromatic disulfide exchange as well as quadruple hydrogen bonding between the urea groups [11d].

Beside dynamic covalent and supramolecular SH concepts also various other supramolecular interactions can be used to create repeatable double SH poly(urethane)s with outstanding mechanical properties. Thus, Burattini et al. [40j] reported an elastomeric supramolecular and self-healable polymer blend comprised of a pyrenyl-functionalized poly(urethane) and a chain-folding polyimide resulting in a nanophase-separated morphology. After

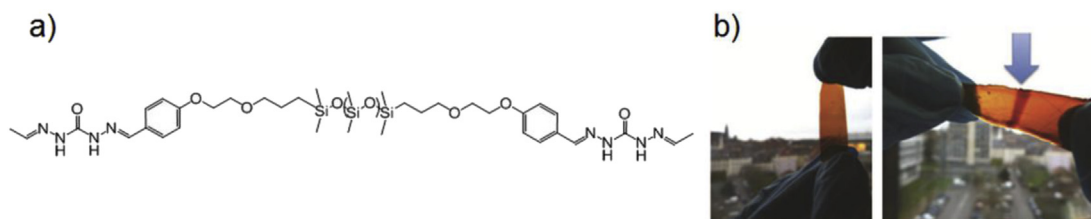


Fig. 6. a) Chemical structure of the condensation product from carbohydrazide and siloxane-based dialdehyde. b) left – virgin soft polymer film; right – cut and healed sample with healed overlapping domain (see arrow). Reprinted from Ref. [12] with permission from John Wiley and Sons.

Inspired by the preparation of SH materials with exchangeable weak covalent bonds [8] the mechanism of strain recovery and the influence of the fraction of labile and permanent bonds was investigated using a hybrid computational model [41a–c]. Calculations have proven a competitive effect between the rate and the extent of strain recovery with increasing energy of the labile bonds. Thus, an increased time scale needed for strain recovery was observed while increasing the labile bond energy resulting in a tougher material. An increasing quantity of permanent bonds enabled improved and faster strain recovery even after several stretch–relaxation cycles. Thus, guidelines for tailoring the toughness and strength of SH polymers and polymer composites were established providing the basis for the development of SH concepts [41a–c].

Consequently, segmented poly(urethane)s prepared by stiff and hydrogen bonded hard peptide segments (acting as one phase) can be reinforced by introducing maleimide groups suitable for thermally reversible covalent crosslinking via Diels–Alder chemistry [41e] in turn achieving a SH response (see Fig. 7). High-performance polymer films with enhanced mechanical properties were obtained which were recycled within 5–20 minutes at temperatures ranging from 160 to 180 °C - a high temperature attributed to the strong poly(urethane) network.

The design of multiphase supramolecular thermoplastic elastomers [19a] composed of two polymer blocks which can undergo phase-separation was realized, where one phase (the stiff phase) acts as a reinforcing structure to the material, whereas the other phase serves as the mobile and in turn SH part of the material (see Fig. 8).

While embedding a hard polystyrene backbone within a soft polyacrylate-amide matrix a SH rubber with outstanding high modulus was obtained. After contacting the cut surfaces, SH proceeded due to reversible hydrogen bonding interactions between the amide groups revealing a recovery of approximately 92% after room temperature healing for 24 h [19a].

A similar approach was reported for an ABA supramolecular block copolymer composed of a poly(*n*-butyl acrylate) soft block and a polystyrene hard block connected via dimerizing 2-ureido-4-pyrimidinone hydrogen bonding moieties [19b]. However, healing required a temperature of 45 °C for 18 h, resulting in a recovery of the tensile strength of about 90%. In contrast, complete healing at room temperature within 24 h was observed for two-phase hard-soft core-shell nanoparticles composed of crosslinked polystyrene nanoparticles and a grafted poly(acrylate amide) shell due to dynamic hydrogen bonds within the shell [41d].

