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Supramolecular Materials

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Hard Autonomous Self-Healing Supramolecular Materials—A Contradiction in Terms?[**]

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hydrogen bonds · mechanical properties · phase separation · self-healing · thermoplastic elastomers

Self-healing and self-repair are crucial to the survival of living species. In contrast, the lifetime of synthetic man-made materials is limited by the occurrence of macroscopic damage or microcracks that severely decrease performance, eventually leading to failure. Intrigued by the beauty and efficiency of natural healing processes, scientists have developed a new research area focusing on synthetic self-healing materials aiming to extend their lifetimes, improve safety, and ensure sustainability.

White and co-workers first reported autonomous self-healing polymeric materials based on so-called thermosets, that is, hard materials with a Young's modulus of 3–10 GPa. Microcapsules incorporated in these materials contain the healing agent while the catalyst for the healing polymerization reaction is dispersed in the polymer matrix.[1] When a crack forms, the capsules are broken and the healing agent is released, pulled into the crack by capillary forces, and exposed to the catalyst, leading to polymerization and crack repair. Although this seminal report initiated the entire field of self-healing materials and this microcapsule approach shows great promise for extending the lifetime of thermoset materials,[2] it is still far away from the sophistication of natural healing mechanisms for two main reasons: 1) Owing to the loss of capsules upon healing, the repair is a one-time healing process rather than a continuous regeneration of the material properties; 2) Microcapsules can only efficiently repair microcracks since insufficient healing agent is available for larger defects. Inspired by nature, White et al. have proposed the use of vascular channels with healing agent to overcome these limitations.[3]

A second major breakthrough in the development of autonomous self-healing materials was achieved by Leibler and co-workers, who developed a supramolecular self-healing rubber (Young's modulus not reported; for soft rubbers it is typically 1–10 MPa), which is held together by hydrogen-bonding interactions.[4] The healing is based on the reversibility of the hydrogen bonds, which are the weakest links and are selectively broken upon rupture. Bringing the cut surfaces back into contact restores the hydrogen-bonding interactions, allowing complete healing of the materials even after complete rupture. More recently, autonomous supramolecular self-healing has been extended towards, for example, hydrogels based on electrostatic as well as host–guest interactions.[5]

The supramolecular self-healing mechanism, which is based on the reversible and dynamic nature of the supramolecular interactions, poses severe limitations to the mechanical properties of the material. The importance of chain dynamics and mobility for self-healing has been nicely illustrated by Sun et al. with a polyelectrolyte multilayer coating that was able to heal only in the presence of water, which decreased the Young's modulus from 12 GPa to 0.44 MPa.[6] One could conclude that autonomous supramolecular self-healing is possible only for soft rubbery materials that have sufficient chain dynamics above the glass transition temperature of the material. Therefore, hard autonomous self-healing supramolecular materials may be considered as a contradiction in terms… or not?

Several relatively hard supramolecular self-healing materials have been developed recently.[6–8] However, these materials require external triggers to induce healing by increasing the mobility of the supramolecular building blocks, thereby enabling reformation of the supramolecular bonds that were broken during rupture. Light-induced self-healing was reported by Rowan, Weder, and co-workers for metallo-supramolecular materials based on very soft oligo(ethylene-*co*-butylene) chains with metal-coordinating ligands as end groups that are chain-extended by metal complexation.[7] Bulk microphase separation, that is demixing on the nanometer length scale, between the soft rubbery polymer phase and the metal complexes yields a thermoplastic elastomer with a storage modulus of 60 MPa. Light irradiation induces selective heating of the metal-complex phase, providing sufficient mobility for self-healing by shifting the supramolecular equilibrium towards uncomplexed species with lower molecular mass, which results in the flow of the material into damaged areas. Upon cooling the complexes are reformed and the original bulk material properties are restored. In

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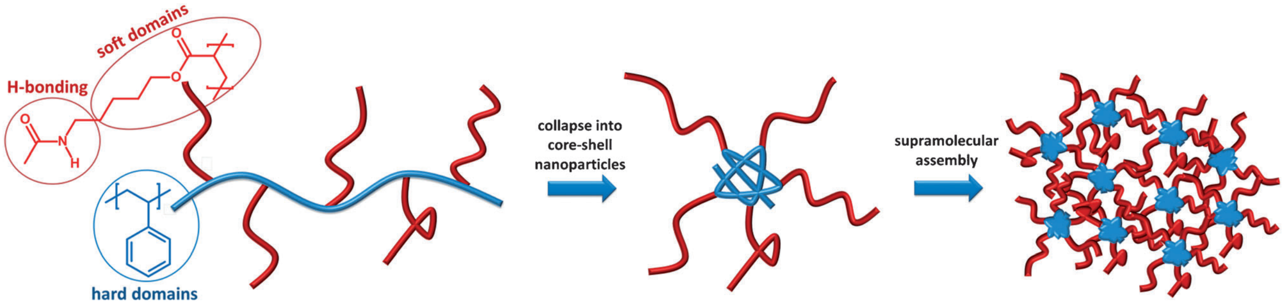

