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BASICS OF SELF-HEALING: STATE OF THE ART

1.1 BACKGROUND

Polymers and polymer composites have been widely used in tremendous engineering fields including aerospace, marine, automotive, surface transport and

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Self-Healing Polymers and Polymer Composites, First Edition. Ming Qiu Zhang, Min Zhi Rong.

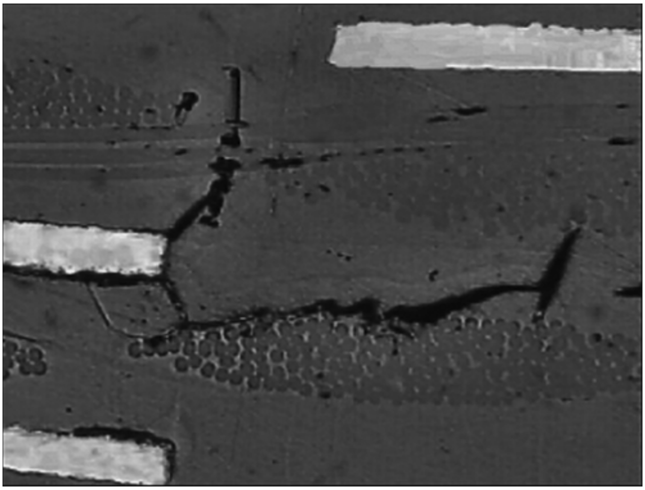
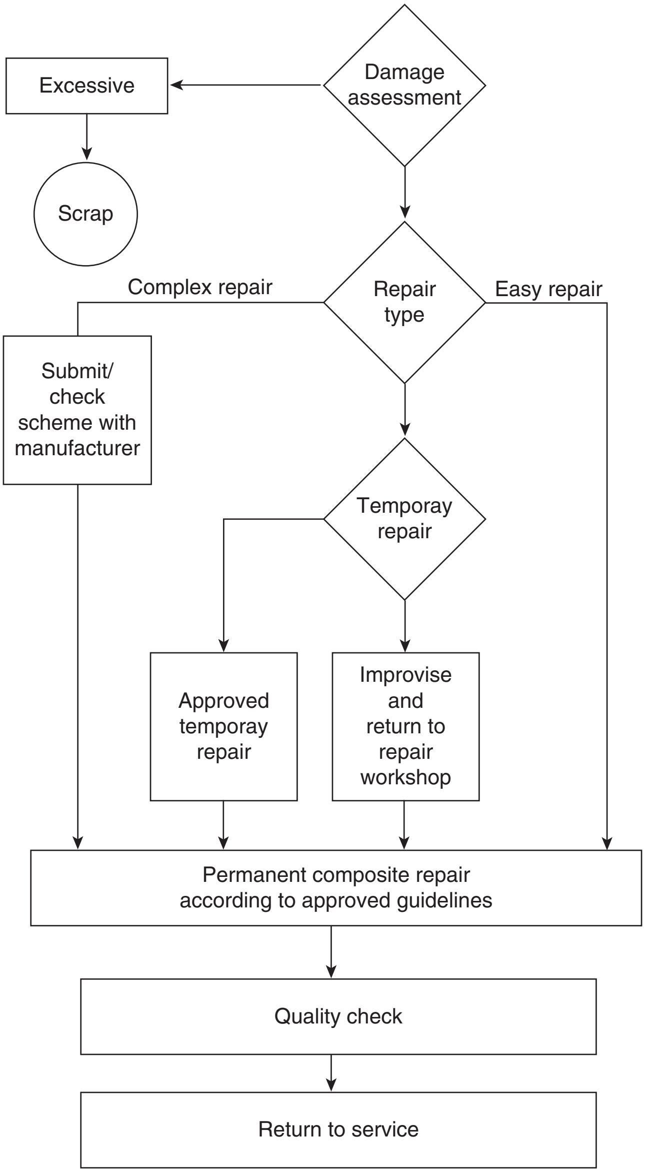


Figure 1.1 Cohesive failures beside plated through holes on copper clad laminates, which used to be produced by thermal stress. (See color insert.)

sports equipment because of their advantages including light weight, good processibility, chemical stability in any atmospheric conditions, etc. However, long-term durability and reliability of polymeric materials are still problematic when they serve for structural application [1, 2]. This is particularly true when impact resistance is concerned, a critical aspect of vehicle design. The lack of plastic deformation in the materials results in energy adsorption via the creation of defects and damages. Besides, exposure to a harsh environment would easily lead to degradations of polymeric components. Comparatively, microcracking or hidden damage is one of the fatal deteriorations generated either during manufacturing or in service as a result of mechanical stress or cyclic thermal fatigue (Fig. 1.1). Its propagation and coalescence would bring about catastrophic failure of the materials and hence significantly shorten lifetimes of the structures.

1.1.1 Adhesive Bonding for Healing Thermosetting Materials

Damaged composites or composite structures should be repaired in time when significant structural degradation is detected [3]. The routine repair procedures for thermosetting composites are shown in Scheme 1.1. Some damage to composites is obvious and easily assessed, but in some cases, the damage may first appear quite small, although the real damage is much greater. Impact damage to a fiber can appear as a small dent on the reinforced composite surface, but the underlying damage can be much more extensive. The decision to repair or scrap is determined by considering the extent of repair needed to replace the original structural performance of the composite [4]. Other considerations are



Scheme 1.1 Flow chart of the key stages for thermosetting composite repair.

the repair costs, the position and accessibility of the damage and the availability of suitable repair materials. Easy repairs are usually small or do not affect the structural integrity of the component. Complex repairs are needed when the damage is extensive and the structural performance of the component needs to be replaced. The best choice of materials would be to use the original fibers, fabrics and matrix resin. Any alternative would need careful consideration of the service environment of the repaired composite, i.e. hot, wet and mechanical performance. The proposed repair scheme should meet all of the original design requirements for the structure. Some repairs need the specialist equipment of the workshop, and some form of improvised repair is needed to return the component to a suitable repair workshop. A temporary repair, usually in the form of a patch, can be fixed to the component. Usually a "belt and braces" approach is taken to ensure safety until the component can be repaired at a later date.

Most damages to fiber reinforced polymer composites are a result of low velocity and sometimes high velocity impact [5]. In metals the energy is dissipated through elastic and plastic deformations, and a good deal of structural integrity is still retained. Whilst in polymer composites the damage is usually more extensive than on the surface. The typical damages are summarized in the following: (i) delamination following impact on a monolithic laminate; (ii) laminate splitting, which does not extend through the full length of the part (its influence on the mechanical performance depends on the length of split relative to the component thickness); (iii) heat damage, a local fracture with separation of surface plies (its effect on the mechanical performance depends on the thickness of the part); (iv) dents in sandwich structure; (v) puncture damage in a sandwich structure and (vi) bolt hole damage, which could be elongation of the hole causing laminate splitting, or damage to the upper plies.

Patch repair, a main technique based on adhesive bonding, involves covering or replacing the damaged portions with a new material [5–7]. It restores the load path weakened or removed by damage or cracking, ideally without significantly changing the original load distribution. Reinforcements or doublers are used to replace lost strength or stiffness, correct design errors, or improve performance [8]. Because the main purpose of composite repair is to fully support applied loads and to transmit applied stresses across the repaired area, the patch repair materials must overlap and be adequately bonded to the plies of the original laminate. In this case, the thickness of the original laminate is made up with filler plies and the repair materials are bonded to the surface of the laminate. The advantages of this approach include (i) quick and simple to do and (ii) minimum preparation, while the repaired laminate is thicker and heavier than the original and careful surface preparation is needed for good adhesion. The degree of property recovery is a function of bonding between the patch and the original material, the presence/orientation of reinforcing fibers and patch thickness [6, 9–12].

In addition to patch repair, there are two similar techniques: (i) taper sanded or scarf repair and (ii) step sanded repair. For the first one, an area around the hole is sanded to expose a section of each ply in the laminate. Sometimes one filler ply is added to produce a flatter surface. Taper is usually in the region of 30–60:1. Comparatively, the repaired version is only marginally thicker than the original. Because each repair ply overlaps the ply that it is repairing, a straighter and stronger load path is obtained. The freshly exposed

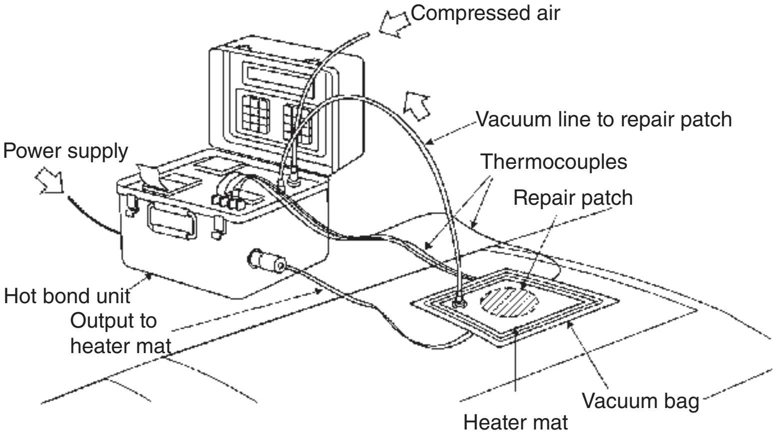


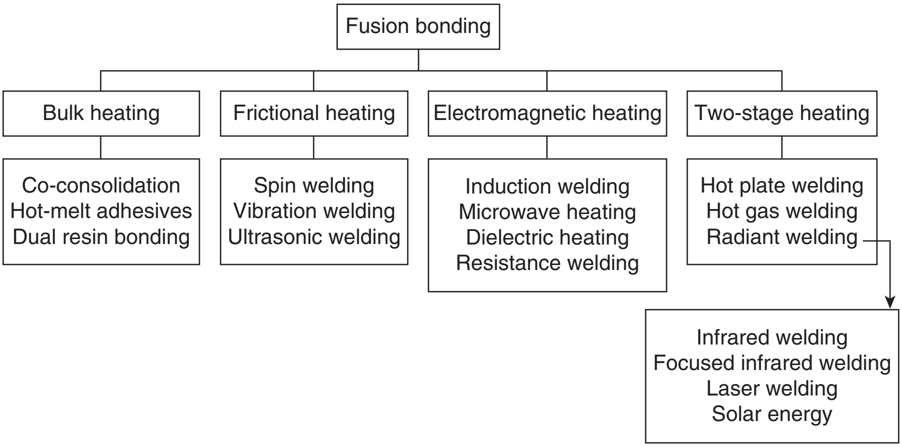
Figure 1.2 Typical lay-up and equipment for one side access repair of thermosetting composites [4].

surfaces help to achieve tight bonds at the interface. With respect to the second method, the laminate is sanded down so that a flat band of each layer is exposed, producing a stepped finish. Typical steps are 25–50 mm per layer. Nevertheless, it is worth noting that the method needs high skill and is difficult to do.

To conduct bonded external patch repair for structural components, equipment and ancillaries have to be employed (Fig. 1.2). The vacuum bag is suited to components with thin sections and large sandwich structures. It involves the placing and sealing of a flexible bag over a composite lay-up and evacuating all of the air under the bag. The removal of air forces the bag down onto the lay-up with consolidation pressure of 1 atmosphere. The completed assembly, with vacuum still applied, is placed inside an oven with good air circulation, and the composite is produced after a relatively short cycle cure.

1.1.2 Fusion Bonding for Healing Thermoplastic Materials

In general, the aforesaid thermosetting adhesive bonding is not directly transferable to thermoplastic polymer based composite. Fusion bonding, or welding, a long-established technology in the thermoplastic industry, offers an effective way for rejoining fractured surfaces with thermal flowability [13]. Although welding may induce residual stresses if performed without adequate control, it eliminates the stress concentrations created by holes required for mechanical fasteners and so does thermosetting adhesive bonding. In addition, welding reduces processing times and surface preparation requirements [14]. However, the high content in carbon fiber reinforcement in the composites, resulting in high thermal and electrical conductivity, imposes difficulties such as uneven heating, delamination and distortion of the laminates. These



Scheme 1.2 Fusion bonding techniques [13]. Reprinted from Ageorges, C., Ye, L., and Hou, M. Advances in fusion bonding techniques for joining thermoplastic matrix composites: a review. *Composites, Part A: Applied Science and Manufacturing 32*, 839–857. Copyright 2001, with permission from Elsevier.

problems become more difficult when bonding large components [15]. In addition, as fiber volume fraction increases, the amount of resin available to melt and reconsolidate into a fused joint is reduced and this can affect the welding quality [16].

Fusion bonding techniques can be classified according to the technology used for introducing heat [13, 16] (Scheme 1.2), namely bulk heating (co-consolidation, hot melt adhesives, dual resin bonding), frictional heating (spin welding, vibration welding, ultrasonic welding), electromagnetic heating (induction welding, microwave heating, dielectric heating, resistance welding) and two-stage techniques (hot plate welding, hot gas welding, radiant welding).

Bulk heating techniques such as autoclaving, compression molding or diaphragm forming are available for performing co-consolidation [17]. Co-consolidation is an ideal joining method as no weight is added to the final structure, no foreign material is introduced at the bond line, essentially no surface preparation is required and the bond strength is potentially equal to that of the parent laminate. However the entire part is brought to the melt temperature, and this generally implies the need for complex tooling to maintain pressure on the entire part and to prevent deconsolidation. Hot melt thermoplastic adhesive films may be inserted at the bond line to improve filling of parts mismatch. Inserting of an amorphous polymer interlayer proved to reduce the scatter of strength [18], which widens the processing window. The dual resin bonding, or amorphous bonding, involves comolding an amorphous thermoplastic film to a semicrystalline thermoplastic matrix laminate prior to bonding [19]. During the joining step, the amorphous polyetherimide (PEI) film can be fused at a temperature above its glass transition, below the melting temperature of the semicrystalline polyetheretherketone (PEEK) polymer, avoiding any deterioration of the bonded structure [20].