2.3. SH nanocomposites

Various other SH concepts based on the incorporation of nanomaterials have been reported in literature [20,42–44] leading to an enhancement of SH properties as well as to an increase of the mechanical stability. Supramolecular hydrogels composed of hard cellulose nanocrystals were reported [20]. While providing mechanical strength as well as sufficient dynamics, fast SH was realized due to host-guest interactions between cucurbit[8]uril and naphthyl- or viologen-functionalized polymers even upon aging of the hydrogels for months. Similar results were obtained by blending poly(vinyl alcohol), nanofibrillated cellulose and borax due to the formation of inter- and intramolecular hydrogen bonds as well as diverse borax complexes [42].

A further increase of mechanical properties can be achieved via superparamagnetic Fe₃O₄-doped SH gels based on host-guest interactions between β -cyclodextrin and *N*-vinylimidazole [44b]. While applying a magnetic field, healing was speeded up from 24 h to 3 h obtaining SH efficiencies of 95%. Control experiments pointed

out that simple heating did not result in increased healing efficiencies emphasizing the impact of the additionally introduced magnetocaloric effect [44b].

Graphene oxide was applied to reinforce double-network composite hydrogels where SH was attributed to hydrogen bonding interactions and to coordination interactions between graphene oxide nanosheets [43a]. Thus, an excellent healing ability was demonstrated with 88% recovery of tensile strength within 24 h [43b]. Self healable thermoreversible elastomers [43c] were obtained, where an incorporation of less than 2 wt% of graphene oxide resulted in an increased mechanical strength while repeated healing was realized within 1 h. Similarly, the incorporation of gold nanoparticles was applied to reinforce the materials properties [44a]. Thus, flexible and tough polymer films were prepared while blending a polydiimide and a pyrene-functionalized polyamide with pyrene-functionalized gold nanoparticles whereas complete healing was achieved within 10 minutes at 50 °C.

3. (Stress-)sensing concepts

Stress-sensing is one of the crucial points in order to prevent catastrophic failure of manmade materials. If a pending damage can be identified and repaired in an early stage, the capability and safety of items can be increased and a too early damage of a material can be avoided. In the best case, stress-sensing and autonomous damage healing should go hand in hand. Beside the well known ultrasonic sensing [47], piezoelectric monitoring [48] and optical fiber-type sensors [49], stress-sensing can be enabled if mechanochemical activatable groups or bonds are incorporated within a material. Such groups can convert a mechanic stimulus, like damage or stress of a material into quantifiable, often optical

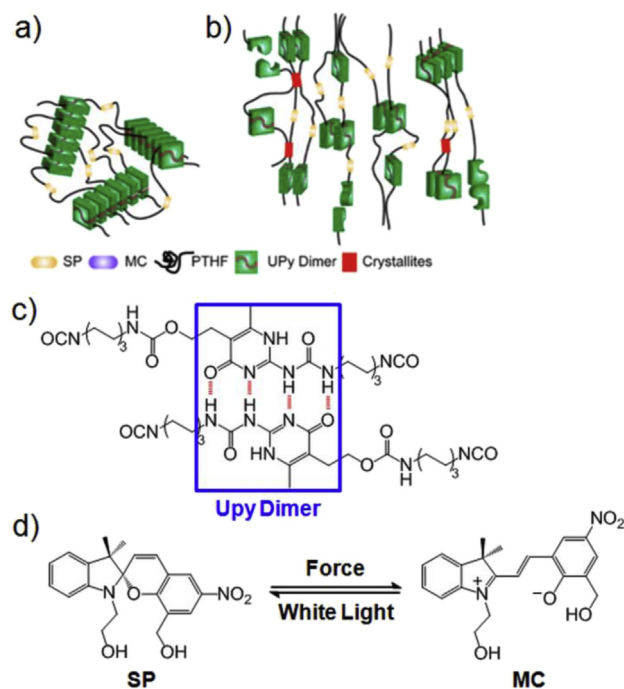


Fig. 9. Proposed mechanism of mechanochemical activation of SP (stretching axis is vertical); virgin state (a) Stretching of the sample leads to strain induced crystallization of pTHF as well as partial decomposition of UPy stacks and/or hydrogen bonds; (b) Activation of SP to MC; (c) Chemical structure of reversible hydrogen bonded physical crosslinker 2-ureido-4-pyrimidinone (UPy); (d) Mechanochemical activation of colorless spiropyran (SP) to colored merocyanine (MC) and white light induced ring-closing from MC to SP. Reprinted from Refs. [52a,f] with permission from the American Chemical Society. Copyright 2014.

