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Improving autonomous self healing via combined chemical/physical principles

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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

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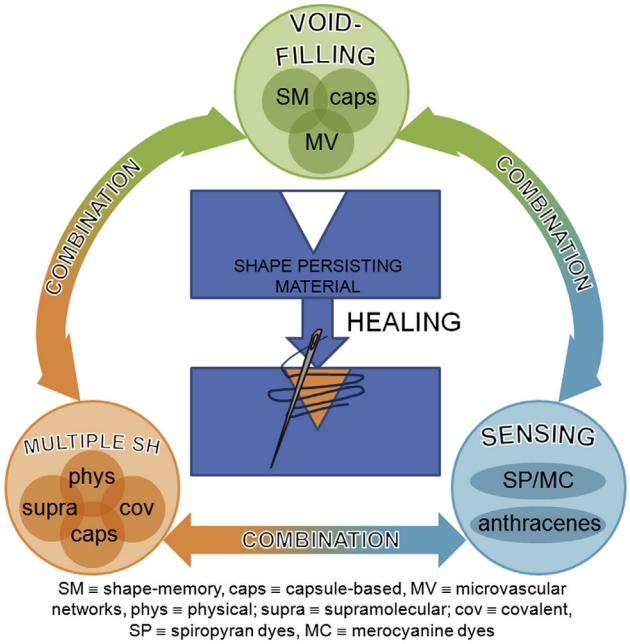

Fig. 1. Combinations of healing principles addressing improved void-filling of cracks via shape-memory (SM) assisted SH, capsule-based (caps) SH, or via microvascular networks (MV) to enable faster and more efficient healing; stress sensing in combination with void-filling or multiple healing concepts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

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