Spin welding and vibration welding have been extensively used in the plastics industry but are less appropriate to joining thermoplastic composites because the motion of the substrates relative to one another may cause deterioration of the microstructure, such as fiber breaking. The process was however investigated for joining carbon fiber/PEEK [16] and glass fiber/polypropylene (PP) [21] systems. Microwave and dielectric welding are available for joining thermoplastics [22], but the fact that heating occurs volumetrically and that multilayer composites are excellent shields in the microwave range [23] make these techniques poorly suitable to the welding of thermoplastic composites particularly when they are reinforced by carbon fibers.

Ultrasonic welding [24], induction welding [25] and resistance welding [26] are the three most promising fusion bonding techniques. Only the welding interface is brought to the melting temperature, and the effect on the rest of the structure is minimized. Welding times are very short. Large-scale welding may be performed through sequential or scanning approaches, and online monitoring of the consolidation is possible.

In two-stage techniques the heating device needs to be removed from between the substrate surfaces between the stages of heating and forging. This aspect involves limitations on size of the component because the whole welding surface must be heated in a single step [27]. Heating times are normally long because they rely on the low thermal conduction of heat through the polymer. Between the heating and forging steps, surface temperature drops and the region experiencing the maximum temperature is located below the skin of the laminate. The high pressure required to consolidate the bond line may cause warpage/flow in the higher temperature inner region [22].

1.1.3 Bioinspired Self-Healing

Although the repair strategies discussed in the last sections have demonstrated their capability of recovering the load bearing property of polymers and polymer composites, the complicated procedures typically represented by Figure 1.2 manifest that they are time consuming and cost ineffective, let alone the losses resulting from malfunction of the components. The possible solution of this problem lies in early elimination of cracks, so that no macroscopic damage would eventually occur. As the cracks deep inside the materials are difficult to be perceived and to repair, the materials had better have the ability of self-healing like biological systems.

In fact, self-healing is almost universal in nature. Most structures can repair themselves, after undergoing nonfatal trauma or injury [28–33]. Exceptions are teeth and cartilage, which do not possess any significant vascularity. It is also true that brains cannot self-repair; however, other parts of the brain take up the lost functions.

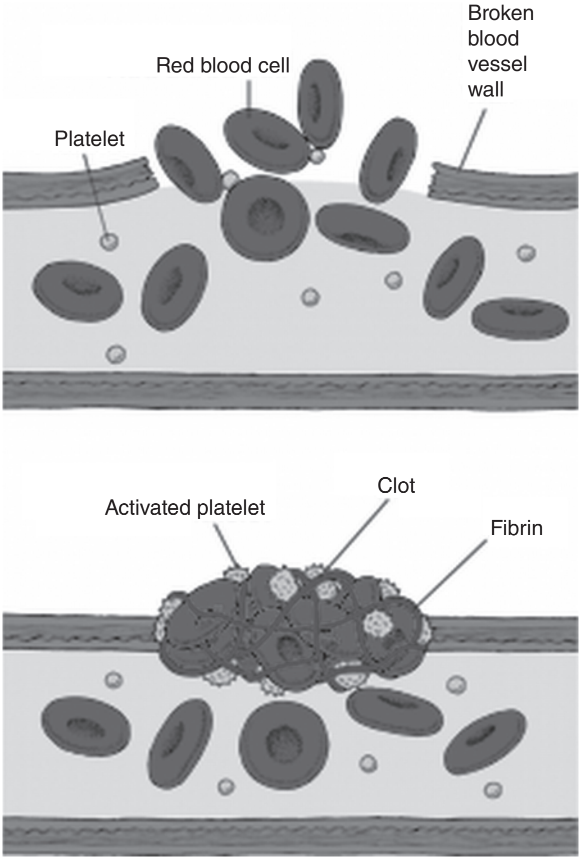


Figure 1.3 Blood clotting in an injured vessel [34]. Reprinted from Porter, R.S. (ed.). *Merck Manual of Medical Information—Second Home Edition*. Copyright 2006, by Merck & Co. Inc., Whitehouse Station, NJ, http://www.merck.com. (See color insert.)

When an injury causes a blood vessel wall to break, for example, platelets are activated. They change shape from round to spiny, stick to the broken vessel wall and each other and begin to plug the break. They also interact with other blood proteins to form fibrin. Fibrin strands form a net that entraps more platelets and blood cells, producing a clot that plugs the break [34] (Fig. 1.3). The blood clotting is factually a protective mechanism that prevents excessive blood from being lost after an injury and also prevents bacteria from getting into the wound. Normal clotting takes place within five minutes. For healing of a broken bone, the following processes are conducted in an autonomic way, including internal bleeding forming a fibrin clot, development of unorganized fiber mesh, calcification of fibrous cartilage and conversion of calcification into fibrous bone and lamellar bone. Clearly, the natural healing in living bodies depends on rapid transportation of repair substance to the injured part and reconstruction of the tissues.

Having been inspired by these findings, continuous efforts are now being made to mimic natural materials and integrate the self-healing capability into polymers and polymer composites. A series of healing concepts that offer the ability to restore the mechanical performance of materials has been proposed and successfully applied in recent years. The healing mechanisms and methods involved in nature, like bleeding, blood cells, blood flow vascular network, were simulated in the form of microcapsules [35], hollow fibers [36], nanoparticles [37] and interconnected microchannels [38], respectively. The timescale for realization of self-healing within engineered structures is considerably reduced by a comprehensive exploration and study of the many examples of how the natural world undertakes the process. Biomimicry of the complex integrated microstructures and micromechanisms found in biological organisms offers considerable scope for the improvement in the design of future multifunctional materials [29]. The progress has opened an era of new intelligent materials.

Among the important achievements, the approach using microencapsulation of fluidic healing agent developed by White et al. in 2001 [35] plays the role of milestone, which is promising to be developed into a practical technique for mass production and application of the smart materials. Since then the numbers of scientific publications on self-healing polymers and polymer composites have been significantly increasing (Fig. 1.4). The year of 2007 is the turning point, meaning an “international race” started, as reflected by both quantities of the published papers and affiliations of the authors.

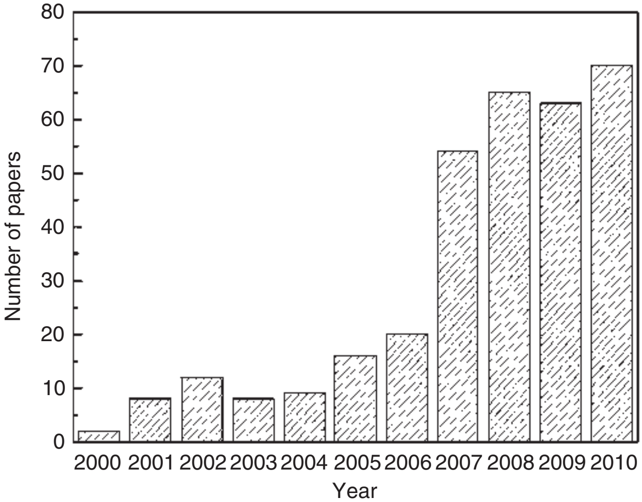


Figure 1.4 Number of research papers on self-healing polymers and polymer composites published between the years of 2000 and 2010 according to the statistics of ISI Web of Knowledge.

So far, in addition to the multiauthored books on self-healing materials (including polymers) [39–41], book chapters [42, 43] and special issues in scholarly periodicals (e.g. *Journal of the Royal Society Interface 4(13)*, 2007 [44] and *Journal of Composite Materials 44(22)*, 2010 [45]), a series of review articles that reflect the newest progresses of self-healing polymeric materials from different angles (e.g. healing theories [46, 47], healing strategies [48–52], healing systems [53–60], healing chemistry [61–66], stimuli responsible for initiation of healing [67], principles of materials design [29, 68] and specific application [69]) is available now. Regular international forums like "International Conference on Self-Healing Materials" (Noordwijk aan Zee, Netherlands (2007); Chicago, United States (2009); Bath, United Kingdom (2011)) have also been established. More and more scientists and companies from various disciplines are interested in different aspects of the topic. The driving forces might come from the rapid consumption of the unrenewable crude oil, ecological concerns, advanced application requirements, miniaturization and integration of products, etc. Taking advantage of this new wave, innovative measures and revolutionary knowledge of the related mechanisms are constantly emerging. It is interesting that the results from different groups complement each other. As a result, the knowledge framework of self-healing polymeric materials is gradually perfected like a jigsaw puzzle.

One thing that needs to be mentioned is that self-healing has been developed in many laboratories in the world, while a universally accepted definition of this issue likely remains yet to be made. We tend to include a wider scope that considers the following two types according to the ways of healing [40]:

- autonomic (without any intervention)
- nonautonomic (needs intervention/external triggering).

Because the present monograph is planned to be devoted to development of new healing chemistry, the focus of review of the state-of-the-art in the subsequent sections of this chapter will be laid on the origination of healing capability and the ways of substance supply and energy supply. Accordingly, self-healing polymers and polymer composites are classified into two categories [48] hereinafter for the convenience of discussion: (i) intrinsic ones that are able to heal cracks by the polymers themselves without the need of additional healing agents and (ii) extrinsic ones in which healing agents have to be intentionally pre-embedded. On the other hand, the prototypes worked out by our group are not analyzed in this chapter but discussed in Chapters 3–7.

Last, as viewed from the ultimate outcomes of repair, self-healing would lead to (i) full-scale restoration and (ii) functionality restoration. The former recovers the materials to their status quo ante, while the latter recovers the principal function of the materials. Self-healing anticorrosion coating that operates relying on the embedded inhibitors is a typical example of the latter effect. The authors of this book are more interested in the former.

1.2 INTRINSIC SELF-HEALING

The so-called intrinsic self-healing polymers and polymer composites are based on specific molecular structures and performance of the polymers and polymeric matrices that enable crack healing mostly under certain stimulation like heating. Autonomic healing without manual intervention is only available in a few cases for the time being. As viewed from the predominant molecular mechanisms involved in the healing processes, the reported achievements consist of three modes: (i) physical interactions, (ii) chemical interactions and (iii) supramolecular interactions.

1.2.1 Self-Healing Based on Physical Interactions

1.2.1.1 Thermal Activation Compared to the case of thermosetting polymers, crack healing in thermoplastic polymers received more attention at an earlier time. Wool and coworkers systematically studied the theory involved [70, 71]. They pointed out that the healing process goes through five phases: (i) surface rearrangement, which affects initial diffusion function and topological features; (ii) surface approach, related to healing patterns; (iii) wetting; (iv) diffusion, the main factor that controls recovery of mechanical properties and (v) randomization, ensuring disappearance of cracking interface. In addition, Kim and Wool [72] proposed a microscopic model for the last two phases on the basis of the reptation model that describes longitudinal chain diffusion responsible for crack healing.

Accordingly, Jud and Kaush [73] tested crack-healing behavior in a series of poly(methyl methacrylate) (PMMA) and poly(methyl methacrylate-co-methyl ethylacrylate) (MMA-MEA copolymer) samples of different molecular weights and degrees of copolymerization. They induced crack healing by heating samples above the glass transition temperature under slight pressure. It was found that full resistance was regained during short-term loading experiments. The establishment of mechanical strength should result from interdiffusion of chains and formation of entanglements for the glassy polymer [74]. Wool [75] further suggested that the recovery of fracture stress is proportional to $t^{1/4}$ (where t is the period of heating treatment). Jud et al. [76] also performed rehealing and welding of glassy polymers (PMMA and styrene-acrylonitrile copolymer (SAN)) at temperatures above the glass transition temperatures and found that the fracture toughness, K_{Ii}, in the interface increased with contact time, t, as $K_{Ii} \propto t^{1/4}$ as predicted by the diffusion model.

It is worth noting that whereas craze healing occurs at temperatures above and below the glass transition temperature [77], crack healing happens only at or above the glass transition temperature [78]. To reduce the effective glass transition temperature of PMMA, Lin et al. [79] and Wang et al. [80] treated PMMA with methanol and ethanol, respectively. They reduced the glass transition temperature to a range of 40–60°C and found that there were two distinctive stages for crack healing: the first one corresponding to the progressive healing due to wetting, while the second related to diffusion enhancement of the quality of healing behavior. Similarly, Hsieh et al. studied crack healing of PMMA induced by cosolvent of methanol and ethanol [81]. The crack tip recession was found to be a linear function of healing time at a given solvent mixture and temperature. The fracture stress increased with decreasing volume fraction of ethanol. By using the same strategy but a different solvent (i.e. carbon tetrachloride), Wu and Lee observed crack healing in polycarbonate (PC) at 40–60°C [82]. Further spectroscopic investigation of solvent healing of PMMA at elevated temperatures indicated that in addition to mechanical locking of the broken chains, the hydrogen bond due to the interaction between methanol and broken polymeric chain promoted the mechanical strength of the healed sample [83]. Kawagoe et al. investigated the effects of case II diffusion on the growing behavior of a surface precrack in a system of PMMA and methanol in relation to the distribution of internal stress induced by surface swelling [84]. At higher ambient temperatures above the glass transition temperature of the swollen polymer, a relatively long crack in the thinner surface swollen layer completely disappeared in the absence of an external load. This phenomenon of crack healing was believed to be brought about by the formation of an interface by contact of crack surfaces under internal compression and the self-diffusion of polymer chains across the interface to make the physical links of chains with the aid of thermal energy.

Yufa et al. reported thermal healing of poly(styrene-b-methyl methacrylate) (PS-b-PMMA) diblock copolymer, which was predamaged by a silicon atomic force microscopy tip [85]. The polymer could heal itself (by molecular flow) significantly faster at elevated temperatures just above the glass transition. Moreover, the fingerprint patterns associated with microphase separation, although initially destroyed by the tip-based lithography, reformed essentially completely upon thermal annealing.