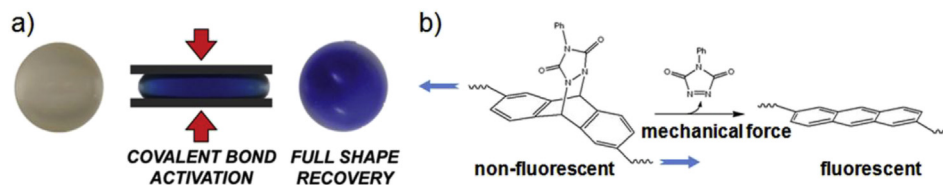


Fig. 10. a) PDMS based networks combining stress-sensing via mechanochemical colorimetric SPs activation with full shape recovery properties; b) Non-fluorescent phenyl-triazolinedione-anthracene adduct acting as stress sensing mechanophore within a PDMS network. Via force-induced retro-Diels-Alder reaction fluorescent 4-phenyl-1,2,4-triazoline-3,5-dione is released. Reprinted from Ref. [55] with permission from the American Chemical Society. Copyright 2014.

signals. Hence, those chromophores display at least two different stages, one “unstressed” inactive and one “stressed” activated. Examples for those functionalities are various proteins [50], poly(3-hexylthiophene)s (P3HT) [51], spiropyranes (SP) [7,52] and 1,2-dioxetanes showing mechano-chemiluminescence [53].

A smart concept combining self-sensing and SH properties was developed by embedding mechanochemical activatable spiropyranes (SP) as chromophore within a physical and chemical crosslinked network based on poly(urethane)s (see Fig. 9) [52a,b,52f]. Spiropyranes can undergo a force-induced 6- π electrocyclic ring-opening reaction from a colorless SP to a colored merocyanine (MC) [7,52] allowing direct spatial and temporal visualization of the concealed damage. Moreover, the light induced ring-closing reaction from MC to SP allows to regenerate the colorless state and thus the recyclability of stress-sensing after accomplished SH. The SH ability of the developed concept is based on the reversible crosslinking of hydrogen bonding 2-ureido-4-pyrimidone (UPy) moieties, additionally incorporated within the poly(urethane) network. The hard/soft character of the formed poly(urethane) network consisting out of soft pTHF and hard UPy segments supports the SH behavior and promotes the activation of the SP stress-sensors. The interplay between stress-sensing and damage event must be tuned carefully, so that the SPs are just activated after fragmentation of the UPy hard domains, thus preventing inadvertent sensing of non-existent damage.

A similar approach is based on the development of a polymeric material possessing damage sensing and SH properties at the same time [52c]. SP moieties and 2,6-bis(1,2,3-triazol-4-yl)pyridine (BTP) are incorporated within the same poly(urethane) backbone. The SP groups again act as stress sensor, while BTP is able to coordinate to various metal ions leading to the formation of a hard/soft segment dominated network. The breaking of metal/ligand interactions as well as the rupture of hard segments and their subsequent reformation leads to SH behavior. A full restoration of mechanical properties can be achieved in the presence of Zn^{2+} ions, however only in the presence of a solvent mobilizing the polymer chains.

Other concepts are based on fluorescent crack sensors [54] where the mechanochemical activation yields fluorescence at the site of the damage. For this purpose, two anthracene derivatives, 9-anthraldehyde and 9-anthracenecarboxylic acid grafted onto poly(vinyl alcohol) can be photo-dimerized, in turn yielding non-fluorescent cyclooctane-type dimers, which act as crosslinking points. Upon cracking, the initial anthracene derivatives were regenerated by mechanochemical cycloreversion and exhibited strong optical absorption and fluorescence emission. Thus, the crack plane can be visualized by fluorescence emission of 500–600 nm when excited with 330–385 nm UV light. The possibility of crosslinking by light induced re-dimerization of the anthracene derivatives revealed potential healing properties.

