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Self-Healing Polymeric Materials: On a Winding Road to Success

Self-healing represents a next-generation technology in response to the common demands of polymeric materials for long-term stability and durability. It mimics the capability of naturally occurring species like living organisms to autonomously recover nonfatal harm. The damages inevitably generated during fabrication and service are allowed to be unconsciously repaired on a microscopic scale, and would no longer develop into macroscopic failures like the case of conventional materials.

In comparison to metals and ceramics, polymers have distinctive molecular structures composed of repeating units typically connected by covalent bonds. Synthesis of macromolecules requires relatively milder conditions (*e.g.*, lower temperature and pressure), so that rehabilitation of polymers and polymer composites may be more easily implemented by taking advantage of various physical, chemical and physicochemical interactions.

The systematic academic exploration of crack self-healing can be traced back to the late 1970s, when R. P. Wool and co-workers studied the healing theory involved in thermoplastic polymers. They pointed out that the healing process goes through five phases: (i) surface rearrangement, (ii) surface approach, (iii) wetting, (iv) diffusion and (v) randomization, and the last two can be described using the reptation model. In 1990s, the investigation was further extended to thermosets. During the repair study of vinyl ester resin, for example, the critical strain energy release rate of the interfaces after crack healing (*i.e.*, annealing above the glass transition temperature) was found to be 1.7% of the virgin value, and lower crosslinking density favored the repair effect. More importantly, the applicability of hollow glass tubes filled with polymerizable medium (such as cyanoacrylate) was identified during this period. Breakage of the brittle-walled vessels upon cracking of the matrix material led to liberation of the included fluidic rejuvenator, which subsequently flowed to the damaged zones *via* the capillary effect and was polymerized to re-bind the cracks.

The worldwide research interests in this aspect were aroused after the publication of the communication about microcapsules aided self-healing of cured epoxy by S. White and his colleagues in the University of Illinois at Urbana-Champaign in the journal *Nature* in 2001. Since then, more and more people have been attracted by the promising field of study. Moreover, an "international race" started at 2007, which is still in the ascendant nowadays, as reflected by the boom of quantities of the studies published, patents filed, and affiliations of the authors/applicants. In the same year, the first special issue on the subject in scholarly periodical appeared in the *Journal of the Royal Society Interface* and the *First International Conference on Self-Healing Materials* was held in Noordwijk aan Zee, Netherlands. Then, for the convenience of further study, the self-healing polymers were classified into two categories in 2008 according to the origination of healing capability. That is, (i) extrinsic self-healing materials in which healing agent has to be pre-embedded, and (ii) intrinsic ones that are able to repeatedly heal cracks by the polymers themselves in principle without worrying about depletion of healing agent like the extrinsic version.

In the case of extrinsic self-healing, the matrix polymer itself lacks intrinsic self-healing mechanism. Healing agent has to be stored in some media (micro-pipelines and microcapsules) and filled into the materials in advance. Many efforts have been made to verify the effectiveness of different types of micro-pipelines. In addition to the hollow glass tubes mentioned above, hollow glass fibers, hollow carbon fibers, hollow polymer tubes, hollow metallic tubes, compartmented fibers and electrospun core-shell nanofibers were successively utilized by different laboratories. The three-dimensional microvascular networks are another type of micro-pipelines. Minor damage to the same area can be repeatedly healed owing to the vascular nature of the supply system.

Similarly, various types of microcapsules were proposed to encapsulate healing agent following the pioneering work of S. White's group: single-capsule system, capsules/dispersed catalyst system, phase separated droplets/capsule system, double-capsules system, and all-in-one microcapsules system. The diverse combinations of the polymerizable chemicals and catalyst/hardener enable different freedoms of materials design and applications. With respect to the fabrication of the healing capsules, although a variety of alternative techniques are available, they have to be tailored to satisfy the requirements of specific self-healing materials. In this context, although polymers used to act as the shell material in most cases, inorganic ones (*e.g.*, silica, glass and metals) have also been employed to construct the capsules shell walls, providing much lower permeability. Besides, the following chemical reactions of healing agent have shown their competent to re-bond the fractured interfaces: ring-opening metathesis polymerization, polycondensation, anionic ring-opening polymerization, cationic polymerization, free radical polymerization, and addition reaction.