In fact, internal microcracks in thermoplastics can be healed by localized viscose flow of the polymer. Corten and Urban, for example, well dispersed γ-Fe_2O_3 nanoparticles into PMMA without sacrificing mechanical properties of the latter [86]. When the superparamagnetic filmy nanocomposite was exposed to the oscillating magnetic field, the magnetic moment of γ-Fe_2O_3 nanoparticles were excited at the frequency of the magnetic field. The magnetic energy resulting from the Néel and Brownian relaxations was converted to thermal energy. Localized amorphous flow occurred and a permanent repair of the physically separated polymeric films was achieved.

Unlike thermoplastics, heating induced healing of thermosetting polymers usually depends on crosslinking of unreacted groups. Healing of epoxy, for instance, has to proceed above the glass transition temperature [87]. Then, the molecules at the cracking surfaces would interdiffuse and the residual functional groups react with each other. A 50% recovery of impact strength can thus be obtained [88]. During the repair study of vinyl ester resin, Raghavan and Wool reported that critical strain energy release rate, G_{IC}, for the interfaces after crack healing (i.e. annealing above the glass transition temperature) was 1.7% of the virgin value. Lower crosslink density favors the repair effect [89]. Interestingly, Aflal et al. showed an example of crack healing in cured epoxy merely through physical interaction [90], which somewhat contradicts the above analysis. They measured fracture loads of compact tension (CT) specimens of epoxy cured by an amine curing agent at stoichiometry. The average healing efficiency for the first fracture was greater than 50% when healing was conducted at 185°C for 1 h. On the basis of results from size exclusion chromatography for the extractable phase, infrared spectroscopy and scanning electron microscopy, it was postulated that healing was primarily due to mechanical interlocking of the nodular topology of a fractured crack interface that occurred in the rubbery state ($T_g = 162°C$) and was set in place by vitrification upon cooling.

Yamaguchi et al. prepared crosslinked polyurethanes (PU) by the reaction between polyester-diol and polyisocyanate with the catalysis of dibutyltindilaurate [91]. By changing the molar ratio of [NCO] to [OH], different crosslinking densities were obtained, so that the number of dangling chains was purposely manipulated. Visual inspection indicated that the cleaved sample sheet made from a proper reaction ratio was rapidly rebound at room temperature within 10 min. The autonomic healing of the weakly gelled polymer (with a gel fraction of 65%, just beyond the critical point) was believed to result from the strong topological interaction (entanglement) of dangling chain ends, while the permanent network prohibited macroscopic flow of the material. In this context, no healing occurred in the case of very high gel fraction (e.g. 91%) because of insufficient dangling chains.

Quantitative characterization of the healing efficiency revealed that 80% of tear strength of the polyurethane produced from a prepolymer having higher molecular weight can be recovered [92]. Well-developed longer dangling chains were considered to be responsible for the mechanical healing.

Although no manual intervention was required for the healing, the core part of the healing mechanism is not different from the “thermal healing” induced chain entanglement of a glassy polymer, because the dangling chains healing proceeded at an ambient temperature, much higher than the glass transition temperature of the polymer (~ −40°C).

Thermoplastic/thermosetting semi-interpenetrating network is factually a material associated with repeatable self-healing ability. The group of Jones introduced a soluble linear polymer to a thermosetting epoxy resin [93–95]. The selected thermoplastic is poly(bisphenol-A-co-epichlorohydrin) (PBE), which is highly compatible with the matrix diglycidyl ether of bisphenol A (DGEBA) resin. Upon heating a fractured resin system, the thermoplastic material would mobilize and diffuse through the thermosetting matrix, with some chains bridging closed cracks and thereby facilitating healing. When this healable resin was compounded with crossply glass fiber, effective healing of composites transverse cracks and delamination has been demonstrated. The requirements for such thermal diffusion of a healing agent were summarized as follows [94]: (i) the healing agent should be reversibly bonded (e.g. through hydrogen bonding) to the crosslinked network of the cured resin below the minimum healing temperature to limit its effect on thermomechanical properties; (ii) the healing agent should become mobile above this minimum healing temperature so that it can diffuse across a hairline crack, such as a transverse crack, to provide a recovery in strength and (iii) the addition of the linear chain molecule should not significantly reduce the thermomechanical properties of the resin matrix.

Similarly, Luo et al. demonstrated a thermoplastic/thermoset blend exhibiting thermal mending and reversible adhesion [96]. The initially miscible blend composed of poly(ε-caprolactone) (PCL) and epoxy, which underwent polymerization-induced phase separation during crosslinking of the epoxy, yielding a brick-and-mortar morphology wherein the epoxy phase existed as interconnected spheres (bricks) interpenetrated with a percolating PCL matrix (mortar). A heating-induced "bleeding" behavior was witnessed in the form of spontaneous wetting of all free surfaces by the molten PCL phase, and this bleeding was capable of repairing damage by crack-wicking and subsequent recrystallization with only minor concomitant softening during that process. The observed bleeding was attributed to volumetric thermal expansion of PCL above its melting point in excess of epoxy brick expansion. The "differential expansive bleeding" effect led to the formation of a PCL patch over the damaged region of the material, restoring a significant portion of the mechanical strength. When a compressive stress (18.7 kPa) was applied to assist crack closure at 190°C, thermal-mending efficiencies exceeded 100%.

By using the thermal adhesivity of poly(ethylene-co-methacrylic acid) (EMAA) copolymer, a new strategy of thermoplastic healing agent was proposed by Meure et al. [97]. They directly added EMAA particles (250–425 μm) into triethylene tetramine (TETA) cured DGEBA epoxy resin. Damaged single edge notched bars and tapered double cantilever beams (TDCB) were healed at 150°C for 30 min to achieve up to an 85% recovery in critical stress intensity and over 100% recovery in sustainable peak load. Optical and scanning electron microscopy revealed that strength recovery in the damaged resin was achieved via EMAA particle healing as well as the formation of an adhesive EMAA layer between adjacent epoxy fracture surfaces. Small bubbles in the EMAA particles acted as a new healing agent delivery mechanism wherein expansion during heating forced larger volumes of healing agent into the damaged region of the resin (Fig. 1.5). Fourier transform infrared spectroscopy study proved that during curing at 50°C, DGEBA and TETA were adsorbed by EMAA via hydrogen bonding and ionic bonding, respectively. During postcuring at 150°C, covalent bonding between the DGEBA and EMAA (acid-oxirane or acidhydroxyl reactions) occurred in addition to the hydrogen/ionic bonding. Based on the availability of acid, oxirane and amine groups in the damaged epoxy resin, it was anticipated that the same types of covalent, hydrogen and ionic bonding identified during curing and postcure were responsible for interfacial strength development during healing [98].

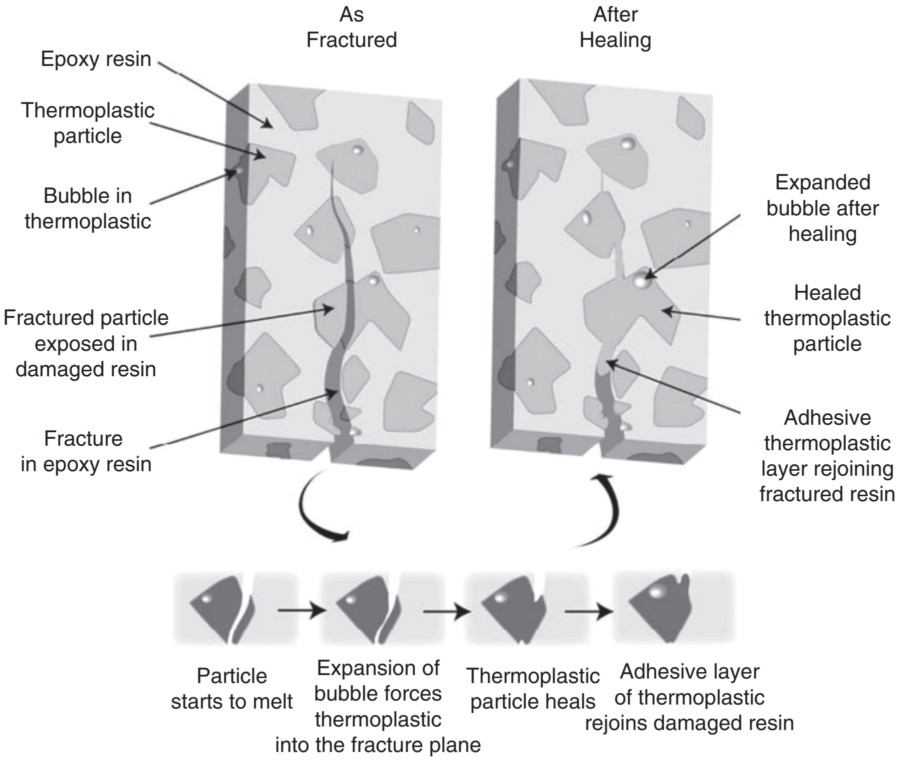


Figure 1.5 Healing agent delivery mechanism used by the mendable epoxy resins containing EMAA particles [97]. Reprinted from Meure, S., Wu, D.Y., and Furman, S.A. Polyethylene-co-methacrylic acid healing agents for mendable epoxy resins. *Acta Materialia 57*, 4312–4320. Copyright 2009, with permission from Elsevier.

In addition, EMMA fibers were also made for being woven into a loose mesh (of approximately 4 mm cubes), which was then placed as an interleaf on woven carbon fiber plies to produce mendable carbon fiber/epoxy laminates [99]. Interlaminar fracture toughness testing carried out on double cantilever beams (DCB) showed that the treatment at 150°C for 30 min of closed DCB yielded 100% restoration of failure energy, G_{IC}, and peak load in a damaged laminate over repeated damage-healing cycles.

1.2.1.2 Ballistic Stimulus Besides simple heating induced healing, thermomechanical healing is valid for some specific polymers, like ionomers. An ionomer is a copolymer that comprises repeat units of both electrically neutral repeating units and a fraction of ionized units (usually no more than 15%). Its properties are governed by ionic interactions within discrete regions of the polymer structure [100]. In terms of microstructure, an ionomer can be considered as a two-phase system of ordered ionic clusters dispersed within a continuous semicrystalline polymer matrix [101, 102]. With a rise in temperature, the polymer exhibits an order-to-disorder transition as a result of which of the ionic clusters, although persisting, lose order and strength. As the temperature is further increased, the semicrystalline polymer matrix melts, even though the disordered clusters remain and continue to provide increased melt strength [103]. These transformations play a vital role in the self-healing process immediately after impact. When the thermal energy of impact dissipates, the aforesaid reversibility ensures rapid solidification while reordering of the ionic clusters and physical crosslinks follows more slowly.

The works by Fall [104] and Kalista et al. [105–108] have shown the unique self-healing response in EMAA, which is beyond the aforesaid external thermal activation induced melting [97, 99]. EMAA films prove to be able to heal upon ballistic puncture and sawing damages. This occurs through a heat generating frictional process, which heats the polymer to the viscoelastic melt state and provides the ability to rebond and repair damage. In contrast, a low speed friction event fails to produce sufficient thermal energy favorable to healing. As a result, thermomechanical healing is not active in the material under the circumstances. The combination of elastic flexibility, high melt strength and spontaneous formation of physical crosslinks gives the ionomers a self-healing behavior upon ballistic impact. After passage of the bullet, a relatively small scar is left on the impact side but the hole formed by the bullet is fully closed, leaving an air- and moisture-tight sample (Fig. 1.6) [109].

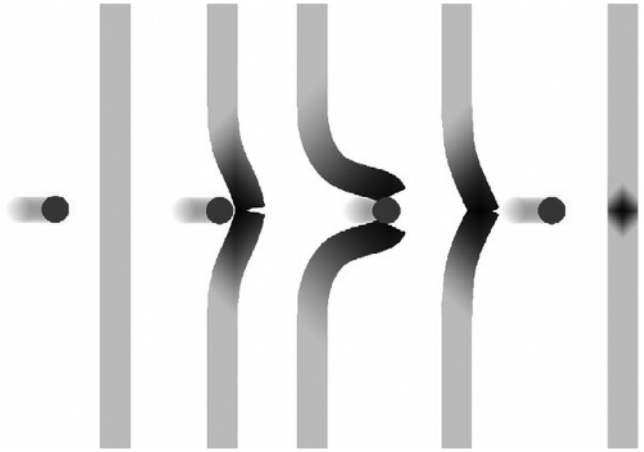


Figure 1.6 Schematic representation of the self-healing process during high-energy impact [109]. Reprinted from Varley, R.J., and van der Zwaag, S. Development of a quasistatic test method to investigate the origin of self-healing in ionomers under ballistic conditions. *Polymer Testing 27*, 11–19. Copyright 2008, with permission from Elsevier. (See color insert.)

It is believed that the ionomeric self-healing arises from a balance of the competing influences of an elastic response and a viscous response during impact.

Varley and van der Zwaag conducted a careful investigation on the mechanism involved in the self-healing process [103]. They found that the outer impact regions exhibited ductile/elastic behavior, while closer to the impact cavity elastomeric and viscous behavior was observed. The viscous healing response showed that, given sufficient molecular mobility and time, polymer chains would diffuse across discontinuous boundaries and heal. The ionomer's response to penetration consisted of three consecutive events: an initial elastic response, ananelastic response and pseudo-brittle failure [110]. The ultimate level of healing was dependent upon the elastic response during impact as well as postfailure viscous flow. Increasing the local temperature at impact consistently increased elastic healing, although further improvements in healing were minor once the local temperature increased beyond the melting point. Below the order-to-disorder transition, severe plastic deformation was perceived while the lack of shape memory reduced the comparative level of elastic healing. Above this temperature, healing was facilitated by elastomeric behavior at the impact site, while above the melting point a combination of elastomeric and viscous flow dominated. In addition, slow relaxational processes occurring postimpact were found to facilitate further recovery in mechanical properties.