Another approach combines stress-sensing of the colorimetric mechanophore SP with shape recovery properties of poly(dimethylsiloxane) (PDMS) networks (see Fig. 10a) [55]. Bis-alkene functionalized SPs were incorporated within a PDMS network via platinum catalyzed hydrosilylation. The reversible activation of the

SP was proven over multiple cycles of tensile elongation with full shape recovery. Shape recovery of soft PDMS materials opens the door for a wide range of application including repeatable activation of stress sensors without loss of activity as well as the opportunity for multiple closing of cracks, created by stress or damage events. Phenyltriazolinedione-anthracene can act as an alternative stress sensing mechanophore within a PDMS network (see Fig. 10b). This mechanophore is able to release 4-phenyl-1,2,4-triazoline-3,5-dione via a force-induced retro-Diels-Alder reaction. The thus induced re-planarization of the anthracene component enables the visualization of damage by fluorescence emission when excited with appropriated UV light [55].

4. Conclusions

Based on the recent efforts a considerable progress in the design of polymers with self healing properties has been achieved, most of all via the many physical and chemical principles of polymer science, accumulated during the past decades. It is obvious that basic research principles (such as e.g. the understanding of polymer dynamics via polymer physics) together with chemical endeavors (such as the knowledge of activation energies or the development of “click”-chemistry or the exploitation of reversible covalent bonds) is required for the successful design of the desired material properties. A clearly visible progress has been achieved in systems, where two or more healing principles are combined in one material/polymer. Especially the use of reversible (supramolecular) bonding principles with covalent chemistry or nanofillers to generate two or more interwoven networks with (partial) reversible properties has lead to materials with nearly unlimited tunability in terms of healing-conditions, triggered healing and still a reasonable mechanical strength. Also the advent of mechanochemical principles enabled to introduce sensing-principles for stress detection or site-specific healing efficiency. It will be decided within the next years whether these highly sophisticated methodologies truly will be reflected in applicable and affordable materials science and technology. Thus, the application of SH materials and SH polymers is transferred to many industrial materials – the future has just begun with a rejuvenated polymer science.

Acknowledgment

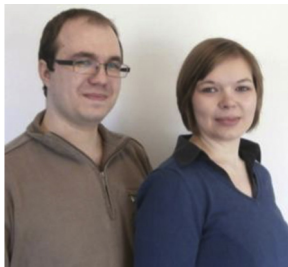
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Diana Döhler was born in Werdau (1988) and **Philipp Michael** was born in Halle (1986). Both studied chemistry at the Martin Luther University Halle-Wittenberg and completed their Master of Science in 2011. They already worked on supramolecular polymers as well as on self-healing materials together with Professor Binder during their Master theses dealing with the investigation and the improvement of room temperature based click-reactions for self-healing applications. Currently, Diana Döhler and Philipp Michael are PhD candidates in the research group of Professor Binder. Now, their current research interests include supramo-

lecular chemistry, self-healing polymers as well as mechanochemistry.



Wolfgang H. Binder is currently full professor of Macromolecular Chemistry at the Martin Luther University Halle-Wittenberg (since 2007). Being born (1969) and raised in Vienna (Austria), he studied chemistry at the University of Vienna and conducted a PhD in organic chemistry (1995). After postdoctoral stays (1995–1997) with Prof. F. M. Menger (Emory University, Atlanta, USA) and Prof. J. Mulzer (University of Vienna), he completed his habilitation at the Vienna University of Technology (TU-Wien, 2004), where he was Associate Professor from 2004–2007. Subsequently he moved to the MLU Halle-Wittenberg as a Full Professor in 2007. His research interests include polymer synthesis, supramolecular chemistry, self-healing polymers and nanotechnology – for

details see www.macrochem.uni-halle.de.