Figure 1. A multiphase autonomous self-healing thermoplastic elastomer based on graft copolymers with a polystyrene backbone and secondary amide containing grafts for hydrogen bonding.[10]

more recent work a porous membrane with pressure-induced self-healing has been developed by Barboiu, Quemener, and co-workers based on ABA triblock copolymers consisting of hard poly(styrene-*co*-acrylonitrile) outer blocks and a soft hydrophilic poly(ethylene oxide) middle block; these copolymers self-assemble into 50 nm flowerlike micelles that pack into a three-dimensional porous structure during spin-coating.[8] The flowerlike micellar structure deforms under flow pressure, enabling the dynamic repair of a 110 μm hole in a 1.3 μm thick porous film. The dynamic repair is ascribed to structural deformation of the micelles as well as exchange of intermicelle crossing triblock copolymers. These two examples demonstrate that harder self-healing supramolecular materials can be obtained based on phase-separated materials. However, in both cases the supramolecularly interacting moieties, that is, metal complexes or physical crosslinks, are located in the hard domains, and thus external stimuli are required to increase chain dynamics and induce healing of the materials.

The apparent intrinsic limitation of autonomous self-healing supramolecular materials, namely that they must be soft rubbers, has recently been overcome by Guan and co-workers, who developed a relatively hard thermoplastic elastomer with a Young's modulus of up to 36 MPa;[9] this material displays autonomous self-healing at ambient conditions, even after complete rupture.[10] This unprecedented combination of materials properties and self-healing ability is based on a multiphase design, in which polystyrene hard domains provide good mechanical properties and a soft matrix featuring supramolecular hydrogen-bonding interactions between secondary amides is responsible for the healing behavior (Figure 1).

Still the question remains, how do these materials benefit from the presence of the hard domains? The answer most likely lies in the multivalent design of the materials that are based on graft copolymers with a polystyrene backbone (100 repeat units) and methyl amide functionalized acrylate side chains (5–10 grafts having 80–200 repeat units) providing up to 1000 amide hydrogen-bonding moieties per polymer chain. Subsequent collapse of these graft copolymers into core–shell nanostructures and supramolecular assembly into phase-separated bulk materials yields stable thermoplastic elastomers (Figure 1), although very slow elongation will result in creep due to slippage of the hydrogen-bonding interactions. Furthermore, the authors demonstrated that the healing ability significantly deteriorates when the time between cutting and healing is extended. This is ascribed to the dynamic rearrangement of the cut surfaces to reform hydrogen bonds and most likely also to the migration of the amide moieties into the material to expose the more hydrophobic aliphatic groups to the surface; similar observations were described by Leibler et al.[4] Very recently, related autonomous self-healing thermoplastic elastomers with a Young's modulus of up to 38 MPa[9] have been reported by Guan et al. based on poly(styrene)-*block*-poly(*n*-butyl acrylate) block copolymers bearing a strong quadruple hydrogen-bonding unit on the poly(*n*-butyl acrylate) terminus which displays multivalent reversible supramolecular association of the soft matrix.[11]

The era of supramolecular self-healing materials has in recent years evolved from autonomous self-healing supramolecular soft rubbers to non-autonomous, quite hard supramolecular materials because of the incompatibility of dynamic supramolecular healing with low chain mobility in hard materials. The work by the Guan group now demonstrates the feasibility of creating relatively hard supramolecular thermoplastic elastomers (Young's modulus up to 38 GPa)[9] with autonomous self-healing abilities at ambient conditions. This demonstrates that hard supramolecular self-healing materials might not be a contraction in terms, after all. Without doubt this work will open up a new class of phase-separated supramolecular self-healing materials with great promise and further extensions towards even harder autonomous supramolecular self-healing materials, possibly even thermoset materials. It should be noted, however, that another yet unavoidable limitation of supramolecular self-healing materials, namely the relatively short time for effective healing, still remains an open challenge in the field.

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