In a recent work, the group of van der Zwaag compounded aliphatic di- and tri-carboxylic acid based modifiers and their analogues with EMAA and studied the effect of cluster plasticization on the autonomous damage elimination [111]. The experiments showed that carboxylic acid modifiers improved healing efficiency by reducing elastic properties and enhancing elastomeric behavior. The ionic clusters were reduced in strength as a result of plasticization yet were able to reform more rapidly below their melting point. The combination of these factors combined to create polymer blends with enhanced elastic healing behavior compared to the unmodified ionomer. In contrast, the neutralized analogue additives and succinamide increased elastic properties, reduced elastomeric behavior and increased ionic cluster strength while reducing the rate of reformation after annealing. The result of these additives was to ultimately reduce healing during penetrative impact. Evidently, plasticizing and increasing the dynamic behavior of the ionic clusters improves healing, while strengthening and reducing the mobility of the ionic clusters reduces healing.

Additionally, Gordon et al. surveyed other commercially available polymers possibly possessing puncture self-healing functionality [112]. Dow Affinity EG 8200 polyolefin elastomer (a saturated ethylene-octene copolymer) and poly(butardiene)-graft-poly(methyl acrylate-co-acrylonitrile) (PB-g-PMA-co-PAN) were found to be able to conduct puncture healing. The effect was improved with increasing temperature, especially when the site of impact temperatures were above glass transition temperatures and melting temperatures of respective polymers.

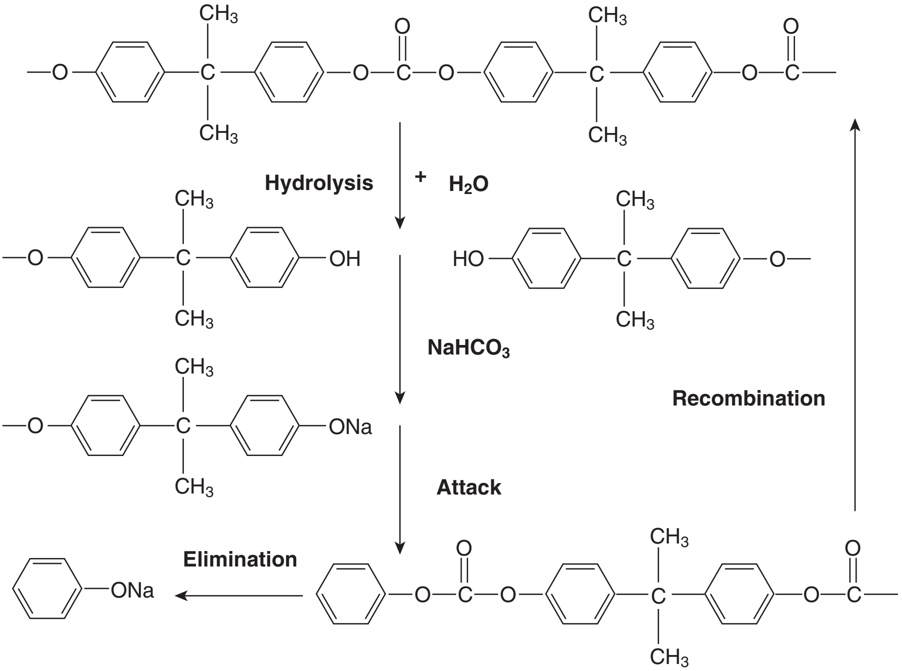
1.2.2 Self-Healing Based on Chemical Interactions

1.2.2.1 Inverse Reactions and Chains Recombination In fact, cracks and strength decay might be caused by structural changes of atoms or molecules, like chain scission. Therefore, inverse reaction, i.e. recombination of the broken molecules, should be one of the repairing strategies. Such method does not focus on cracks healing but on "nanoscopic" deterioration. One example is PC synthesized by ester exchange method. The PCs were treated in a steam pressure cabin at 120°C prior to the repair [113–115]. As a result, molecular weight of the PCs dropped by about 88% to 90%. After drying them in a vacuum cabin, the repairing treatment was done in an oven at 130°C with N_2 atmosphere under reduced pressure. The reduced tensile strength due to the deterioration treatment can thus be gradually recovered. The repairing mechanism was considered as the following procedures. Firstly the carbonate bond was cut by hydrolysis, and then the concentration of the phenoxy end increased after deterioration. The (-OH) end-group on the chain was substituted by sodium ion. The (-ONa) end might attack a carbonate bond at the end of one of the other chains, leading to a recombination of these two chains with the elimination of the phenol from PC (Scheme 1.3). The repairing reaction was accelerated by a weak alkaline, such as sodium carbonate. It suggested that two conditions are required for the PC to recombine the polymer chains. One is the chemical structure of the chain end, and the other is the catalyst (Na_2CO_3) for acceleration of the reaction.

Another example is poly(phenylene ether) (PPE) in which the repairing agent was regenerated by oxygen [114, 116]. The polymer chain of the PPE was cut by a deterioration factor (such as heat, light, and external mechanical force) to produce a radical on the end of the scission chain. Subsequently, a hydrogen donor stabilized the radical. The catalyst existing in the system, Cu (II), would react with each end of the scission chains to form a complex. Then, the chains combined by eliminating two protons from the ends, and the copper changed from Cu (II) to Cu (I). Afterward, two Cu (I) reacted with an oxygen molecule to be oxidized to Cu (II), and an oxygen ion reacted with two protons to form a water molecule that went out from the specimen.

Cracked poly(ether ketone) (PEK) can be repaired by the same strategy. Two kinds of reactions are involved. One is the ester exchange reaction, and the other is the recombination reaction of two polymer ends [114, 116].

The above examples show that PC or PPE might be designed as a self-repairing material by means of the inverse reactions. The deterioration is expected to be minimized if the recovery rate is the same as the deterioration rate. However, the systems in these studies are not sufficient for construction of real self-repairing composites because the recovery of the broken molecules needs higher temperature and other rigorous conditions. A much more effec-

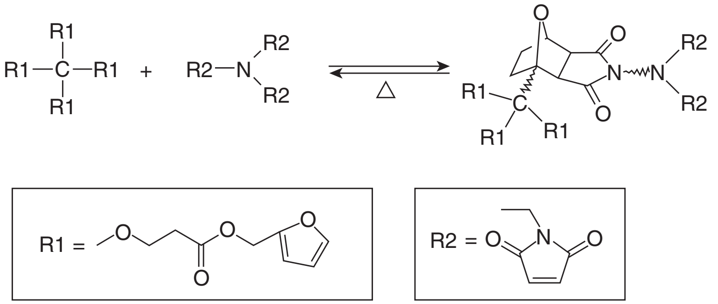


Scheme 1.3 Hydrolysis and recombination reaction of PCs with the catalyst of $NaCO_3$.

tive catalyst should be found out, which is able to activate the recombination of degraded oligomers at room temperature.

Ghosh and Urban reported the development of heterogeneous PU networks based on oxetane-substituted derivative of chitosan (OXE-CHI) [117]. Upon mechanical damage of the network, four-member oxetane rings open to create two reactive ends. When exposed to ultraviolet light (power: 120 W, wavelength: 302 nm), chitosan chain scission occurs, which forms crosslinks with the reactive oxetane ends, thus repairing the network within one hour. Because of the thermosetting characteristics of the networks, however, if exactly the same previously repaired spot is damaged again, the ability for further repair is limited.

1.2.2.2 Reversible Bonds Reversible polymers share one property in common—reversibility, either in the polymerization process or in the crosslinking process [63, 64]. Such a feature offers versatile possibilities of repeated healing on molecular scale. For example, thermally reversible crosslinking behavior has been known for quite a while [118, 119]. Wudl et al. combined this with the concept of “self-healing” in making healable polymers [120, 121]. They synthesized highly crosslinked polymeric materials with multi-furan and multi-maleimide via Diels-Alder (DA) reaction (Scheme 1.4). At temperatures above 120°C, the “intermonomer” linkages disconnect (corresponding to



Scheme 1.4 Thermally reversible crosslinking based on Diels-Alder reaction.

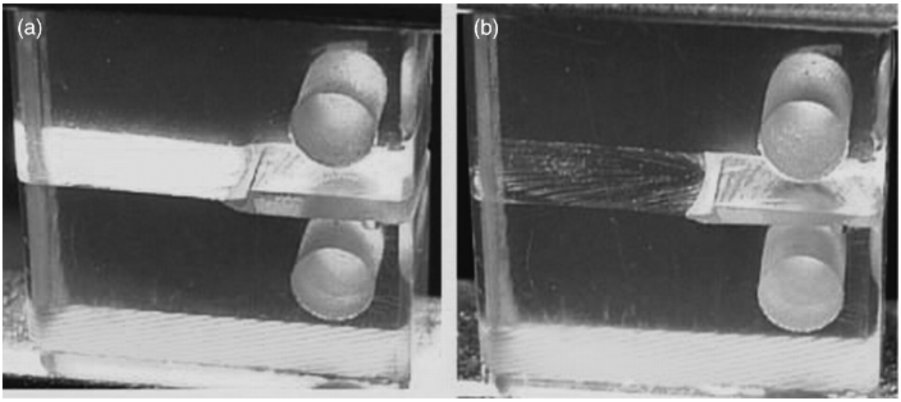


Figure 1.7 Images of a broken compact tension test specimen (a) before and (b) after thermal treatment, showing disappearance of the crack due to the reversible DA bonds [67]. Reprinted from V Murphy, E.B., and Wudl, F. The world of smart healable materials. *Progress in Polymer Science 35*, 223–251. Copyright 2010, with permission from Elsevier. (See color insert.)

retro-DA reaction) but then reconnect upon cooling (i.e. DA reaction). This process is fully reversible and can be used to restore fractured parts of the polymers (Fig. 1.7). The polymers are transparent and possess mechanical properties comparable to commercial epoxy and unsaturated polyester. In principle, an infinite of crack healing is available without the aid of additional catalysts, monomers and special surface treatment.

Subsequently, composite panels were prepared by sandwiching the DA monomers between carbon fiber fabric layers [122]. Microcracks that were induced on the resin-rich surface of the composites disappeared after treatment at 180°C for one hour as a result of resistance heating. The experiments demonstrated the self-healing ability of the remendable polymers in both bulk form and fiber composites. Owing to the fast kinetic rate of the reaction of the polymer constituents, which requires a fast injection of the healable resin into the carbon fiber perform, a modified resin transfer mold (RTM) technique was developed accordingly [123]. Besides, Plaisted et al. proposed the concept of multifunctional composites [124], in which the crosslinked polymer from multi-furan and multi-maleimide [120] serves as the matrix, arrays of straight copper wires and copper coils as the conductive electromagnetic scattering elements and synthetic fibers as the reinforcement. The scattering elements provide controlled electromagnetic response for tasks such as tuning the dielectric constant and filter radio frequency radiation. Internal damage, in the form of polymer matrix cracking, may be repaired when heat is applied through the metallic wires.

In the meantime, Kwok and Hahn carefully studied the influential factors when using carbon fibers as a resistive heating network for activating the self-healing function [125]. Various electrode methods were tested in an attempt to reduce the contact resistance that caused localized heating around the electrode. Besides, Park et al. confirmed multiple healing and shape memory effects of the composites after electrical resistive heating [126].

Using the concept of thermal reversibility induced repair, powder coatings can be applied in their crosslinked state, which has distinct advantages with respect to their storage stability, as demonstrated by the crosslinked material based on acrylate copolymers [127]. When heated above the threshold temperature flow should be sufficient to enable proper film formation. As soon as the surface is of sufficient quality, crosslinking can be started by cooling down. In a fully crosslinked state of a powder coating system, i.e. below a certain threshold temperature, the coating will exhibit its essential properties with respect to mechanical strength, etc., but in its (partly) decrosslinked state, above the threshold temperature, it will show a certain level of plasticity and flow. This plasticity will decrease problems in the area of film formation of powder coatings and will enable repair of the coating using their self-healing properties [68].

In the work by Liu and Hsieh [128], Wudl's approach was modified. The multifunctional furan and maleimide compounds were prepared in simple routes, using epoxy compounds as precursors. The furan and maleimide monomers could be therefore considered as epoxy-based compounds, so as to incorporate the advantage characteristics of epoxy resins, including solvent and chemical resistance, thermal and electrical characters and good adherence, to their corresponding cured polymers. Furthermore, Liu and Chen prepared polyamides (PA) possessing furan pendent groups (PA-F) from reacting furfuryl amine with maleimide containing polyamides (PA-MI) via a Michael addition reaction [129]. Thermally reversible crosslinked polyamides were obtained from PA-MI and PA-F polyamides by means of DA and retro-DA reactions. The thermally reversible crosslinked polyamides also exhibited a self-repairing property as well as the ability of mechanical property recovery.

Kavitha and Singha applied click chemistry to make polymethacrylate (PMA) bearing reactive furfuryl functionality, which was then reacted with bismaleimide (BMI) to form crosslinked poly(furfuryl methacrylate)-bismaleimide (PFM-BMI) [130]. DA bonds acted as the crosslinking sites, so that the polymer can be decrosslinked through the retro-DA reaction. Accordingly, a complete notch (knife-cut) recovery to regain the original structure was detected by scanning electron microscope on PFM-BMI film after treatment at 120°C for 4 h.

By using Paal-Knorr reaction of polyketones (PK) and furfurylamine, Zhang et al. converted polyketones to furan derivatives in bulk under mild conditions without the need for a catalyst or a solvent, whereas the degree of furan functionality can be tuned well by changing the initial reaction conditions [131]. As a result, a thermosetting material was obtained by mixing the furan-containing polymer with BMI. The furan-functionalized polyketones (PK-furan) could be repeatedly crosslinked and decrosslinked with BMI under the stimulus of heating. Three-point bending tests showed that the highly crosslinked polymers can be thermally remended to complete recovery in fracture loading, whereas the remending process can be repeated multiple times without any loss in mechanical properties. Another interesting issue of this work lay in the way of healing efficiency characterization. Instead of healing the fractured sample and retesting to determine healing efficiency, as is often the case in this field, the fractured material was shredded into small granulates and a new specimen was fabricated (by compression molding of the crosslinked PK-furan granulates into rectangular bars at 120°C for 20 min under a pressure of about 4 MPa, followed by the thermal treatment at 50°C for 24 h in an oven). The new sample was retested, so that healing efficiency can be calculated by comparing the fracture loads of the original sample and the new sample.