As for intrinsic self-healing, which initially took care of repairing of thermoplastics *via* thermal activation induced macromolecular chains entanglements across the cracked interface, proved to be applicable to ionomers and crosslinked polymers in the early 2000s. Particularly, intrinsically self-healable polymer networks based on reversible covalent chemistry or supramolecular interactions have become the main subject of study. For example, Diels-Alder (DA) cycloaddition between multi-furan and multi-

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maleimide monomers was used to produce a thermally remendable crosslinked polymer. No catalyst was needed for the crack healing of the material. Furthermore, complete restoration of tensile properties was observed in a supramolecular rubber formed in the mixture of a large number of di- and tri-functional building blocks with various strong hydrogen bonding urea and amide molecules. Driven by these attempts, a series of other reversible bonds and reversible reactions, such as photo-reversible cycloaddition, hydrolysis-bonding equilibrium, exchange reactions of disulfide, boronic ester and C=N bonds, homolysis of alkoxyamine, transesterification, π-π stacking, ionic interaction, host-guest interaction, and metal ligand coordination, were introduced into a variety of networked polymers and enabled self-healing under different stimuli.

The recent progress indicates that the objective of self-healing lies in restoration of not only mechanical performance but also functionalities (*e.g.*, electrical, optical and physicochemical properties), and the latter accounts for a remarkably increasing proportion. Self-healing skin-inspired electronics, for example, which allow for advanced health monitoring, disease detection, medical therapies and human–machine interfacing, have been developed. Meanwhile, self-healing wearable electronics, self-healing energy storage devices and self-healing supercapacitors are also receiving growing attention. Both extrinsic and intrinsic self-healing have contributed to the relevant healing paradigms. Accordingly, the microencapsulated healing agent was changed from reactive chemicals to the suspension containing carbon nanotubes or even low-melting point metals for reconstruction of the broken electrical pathways in conducting composites. Another example showing the works correlated to self-healing functional materials towards recovery of deteriorated functions can be the transparent poly(ethylenimine)/poly(acrylic acid) film. The reduced transmittance of the material due to abrasion can be repeatedly regained by making use of water assisted electrostatic and hydrogen interactions. On the whole, self-healing has been a standard configuration of many new materials and devices.

Self-healing materials have opened up broad prospects for key engineering communities and cutting-edge technologies. Furthermore, a few new spin-off techniques were also derived, like reprocessing, reshaping and recycling, topology rearrangement of traditionally non-reworkable thermosetting polymers. The new possibilities go beyond the scope of classic polymer engineering and enrich the measures of material diversification.

It is worth noting that, however, there has not yet been a landmark example of commercial application in this aspect. The forecast about rapid growth, which was made about two decades ago when self-healing was in an embryonic stage, turns out to be over-optimistic. It means that great efforts have to be made to tackle the challenges from multiple sources, as partially illustrated by the representative cases hereinafter. (i) Coupling self-healability with high strength. Self-healing fiber-reinforced polymer composites have been an important target of aviation and automobile industrials. Nevertheless, the intrinsic self-healing systems developed so far have not yet reached the strength of commercial one, and the healing efficiencies of extrinsic self-healing composites are mostly lower than the intrinsic versions. (ii) Autonomously triggerable intrinsic self-healing. Mostly, intrinsic self-healing of polymers cannot take effect upon damaging like the extrinsic self-healing materials by making use of crack response of healing capsules. A possible solution lies in the application of mechanochemistry. It was showed that the mechanochemically initiated cascading variation of metal-ligand coordination bonds enables self-blocking and self-healing of early minor damages in polymers. (iii) Mass production methods. The research activities so far have rarely dealt with preparation of self-healing materials in terms of industrial technologies. The issues like cost effectiveness, processing windows, accessibility of raw materials remain open. Therefore, a large number of people with engineering backgrounds should join the research ranks. (iv) Longevity. The topic is critical for application but very few studies were carried out, probably because of the time-consuming experiments. The main concern lies in the gradual reduction of the healing efficiency induced by the deactivation and leakage of encapsulated healing agents during storage or the decay of reversibility of the reversible bonds.

In China, the researches on self-healing have become an active branch of polymer science and engineering, and a few latest achievements were included in a special issue of the *Chinese Journal of Polymer Science* in 2021. Chinese researchers play an important role in this area. As the next step, the transfer of the results of basic research to industrialized applications should be the focus. There is a greater need for comprehensive investigations on larger scale that consider practical scenarios, besides the laboratory-scale studies dealing with proof-of-principle experiments, prototype formulations and molecular structures. Only when the knowledge of self-healing is brought into play in market, its value for promoting development of sustainable society can be embodied.

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The views expressed in this editorial are those of the author.

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