Recently, Murphy et al. simplified the dual monomer route for the synthesis of remendable polymers from DA adducts by replacing furan-maleimide pair with a single monomer that contained a dicyclopentadiene (DCPD) core unit [132]. The new single-component remendable polymer system used the dicyclopentadiene moiety as both diene and dieneophile in the thermally reversible DA cycloaddition reaction. Additionally, the Staudinger crosslinking of the dienophilic DA dimer adduct double bond of the growing polymer chains was found to be the key to the strength of the materials. Fracture tests showed that the healing treatment of 120°C for 20 h in an argon atmosphere led to an average of 46% healing efficiency.

Similar to the above work by Wang et al. [122], thermally remendable composites with the dicyclopentadiene-based polymer as the matrix and graphite fibers as the reinforcements were also fabricated [133]. Because the graphite fibers can act as electrical conductors to provide the necessary heat to the polymer, resistance heating was used to stimulate the healing. It was found that microcracks can be healed within minutes at temperatures ranging from 70 to 100°C.

Syrett et al. used DA chemistry to synthesize polymerization initiators and a dimethacrylic crosslinker that leads to cleavage and reformation required by self-healing [134]. The linker exhibited cleavage properties with 50% reformation occurring upon the reheating cycle. Linear and star methyl methacrylate polymers bearing DA adducts within their macromolecular backbone prepared via living radical polymerization were also preliminarily evaluated to check their ability to cleave and reform under external thermal stimuli.

In consideration that endo/exo stereoisomers of furan-maleimide DA-adducts might influence thermal reversibility and hence thermal remendability of polymer networks based on a DA crosslink reaction, Canadell et al. synthesized and characterized a number of model compounds containing DA-adducts derived from furan and maleimide groups [135]. It was established that the endo and exo DA stereoisomers show significantly different thermal responses: the retro-DA of the endo DA-adducts typically takes place at 20–40 K lower temperatures than that of the corresponding exo DA-adducts in all cases, with the exception of some aromatic maleimides. In general, the stereoisomeric effect was not expected to influence the thermoremendability of DA-crosslinked networks being dependent on two separate stereoisomeric retro-DA steps.

Besides, thermal reversibility can also be imparted to rubbers. Chen and Jiao used diglycidyl dicyclopentadienedicarboxylic acid ester (DGDCA) as a crosslinking monomer in alkyl aluminum system catalyzed copolymerization with epoxide monomers like epichlorohydrin (ECH) [136]. The resultant polyether thermoplastic elastomer can be molded into sheets at 215°C. When the opposite parts of a broken specimen were joined together, the crack became invisible under certain conditions. It means that decrosslinking of the crosslinked copolymer occurred at an elevated temperature, leading to melting and plastic flow. When the material was cooled down, the DA cycloaddition between the side group cyclopentadiene rings reconstructed the elastic crosslinking networks.

Yoshie and coworkers developed network polymers with recyclability using telechelic prepolymers with reversible reactivity [137]. On the basis of the research, they produced an elastomer from bisfuranic terminated poly(ethylene adipate) (PEA) and tris-maleimide through DA reaction at 60°C [138]. The resultant polymer, PEAF2M3, possessed a glass transition temperature of –34°C and can be decrosslinked by retro-DA reaction at 145°C for 20 min. When a film sample was cut into two pieces and the cut surfaces were kept in contact with each other at 60°C, rejoining of the cut pieces was observed. This mending was believed to be induced by the following three mechanisms: (i) the reversible crosslinking reaction bridged the cut surfaces (at the cut front, the weak DA-adducts were selectively dissociated sacrificially to release the stress so as to protect the chemical structure of the prepolymer and the linker against the scission or degradation); (ii) exchange of the maleimide (furan) group in a DA-adduct with that in another DA-adduct and (iii) entanglement of dangling chains.

In general, thermal reversibility induced remend of polymers is achieved by external heating. Nevertheless, the organometallic polymers comprising

N-heterocyclic carbenes and transition metals, proposed by Williams et al. [139], enable crack repair through inductive heating. The polymers possess a network with reversible interactions to allow for healing and conjugation to meet conductivity requirements (~10^{-3} S/cm). Upon the formation of a microcrack, the total number of electron percolation pathways within the material decrease, leading to an increase in the inherent resistance. When an electric current is applied, this resistance can lead to ohmic heating of the material, which should facilitate depolymerization into fluidic monomers. The monomers could then flow into the voids and ultimately restore the material's original structural and electronic properties.

The group of Lehn screened condensation reactions between various dienes and dienophiles for reversibility [140]. They found that functionalized fulvenes, bearing in particular biological groups, and cyanolefins can react rapidly and reversibly, in the temperature range from –10 to 50°C. The results paved the way for the generation of room-temperature dynamers, e.g. bis(fulvene) and bis(dicyanofumarate) [141]. Soft films (with T_g lower than room temperature) of these two dynamers were cut into two pieces, and then the pieces were laid on top of each other and pressed gently to ensure a microscopic contact. Ten seconds after this the two pieces could no longer be separated by pulling them apart but reacted to the constraint by elongating themselves. No heating was needed during the healing. It is worth noting that this room temperature self-healing took place between the surfaces of the films, not only at the freshly cut surfaces. The surface of the film represented an area at thermodynamic equilibrium, as a result of low equilibrium constants for the interaction between the fulvenes and the cyanoolefins used. The constants were high enough to permit the formation of a material made of small molecules and low enough to allow the scrambling of the chains to take place even in the condensed phase. Consequently, the dynamer constantly created new chain ends and formed new connections, thus building a material that can self-repair across all of its volume.

Following the concept dynamic covalent chemistry, Deng et al. produced reversible polymer gels with self-healing properties [142]. By condensation of acylhydrazines at the two ends of a poly(ethylene oxide) (PEO) with aldehyde groups in tris[(4-formylphenoxy)methyl]ethane, a network with acylhydrazone bonds as crosslinks was generated. Acylhydrazone bonds are covalent in nature, but acylhydrazone formation displays reversibility under mild conditions with an acid catalysis, breaking down the network and regenerating the starting reagents. By adjusting the acidity of the system, this chemical gel revealed reversible sol-gel phase transitions. This dynamic character can be used to reshape a strong chemical gel.

Photoreversibility is an important aspect of reversibility of macromolecules. The chemicals that are able to take part in photoreversible reaction include coumarin and its derivatives, anthracene, cinnamic acid, pyrimidine, etc. In general, most photoreversible reactions involved in polymers belong to [2 + 2] cycloaddition-elimination ones. Chung et al. chose photochemical [2 + 2] cycloaddition of cinnamoyl groups as the healing reaction [143] because the photocycloaddition to form cyclobutane structure [144] and the reversion of cyclobutane to C=C bonds [145] readily occur in solid state. They synthesized a photocrosslinkable cinnamate monomer, 1,1,1-tris-(cinnamoyloxymethyl) ethane (TCE) by reacting 1,1,1-tris(hydroxymethyl)ethane with cinnamoyl chloride. It was expected that the cyclobutane would reverse to original cinnamoyl structure upon crack formation and propagation, and crack healing could be accomplished by the recycloaddition of cinnamoyl groups. Crack healability characterized by bending tests indicated that the average flexural strength of the healed specimens (healing condition: light irradiation with $\lambda < 280$ nm for 10 min) was 5.8 MPa, which was higher than that of the cracked ones (i.e. 3.1 MPa) but lower than that of the original ones (i.e. 42.1 MPa).

To quantify the degree of structural restoration after damages have been repaired, characterization of healing efficiency is necessary, but no specific testing standard is available now. Different testing procedures sometimes give different results [94]. When Wudl's group measured healing efficiency of their thermally reversible crosslinked polymers, fracture toughness from compact tension tests was used [120]. Values for the original and healed fracture toughness were determined by the propagation of the starter crack along the middle plane of the specimen at the critical load. In consideration of the difficulties in (i) precise registration of the fracture surface and (ii) protection of prenotching, Plaisted and Nemat-Nasser [146] applied the double cleavage drilled compression (DCDC) method [147] to evaluate mending efficiency of the reversibly crosslinked polymer based on DA cycloaddition. The testing geometry allowed for controlled incremental crack growth so that the cracked sample remained in one piece after the test, improving ability to realign the fracture surfaces prior to healing.

The above-mentioned self-healing polymers based on reversible DA reactions were studied as bulk materials. However, the work by Peterson et al. demonstrated another form of application of the polymers [148]. They synthesized a thermally reversible crosslinking gel by the addition of a stoichiometric amount of 1,1'-(methylenedi-4,1-phenylene) bismaleimide to furfurylamine (FA)-DGEBA oligomer. Then, the gels served as a healing agent for traditional epoxy-amine thermosets. Direct application of the reversibly crosslinking network to a crack surface in an epoxy-amine thermoset resulted in the recovery of 37% of the initial epoxy-amine network's strength. Composites in which the reversibly crosslinking gel was incorporated as a secondary particulate phase recovered 21% of the initial composite strength after the first healing cycle. The healing mechanism, which was governed by the DA reaction, lay in that heating caused the secondary gel phase to liquefy and flow into the crack surface, and upon cooling crosslinks reformed. Moreover, Peterson and coworkers used an N,N'-dimethylformamide (DMF)-based BMI solution to manually heal the furan-functionalized epoxy-amine thermosetting materials that was obtained by mixing a certain amount of furfuryl glycidyl ether into epoxy resin before curing [149]. Healing at room temperature was available as a result of physical and covalent bonding. Solvent-induced swelling and softening of the crack surfaces allowed for mechanical interlocking, while compatible functionalization of the polymer network and healing agent caused covalent bonding through the DA reaction of furans and maleimides. They are considering the methods to store BMI solutions for in situ healing, including hollow glass fibers and polymer microcapsules. Besides, the idea is going to be used to build up reversible interfaces in composites. That is, maleimide-functionalization of glass fibers within a furan-functionalized polymer network will result in a thermoreversible, and healable, fiber-network interface.

1.2.3 Self-Healing Based on Supramolecular Interactions

Intrinsic self-repair without the aid of healing agent or external stimuli requires high chain mobility and therefore seems to be in direct contradiction with the fixation needed to form covalent bonding in polymers [150]. Nevertheless, Chino and Ashiura synthesized a thermally reversible crosslinking rubber to have similar mechanical properties to a vulcanized one by using supramolecular hydrogen bonding networks [151]. The molecules can be rearranged in the heated state, while the network can be reformed when cooled down. Recently, Leibler and coworkers further demonstrated complete restoration of tensile properties of a thermoplastic elastomer by simply bringing together fractured surfaces [152, 153] (Fig. 1.8). The system was characterized by indefinitely repeatable healing with thermoplastic behavior in the melt and presumably with low toxicity. Dimer and trimer fatty acids from vegetable oils were reacted with diethylene triamine and subsequently with urea. This reaction yielded a transparent glassy material with a glass transition temperature of 28°C. A supramolecular network was formed in the mixture of a large number of di- and trifuctional building blocks with various strongly hydrogen bonding urea and amide molecules. Crystallization was prevented by the presence of a multitude of different species, which warranted rubbery properties at higher temperatures. The temperature-dependent strength of the hydrogen-bonding units resulted in a strong decrease of the viscosity of the material at high temperatures, thus the material can easily be melt-processed. While adhesion was almost immediately sufficient for the pieces to sustain their own weight, the bonding gradually increased over time to reach the initial strength after only three hours. The key mechanism responsible for the self-healing was related to the dynamics and the density of strongly associating hydrogen-bonding groups. When the elastomer failed by rupture, these hydrogen bonds, rather than covalent bonds, were broken, leading to a high density of nonassociated groups at the interface. The nonassociated hydrogen bonds remained in their free state for a significant time, waiting to find a new partner when brought into contact with another freshly cut surface. Relatively fast recombination of a high density of groups at the surface gave rise to a unique repair mechanism that did not rely on reptation of complete polymer chains to recover mechanical strength.

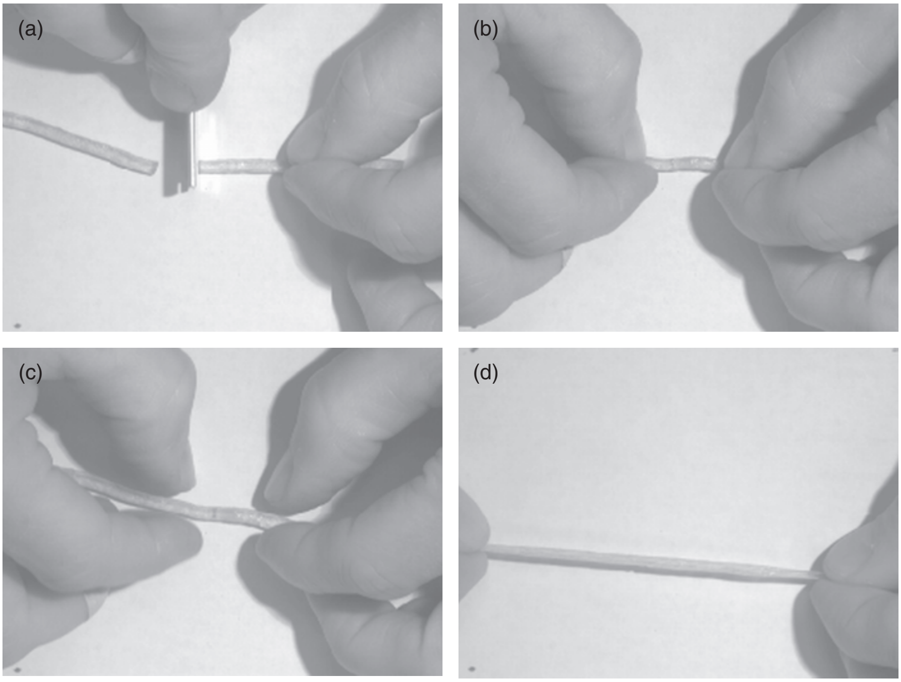


Figure 1.8 Sequential photos showing self-healing of the supramolecular rubber. (a)–(d): Cut, join, mend and stretch [152]. Copyright 2008, reprinted by permission from Macmillan Publishers Ltd: Nature.

The above synthetic pathways relied on grafting H-bonding moieties onto previously synthesized appropriate backbones. The group of Leibler developed a facile one-pot synthesis of supramolecular plastics and self-healing rubbers [154, 155]. By combining and controlling the backbone building, with the grafting of the functional groups, a large variety of supramolecular materials were obtained from the same one-pot reaction by merely varying the stoichiometry of the reactants.

Harreld et al. synthesized a self-healing noncovalently crosslinked organosiloxane-polypeptide block copolymer [156]. The key issue lay in coupling of an aminopropyl-functionalized polydimethylsiloxane (PDMS) with protected polypeptide. The polypeptide segments not only provided toughness to the material, but also allowed for rehealing by allowing reforming of the crosslinks (by virtue of ionic or hydrogen bonding) after a disruptive stress incidence.

In contrast to the supramolecular hydrogen bonded self-healing systems, a healable supramolecular polymer blend, which assembles via π–π stacking interactions, was reported by Burattini et al. [157, 158]. They used two relatively low molecular weight polymers—a polydiimide that is capable of adopting a chain-folded conformation, thereby generating π-electron deficient "tweezer-type" receptor units and a linear polysiloxane that features complementary π-electron rich pyrene end-groups. The blend of these two polymers cast from solution afforded a thermodynamically stable material capable of autonomous healing when exposed to temperatures above ambient (Fig. 1.9). The complementary π-electron-rich and -poor receptors exhibited rapid and reversible complexation behavior in solution and healable characteristics in the solid state in response to temperature. A mechanism was proposed for this thermoreversible healing behavior that involved disruption of the intermolecular π–π stacking crosslinks as the temperature of the supramolecular film was increased. The low T_g polysiloxane component can then flow and as the temperature of the blend was decreased, π–π stacking interactions drove formation of a new network and so led to good damage-recovery characteristics of the two-component blend.

It is worth noting that many natural self-healing mechanisms of great efficiency and simplicity are based on self-assembly [49]. Self-assembly occurs when the building blocks of the system spontaneously organize in an ordered structure by means of physical interactions. Such a manner in artificial materials has been explored for years, but has not yet become a mainstream measure for obtaining self-healing. Nevertheless, design of a material with auto-assembly properties implies the built-in self-healing ability might be associated as a side-effect. Tsukruk et al. prepared compliant nanocomposite membranes with molecular precision by time-efficient, spin-assisted layer-by-layer assembly of polymeric monolayers with a gold nanoparticle intralayer, with a thickness of 35–55 nm and a diameter of hundreds of micrometers [159]. After plastic deformation, the membranes showed autonomous recovery of their properties, which was possible by means of a reversible polymer–nanoparticle self-organization process.

Skrzeszewska et al. also prepared well-defined self-assembled physical gels by telechelic polypeptides with nodes formed by collagen-like triple helices [160]. When the gels were sheared, fracture occurred at a critical stress that increased logarithmically with increasing shear rate. When a constant stress was applied, a fracture occurred after a delay time that decreased exponentially with increasing stress. It was believed that fracture in these systems was due to stress-activated rupture of triple-helical junctions. After rupture, the physical gels healed completely.

In a recent work, South and Lyon reported self-healing of hydrogel film [161]. They employed spherical, submicrometer-sized, poly(ethylene glycol) diacrylate based hydrogel particles (microgels) as the main building block in the layer-by-layer polyelectrolyte assembly procedure to fabricate continuous, multilayered hydrogel films. The films were deposited on an elastomeric substrate of PDMS, which allowed for the controlled mechanical manipulation of the substrate and its associated microgel coating. Four microgel layers were assembled using alternating layers of anionic microgels and poly (diallyldimethylammonium chloride) (PDADMAC), a cationic quaternary amine. When damage was introduced by multiple "stabs" with a 5 μL pipette

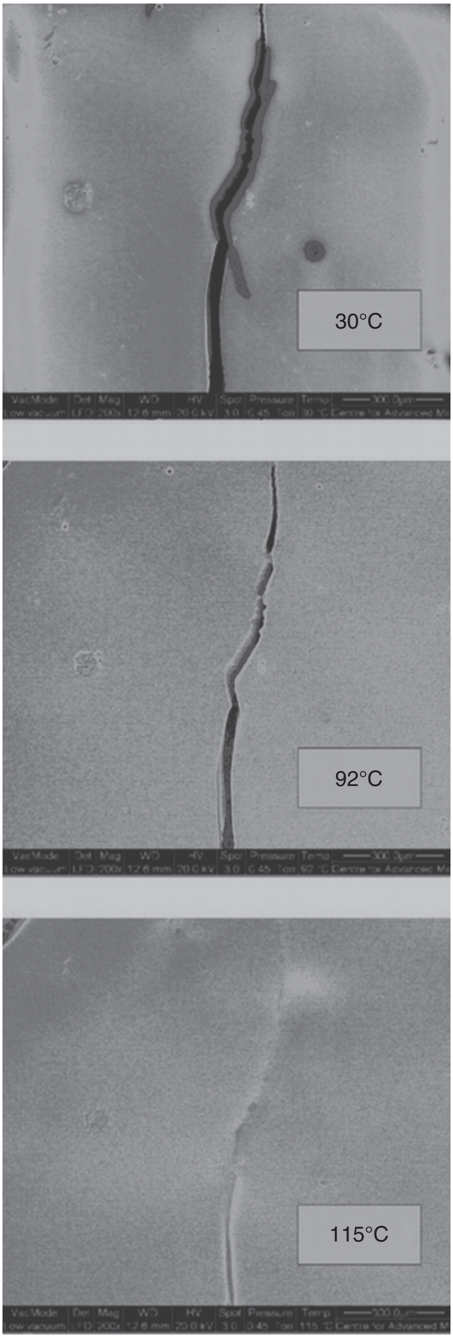


Figure 1.9 Temperature dependent crack healing behavior of the cast blend of the chain-folding polydiimide and the pyrene end-capped siloxane [157]. Reproduced with permission from the Royal Society of Chemistry. (See color insert.)

tip, addition of water to the film rapidly erased the defects on a timescale of seconds. The observation showed the ability of microgel-based polyelectrolyte multilayers to reorganize after damage. Redistribution of the microgels to a less energetic state associated with reformation of the polyanion–polycation interactions was believed to account for the self-healing manner.

1.3 EXTRINSIC SELF-HEALING

In the case of extrinsic self-healing, the matrix resin itself lacks an intrinsic self-healing mechanism. Healing agent has to be stored in some media and embedded into the materials in advance. As soon as the cracks destroy the fragile reservoirs, the healing agent would be released into the crack planes due to a capillary effect and heal the cracks. In accordance with types of the containers, there are two main modes of the repair activity: (i) self-healing in terms of healant loaded pipelines and (ii) self-healing in terms of healant loaded microcapsules. Taking the advantages of crack triggered delivery of healing agent, manual intervention (e.g. heating that used to be applied for intrinsic self-healing) might be no longer necessary.

1.3.1 Self-Healing in Terms of Healant Loaded Pipelines

1.3.1.1 Hollow Glass Tubes and Glass Fibers The core issue of this technique lies in filling the brittle-walled vessels with a polymerizable medium, which should be fluid at least at the healing temperature. Subsequent polymerization of the chemicals flowing to the damage area plays the role of crack elimination. Dry first identified the potential applicability of hollow glass tubes [162–165]. A similar approach was adopted by Motuku et al. [166] and Zhao et al. [167]. Because the hollow glass capillaries have diameters (on a millimeter scale) much larger than those of the reinforcing fibers in composites, they have to act as initiation for composites failure [36]. Instead, Bleay et al. employed hollow glass fiber (with an external diameter of 15 μm and an internal diameter of 5 μm) to minimize the detrimental effect associated with large diameter fibers [36]. Complete filling of healing agent into the tiny tubes was achieved by vacuum assisted capillary action filling technique.

Accordingly, three types of healing systems were developed (Fig. 1.10) [162–177]: (i) single-part adhesive: all hollow pipettes contained only one kind of resin like epoxy particles (that can be flowable upon heating and then cured by the residual hardener) or cyanoacrylate (that can be consolidated under the induction of air); (ii) two-part adhesive: in general, epoxy and its curing agent were used in this case; they were filled into neighboring hollow tubes, respectively and (iii) two-part adhesive: one component was incorporated into hollow tubes and the other in microcapsules.

With the aid of the pre-embedded healing system in hollow pipettes, Motuku and coworkers studied the healing ability of glass fiber/unsaturated polyester

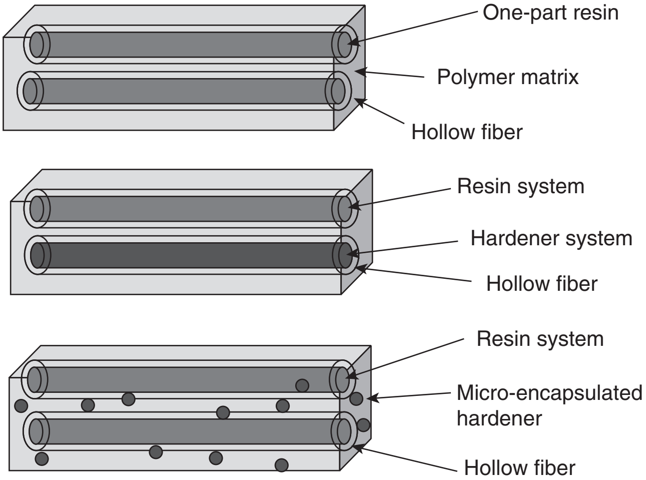


Figure 1.10 Schematic diagram of repair concept for polymer matrix composites using pre-embedded hollow tubes [36]. Reprinted from Bleay, S.M., Loader, C.B., Hawyes, V.J., Humberstone, L., and Curtis, P.T. A smart repair system for polymer matrix composites. *Composites, Part A: Applied Science and Manufacturing 32*, 1767–1776. Copyright 2001, with permission from Elsevier.

composites subjected to low velocity impact [166, 172]. The species of the healing agent, characteristic parameters of the hollow pipes (amount, type of tubing materials and spatial distribution), composites panel thickness and impact energy level were found to be critical to the healing efficiency. Meanwhile, Bleay et al. proved that the epoxy based composites reinforced by hollow glass fibers containing solvent diluted two-part epoxy became repairable as assessed by a compression after impact (CAI) test [36].

Recently, Trask et al. [176] considered the placement of self-healing hollow glass fiber layers within both glass fiber/epoxy and carbon fiber/epoxy composite laminates to mitigate damage and restore mechanical strength. The hollow fibers were bespoken with diameters between 30 and 100 µm and a hollowness of approximately 50%. The study revealed that after the laminates were subjected to quasistatic impact damage, a significant fraction of flexural strength can be restored by the self-repairing effect of a healing resin stored within hollow fibers. More details of such healing system can be found in ref. [173–175, 177–179]. For example, Pang et al. added UV fluorescent dye to the healing resin within the hollow fibers so that bleeding of the repair substance in the composites can be visualized [173]. Williams et al. demonstrated the importance of optimizing the location and amount of healing resin filled hollow glass fibers to provide an effective self-healing function within carbon fiber reinforced epoxy laminates [178]. Kousourakis and Mouritz carefully assessed the influence of hollow glass fibers (external diameter = 170, 320, 430 and 680 µm, wall thickness = 0.6–1.5 µm) on mechanical properties of continuous carbon fibers/epoxy composites because ply waviness and resin-rich zones are changed [179]. Their results indicate that tension and compression properties of the composites are not significantly affected when the hollow fibers are aligned parallel to the load-bearing plies. However, the static strength properties are reduced at relatively large fiber sizes (above ~200 µm) when aligned normal to the load-bearing plies.

On the other hand, a step type multimode quartz optical fiber consisting of hollow fiber, cladding and coating have been successfully applied in building up smart composites structures. When the materials were damaged, the pre-embedded hollow optical fibers had to be ruptured leading to significant reduction in the output light intensity. This favored to locate the cracked portions. In case the hollow optical fibers were infused with uncured resin and embedded within polymer composites, real-time monitor, diagnosis and repair of damages would be simultaneously completed. Guided by this idea, Yang and coworkers manufactured glass fiber laminates with self-diagnosis and self-healing functionality, in which ethyl cyanoacrylate served as the healant. Recoveries of initial tensile strength of about 1/3 and initial compressive strength of about 2/3 proved the feasibility of this approach [180–182]. Moreover, shape memory alloy (SMA) filaments were also introduced into the system (Fig. 1.11), which could generate localized compression under the stimulus of a control circuit driven by the data acquired from the signals of the optical fibers network, helping to squeeze the fluidic healing agent out of the hollow optical fibers [183, 184]. Here the hollow optical fibers play a dual role. They act as sensors to detect the sites, types and degrees of any possible internal damages and as reservoirs to store the healing agent.

In fact, SMA itself can also be employed for crack healing by exerting closure force on the cracks [185–187], because it exhibits a thermoelastic

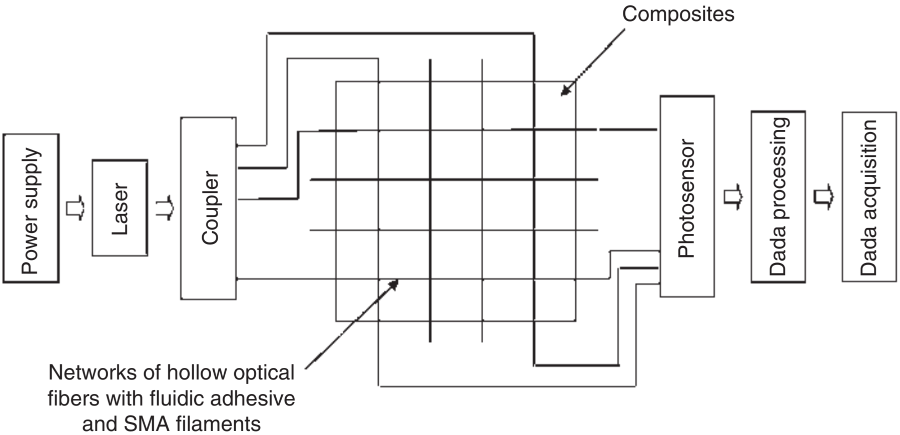


Figure 1.11 Smart composites structure capable of autonomic self-diagnosis and self-healing based on hollow optical fibers and SMA filaments.

transformation from martensite to austenite when heated above the transformation temperature. However, the literature shows that SMA fibers used to play a supporting role and worked together with other healing mechanisms, probably due to the fact that the shape of the specimen with SMA fibers alone would change after repair [188].

Property matching is important for hollow glass fibers/matrix polymer pairs, which decides breakage of the hollow fibers and release of the healing agent. Zhao et al. showed that for the epoxy/polyamide compounds with healing agent loaded hollow plastic fiber, the plastic tubes did not fracture even when the matrix was completely broken [167]. No healing effect could be observed as a result. One of the possible solutions of this problem lies in covering the hollow repair fiber with a thin polymeric layer [168, 189]. By tuning species and thickness of the polymer coating, one might be able to control fracture mode and time of the containers, giving out healant at the right moment.

Flowability of the released healing agent inside materials to be healed is another problem that might be encountered in practice. Besides diffusivity of the healing agent itself, internal pressure within the repair tubes should also be considered. Having carefully studied dependences of the spillage of healing fluid and the repair area, Zhao and coworkers indicated that 95% of the crack planes can be healed when the internal pressure reached 0.2 MPa [167].

1.3.1.2 Three-Dimensional Microvascular Networks Conventional extrinsic self-healing composites are hard to conduct repeated healing, because rupture of the embedded healant-loaded containers would lead to depletion of the healing agent after the first damage. To overcome this difficulty, Toohey et al. proposed a self-healing system consisting of a three-dimensional microvascular network capable of autonomously repairing repeated damage events (Fig. 1.12) [38]. Their work mimicked architecture of human skin. When a cut in the skin triggers blood flow from the capillary network in the dermal layer to the wound site, a clot would rapidly form, which serves as a matrix through which cells and growth factors migrate as healing ensues. Owing to the vascular nature of this supply system, minor damage to the same area can be healed repeatedly. The 3D microvascular networks were fabricated by deposition of fugitive ink (a mixture of Vaseline/microcrystalline wax (60/40 by weight)) in terms of direct-write assembly [190] through a cylindrical nozzle. Then, the yielded multilayer scaffold was infiltrated with epoxy resin. When the resin was consolidated, structural matrix was obtained. With the help of heating and a light vacuum, the fugitive ink was removed and 3D microvascular networks were created. By inserting a syringe tip into an open channel at one end of the microvascular networks, a fluidic polymerizable healing agent was injected into the networks.

The healing chemistry of this method used ring-opening metathesis polymerization of dicyclopentadiene monomer by Grubbs' catalyst, benzylidenebis (tricyclohexylphosphine) dichlororuthenium, which was used successfully in microencapsulated composites [35]. In the crack plane, the healing agent

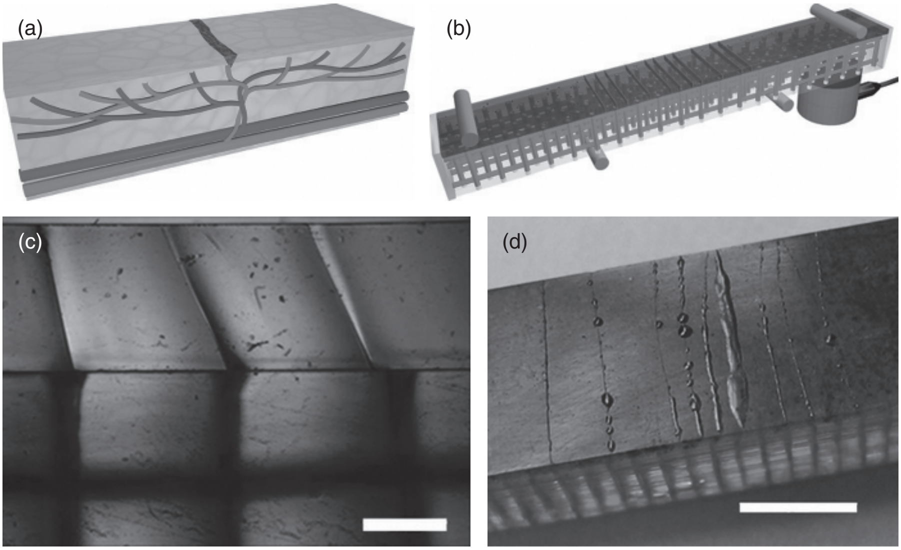


Figure 1.12 Self-healing materials with 3D microvascular networks [38]: (a) schematic diagram of a capillary network in the dermis layer of skin with a cut in the epidermis layer; (b) schematic diagram of the self-healing structure composed of a microvascular substrate and a brittle epoxy coating containing embedded catalyst in a four-point bending configuration monitored with an acoustic-emission sensor; (c) high-magnification cross-sectional image of the coating showing that cracks, which initiate at the surface, propagate toward the microchannel openings at the interface (scale bar = 0.5 mm); (d) optical image of self-healing structure after cracks are formed in the coating (with 2.5 wt% catalyst), revealing the presence of excess healing fluid on the coating surface (scale bar = 5 mm). Copyright 2007, reprinted with permission from Macmillan Publishers Ltd: Nature Materials. (See color insert.)

interacted with the catalyst particles in the composites to initiate polymerization, rebonding the crack faces autonomically. After a sufficient time period, the cracks were healed and the structural integrity of the coating was restored. As cracks reopened under subsequent loading, the healing cycle was repeated.

By means of four-point bending configuration monitored with an acoustic-emission sensor, the above approach proved to be feasible. The authors imagined extending this approach further to integrate pumps, valves and internal reservoirs, as well as to introduce new functionalities, including self-diagnosis or self-cooling, through the circulation of molecular signals, coolants or other species [38].

As pointed out by Toohey et al. [191], however, one drawback of the above design is the restricted availability of the solid-phase catalyst, which eventually becomes depleted upon repeated healing of the same crack. Accordingly, they proposed a new approach by building up two sets of independent vascular networks through direct-write assembly and selective photopolymerization, which contain epoxy resin and amine-based curing agents, respectively. Healing efficiencies of over 60% were achieved for up to 16 intermittent healing cycles of a single crack in epoxy coating, as reflected by the specific assessment protocol [192].

In the meantime, Hansen et al. made advancements in direct-write assembly—dual ink deposition and vertical ink writing [193]. They independently deposited two fugitive organic inks to construct a 3D interpenetrating microvascular network to enable repeated, autonomous healing of mechanical damage in a biomimetic coating/substrate architecture. A healing efficiency of ~50% was retained after 30 cycles of healing, which compared favorably with the self-healing microcapsule and single-network geometries.

To provide theoretical understanding of how to vascularize a self-healing composite material so that the healing fluid reaches all of the crack sites that may occur randomly through the material, Bejana et al. studied the network configuration that is capable of delivering fluid to all of the cracks the fastest (for more details, see Chapter 2) [194]. When crack site dimension and total volume of the channels were fixed, it was argued that the network must be configured as a grid and not as a tree. In addition, it is beneficial to use a grid structure that has two channel sizes, D_1 and D_2, provided that the ratio D_1/D_2 is optimized. The crack-filling time can be reduced to 50% of the time required when the grid contains channels of only one size.

On the other hand, the reliability of the self-healing vascular network for engineering applications was evaluated by identifying the critical failure modes via a failure modes, effects and criticality analysis (FMECA) [195]. This technique has also been applied to the human circulatory system to gain insight and understanding. Plant vasculature was mimicked to propose a segregated network to address the risk of fluid leakage. The approach could allow a network to be segregated into six separate paths with a system mass penalty of only approximately 25%. Fluid flow interconnections that mimic the anastomosis of animal vasculatures can be used within a segregated network to balance the risk of failure by leakage and blockage. These biomimetic approaches defined a design space that considered the existing published literature in the context of system reliability. Hamilton studied the issue at a different angle in terms of experiments [196]. They explored the interaction of cracks with a vascular system of microchannels (ca. 200 μm) embedded in a bulk epoxy structural material. Mechanical recovery from multiple cycles of damage was observed owing to the continuous supply of healing agents despite the intersection of crack damage with individual microchannels and subsequent disruption of the vascular network.

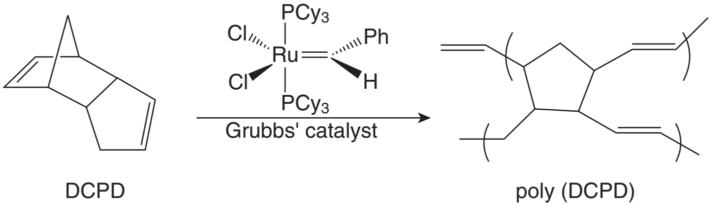
As an extension of the hollow glass fiber approach, vascular networks were also developed by the Bond's group in the University of Bristol for providing a replenishable and repeated self-healing function [197, 198]. They firstly worked out glass fiber/epoxy laminates with a vascular sandwich core, giving a relatively thin skinned configuration [197]. The healing networks consisted of tubing bonded into the midplane of the core and vertical risers supplying the skin-core bond region. The distribution of the vertical risers can be varied by design. In another work of them on the same topic [198], a vascular sandwich structure with horizontal supply channels and vertical riser channels in a closed-cell foam core was prepared. Such a network had a negligible effect on the baseline static mechanical properties of the composite panel. Rupture of the vessels released the healing fluid, filling the void that formed as a result of impact damage on the sample, as characterized by a complete recovery of compressive stress at failure after impact damage.

Even more recently, the researchers in Bristol proposed to construct vascular networks in composites following a biomimetic concept of "ray cell" structure [199, 201], analogous to vasculature in hardwoods. In addition to the analytical assessment that proved the eligibility of such plantae vascules for creating self-healing functionality [199], a prototype of this system was introduced within a carbon fiber reinforced epoxy polymer composite laminate [200, 201]. The vascules were formed by a "lost-wax" type process using low melting temperature solder wire (0.25 mm diameter, Sn 60%, Pb 40%) positioned at key interfaces between plies to form parallel channels within the laminated composite before autoclave processing. The solder wire was selected such that it could survive exposure to the manufacturer's recommended cure cycle for the composite resin system and was subsequently removed under the application of a postcure process of 190°C for 2 h whilst held under vacuum. Once removed open channels or vascules were created. The results of this conceptual study showed that damage morphology is influenced by vascule orientation and that a 10 J low-velocity impact damage event is sufficient to breach the vasculature; a prerequisite for any subsequent self-healing function [201]. The residual compressive strength after a 10 J impact was found to decrease to 70% of undamaged strength when vasculature was aligned parallel to the local host ply and a value of 63% when aligned transverse. Such a vasculature might offer a self-healing function with minimum mass penalty, without initiating premature failure within a composite structure.

1.3.2 Self-Healing in Terms of Healant Loaded Microcapsules

The principle of this approach resembles the aforesaid pipelines, but the containers for storing healing agent are replaced by fragile microcapsules. Because the technique of microencapsulation has been rapidly developed since its emergence in the 1950s [202, 204] and mass production of microcapsules can be easily industrialized, self-healing composites might thus be used in practice accordingly.

1.3.2.1 Diene Monomers The group of White et al., the pioneer in developing self-healing polymeric materials, systematically investigated a self-healing strategy based on ring opening metathesis polymerization (ROMP) of microencapsulated endo isomer of DCPD and reported a series of impor-



Scheme 1.5 Ring opening metathesis polymerization of DCPD.

tant findings [35, 205–216]. Healing was triggered when damage in the form of a crack ruptured the microcapsules, causing DCPD to be released into the crack plane where it came in contact and mixed with the pre-embedded Grubbs' catalyst (Scheme 1.5 and Fig. 1.13). For increasing catalysis efficiency, the catalyst was capsulated by wax and recrystallized, respectively [208, 209]. Delamination [210, 211], low-velocity impact damages [217] and indentation induced interpenetrating crack networks [218] in fiber reinforced epoxy composites were found to be successfully repaired by the healing agent. In addition, fatigue crack growth in epoxy [212–214] can also be retarded by the released fluid.

Aldridge et al. carefully investigated the cure kinetics of DCPD using a combination of inelastic light scattering measurements and molecular-scale simulations [219]. Structural evolution of the curing network was monitored both in terms of network connectivity and the concentration of chemical species present. The reaction rate was found to be dependent on the square of Grubbs' catalyst concentration, and there was a need to exceed a minimum catalyst concentration for the ROMP reaction to progress at all. Moreover, the rate coefficients for opening the norbornene and cyclopentene rings are almost equal.

Sanada et al. assessed the efficiency of aforesaid DCPD-Grubbs' catalyst pair for healing interfacial debonding in unidirectional carbon fiber reinforced epoxy laminates [220]. The composites were manufactured by coating carbon fiber strands with an epoxy mixture containing 30 wt% DCPD-loaded microcapsules and 2.5 wt% Grubbs' catalyst through manually dipping. The maximum healing efficiency was 19% for the specimens subjected to transverse tensile tests. The presence of carbon fibers changed the stress state around the microcapsules, so that a higher percentage of the microcapsules was broken releasing more healing fluid into the fracture plane. By using microcapsules with much smaller sizes than those applied in ref. [220], Sottos and coworkers proved the feasibility of recovery of fiber/matrix interfacial bonding in a model single fiber composite with obviously improved healing efficiency [221]. That is, 1.5 μm diameter DCPD filled capsules and recrystallized Grubbs' catalyst were attached to glass fiber surface in advance. Up to 44% average recovery of interfacial shear strength was achieved in the samples after full interfacial debonding.

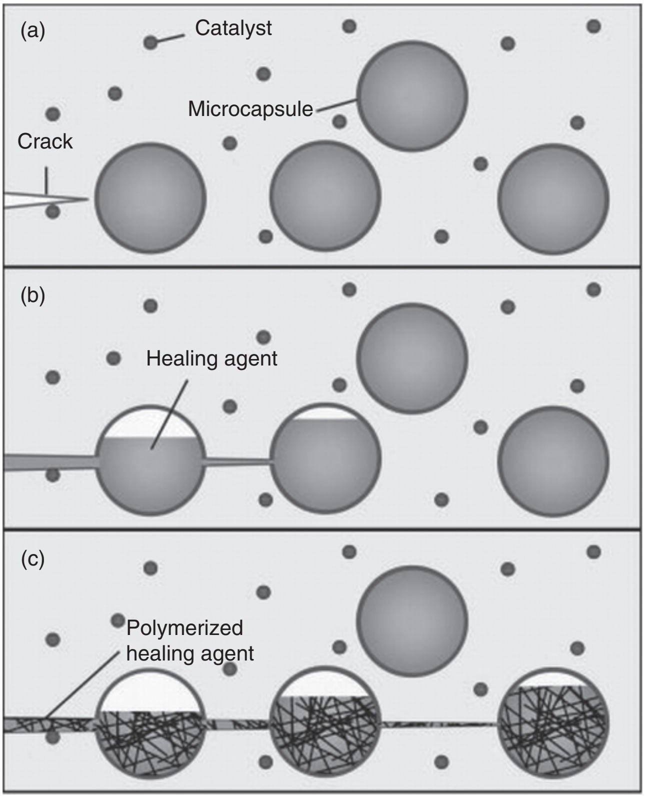


Figure 1.13 The autonomic healing concept [35]. A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent: (a) cracks form in the matrix wherever damage occurs; (b) the crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; (c) the healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed. Copyright 2001, reprinted with permission from Macmillan Publishers Ltd: Nature. (See color insert.)

Biggs et al. applied the approach invented by White et al. [35] to fabricate self-healing acrylic bone cement for use in cemented joint replacements [222, 223]. Microencapsulated DCPD and particulate Grubbs' catalyst were incorporated into PMMA based bone cement. The polymerization rate of the curing cement at 37°C (body temperature) was found to increase significantly with the decrease in the size of Grubbs' catalyst particles [223]. It was expected that the *in vivo* longevity of these arthroplasties would increase which, in turn, would translate to increased patient satisfaction and decreased hospital costs. Similarly, Chipara et al. prepared self-healing high elasticity block copolymers (polystyrene-block-polybutadiene block-polystyrene (SBS)) by dissolving the polymer in a solvent that neither dissolved the microcapsules nor deactivated the Grubbs' catalyst [224]. The self-healing block copolymer has been obtained by mixing the polymer, the solvent, the microcapsules filled with DCPD and the Grubbs' catalyst followed by the evaporation of the solvent. Raman spectroscopy and mechanical data suggested that the block copolymer exhibited self-healing features, and the addition of self-healing capabilities improved the elongation at break and tensile strength. Wertzberger et al. evaluated healing efficiency of a model dental composite formulated to autonomically heal cracks with encapsulated DCPD and Grubbs' catalyst [225]. The visible light cured base resin consisted of triethyleneglycol dimethacrylate (TEGDMA):urethane dimethacrylate (UDMA):bisphenol-A-glycidyl dimethacrylate (Bis-GMA) (1:1:1) at 45% w/w with silanated barium borosilicate glass particles (~7 µm). A 57% average recovery rate of original fracture toughness was determined after healing for seven days.

To enhance interfacial bonding between DCPD-loaded capsules and polymer matrix in composites, Wang et al. attached 3-aminopropyltriethoxy silane [226] and γ-glycidoxypropyltrimethoxy silane [227, 228] to the surface of poly(urea-formaldehyde) (PUF) capsules containing DCPD, respectively. The resultant microcapsule size was in the range of 40–190 µm with an average of 125 µm. The microcapsules wall thickness varied between 2 and 5 µm, and the core content of microcapsules was about 60%. Moreover, silanol functional groups were grafted onto the capsules. The chemical bond (Si-O-C) and hydrogen bond were formed at the interface by the reaction between Si-OH and the hydroxyl group of PUF microcapsules surface. Tensile strength and impact resistance of the epoxy composites filled with the surface modified PUF capsules were improved accordingly [228].

For purposes of stabilizing and preventing aggregation of capsulated DCPD and Grubbs' catalyst during composites manufacturing, Jackson et al. developed a generalized silica coating scheme on the basis of fluoride-catalyzed silica condensation chemistry [229]. The Grubbs' catalyst particles were wrapped by both polystyrene (PS) and PMMA in advance, rather than wax protection as reported in ref. [208]. It was shown that the coated PUF capsules and catalyst particles were well dispersed in epoxy without significant loss of the healing agent. A modest recovery of mechanical properties was observed through self-healing.

Considering that exo-stereoisomer of DCPD (i.e. exo-DCPD) has a much faster olefin metathesis reaction rate with Grubbs' catalyst, Mauldin et al. compared the kinetics of damage repair for endo- and exo-DCPD [230]. Using Grubbs' catalyst loading levels previously reported to be effective for endo-DCPD, exo-DCPD was found to heal approximately 20 times faster than the endo-isomer, but with a lower healing efficiency because of the decreased gelation time of exo-DCPD, which does not allow sufficient time to dissolve the wax or a sufficient quantity of the embedded catalyst. Nevertheless, the combination of fast kinetics and high healing efficiency was demonstrated by appropriate blending of exo/endo-DCPD healing agents and by adjusting catalyst loadings to optimal levels.

Besides DCPD, ethylidene norbornene (ENB) might be a potential candidate for the polymerizable monomer of the two-component healing agent operating by the ROMP mechanism, due to its rapid polymerization and lower costly Grubbs' catalyst loading requirements [231–238]. Furthermore, ENB has low viscosity, favoring full infiltration in the cracked parts for high healing efficiency. Guadagno et al. indicated that the pair of ENB-loaded microcapsules and Grubbs' catalyst can form metathesis product at low temperature in cracked epoxy material [237, 238]. Considering that the polymer resulting from ENB possesses a linear molecular structure, with physical properties that may not be sufficient to effectively heal microcracks, either norbornene-based ROMP crosslinking agents [233] or DCPD [234, 235] should be incorporated to improve adhesive properties of the resultant polymer. Toward development of a new healing system, Liu et al. synthesized melamine-urea-formaldehyde walled microcapsules containing ENB and its crosslinking agent by in situ polymerization in an oil-in-water emulsion [236]. Healing functionality of these capsules in polymer composites yet remains to be characterized.

In view of the fact that one of the economic obstacles of using Grubbs' catalyst for the aforesaid ROMP healing chemistry results from its poorer solubility in monomers, Mauldin and Kessler developed a model to make predictions regarding the dissolution of Grubbs' catalyst in a library of ROMP-active norbornenyl-based healing monomers [239]. They hoped to reduce the amount of the catalyst required to achieve maximum healing potential by increasing the dissolution rate of Grubbs' catalyst. Hansen solubility parameters were calculated for the norbornenyl-based monomers, which are generally reactive via the ROMP reaction. The Grubbs' catalyst was found to have two sets of Hansen parameters, and blends of healing monomers created to match these parameters were found to dissolve the catalyst rapidly.

At the early stage of using ROMP-based self-healing, typically in ref. [35], the Grubbs' catalyst serving as the polymerization initiator belongs to the first generation. Nevertheless, the use of this catalyst imposes limitations due to the catalyst's chemical and thermal instability typically encountered in processing and curing of epoxy resins [240]. To expand the scope of the healing chemistry to more challenging application conditions, Wilson et al. conducted a careful comparative investigation on three variations of Grubbs' catalysts (first generation (benzylidene-bis(tricyclohexylphosphine)dichlororuthenium), second generation (benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine)ruthenium), and Hoveyda-Grubbs' second generation (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)ruthenium)) for use in self-healing polymers [240, 241]. Owing to the thermal stability and functional group tolerance, the second generation Grubbs' catalyst emerged as the most versatile catalyst especially for high temperature applications and use with healing chemistries aimed at improving self-healing performance via noncovalent interactions. Liu et al. also studied rheological behavior of ROMP triggered by the first and second generation Grubbs' catalyst suspended in various thermosetting resins with an oscillatory parallel plate rheometer [242]. Their results showed that the first generation catalyst was more effective than the second generation in all of the epoxy matrices.

In addition to the optimization of Grubbs' catalyst, efforts were made to find out its replacement. Kamphaus et al. examined the use of WCl_6 as a catalyst precursor for ROMP of exo-DCPD [243], in hopes of establishing healing chemistry that is cost effective, widely available and tolerant of moderate temperature excursions. WCl_6 is widely available and has a melting point of 275°C, which is significantly higher than that of Grubbs' catalyst (153°C). Preliminary in situ healing experiments using 12 wt% as-received WCl_6 and 15 wt% 188 μm microcapsules containing exo-DCPD, 0.5 wt% phenylacetylene (coactivator, alkylating the tungsten to convert WCl_6 into an active catalyst) and 1.0 wt% nonylphenol (dissolution agent, helping to dissolve WCl_6 in the released DCPD) yielded approximately 20% healing efficiency.

In general, the powdery catalysts for ROMP of DCPD or ENB were predispersed in matrix material. The inevitable agglomeration of the particles has to result in heterogeneous degree of polymerization throughout the composite. Skipor et al. suggested constructing microcapsules containing DCPD with Grubbs' catalyst attached to the exterior of the microcapsules [244]. The overall healing efficiency was claimed to be raised in this way.

The effect of the DCPD loaded microcapsule size on the performance of self-healing polymers was conducted [216]. Rule et al. indicated that the amount of liquid that microcapsules deliver to a crack face changed linearly with microcapsule diameter for a given weight fraction of capsules. Self-healing performance reached maximum levels only when sufficient healing agent was available to entirely fill the crack. Based on these relationships, the size and weight fraction of microcapsules can be rationally chosen to give optimal healing of a predetermined crack size. By using this strategy, self-healing was demonstrated with smaller microcapsules and with lower weight fractions of microcapsules. Blaiszik et al. further produced smaller capsules (down to 220 nm) using sonication techniques and an ultrahydrophobe to stabilize the DCPD droplets [245]. It is believed that the nanocapsules will make self-healing materials responsive to damage initiated at a scale that is not currently possible and compatible with composites where the reinforcement spacing requires smaller capsules for applications such as self-healing thin films, coatings, and adhesives.

Nevertheless, the results of Rule et al. revealed that the healed fracture toughness fell off substantially at low microcapsule sizes and concentrations due to the failure to completely fill the crack volume with healing agent [216]. To allow the entire crack to be filled with a small volume of the healing agent, reducing the crack size during the healing period by means of SMA wires is a proper measure. Kirkby et al. showed that significant improvement in healing performance was achieved in epoxy samples containing SMA wires and Grubbs' catalyst by manually injected DCPD [246]. The SMA wires bridged the fracture plane and were activated by resistive heating to 80°C for 30 min following the virgin fracture event. Consequently, the crack volume was greatly decreased, thus allowing better healing performance with low amounts of the healing agent. In the subsequent work of Kirkby et al. [247], comparable improvements in healing performance were observed with SMA wires when the DCPD healing agent was delivered autonomically from microcapsules. The contributions were made by the reduction of crack volume as a result of pulling the crack faces closed and more complete polymerization of the healing agent due to the heat produced by the activated SMA wires.

Comparison of fracture toughness of the original specimen with that of a healed one was used as a measure of the healing effect. Conventional single-edge notched bending (SENB) and CT tests might be problematic in this case, as the prenotches would be partly closed after the healing process and an accurate measurement cannot be guaranteed. To overcome the difficulty, White et al. proposed a testing protocol with a TDCB configuration (Fig. 1.14) [205, 207]. The specific geometry ensures that the measured fracture toughness is nearly independent of precrack length, so that healing efficiency can be precisely determined.

The research so far suggest that one of the key issues of self-healing composites by means of microencapsulation lies in rigidity of the shell substance and matrix. Like the case of hollow tubes discussed hereinbefore, crack trigger in microsphere embedded composites depends on matching of deformation characteristics of the related materials. Route of crack propagation is a function of the stiffness ratio of microcapsules and matrix [35]. If the inclusion has higher modulus than the matrix, the approaching crack tends to round microcapsules; conversely, the crack could penetrate the microcapsules when the matrix is stiffer. On the other hand, simulation experiments manifest that the difference in fracture toughness of the microcapsules and matrix should be less than $0.11\,\mathrm{MPa\,m}^{1/2}$ [248]. Otherwise, cracks would not pass through the microcapsules.

The other critical factors include (i) good adhesion between microencapsulated healing agent and the matrix, (ii) size and concentration of microencapsulated healing agent, (iii) rate and degree of polymerization of the released healing agent and (iv) shell thickness and core content of the microencapsulated healing agent.

1.3.2.2 Miscellaneous Chemicals Jung et al. prepared a self-healing polyester composite with pre-embedded poly(oxymethylene urea) (PMU) microspheres [249]. The crack repair agent is mostly composed of styrene monomers and high molecular weight PS. The latter helps to lower the rate of diffusion of styrene or diethenyl benzene into a polyester matrix. The system of 23% PS ($M_n = 2.5 \times 10^5$), 76.99% styrene and a trace amount of inhibitor proved to offer the optimum healing efficiency. Jung et al. also tried to use epoxide monomer loaded PMU microcapsules for rebinding the cracked faces in the polyester matrix [249]. Solidification of the epoxy resin (i.e. the repair action) was triggered by the naturally occurring functional sites or embedded amine

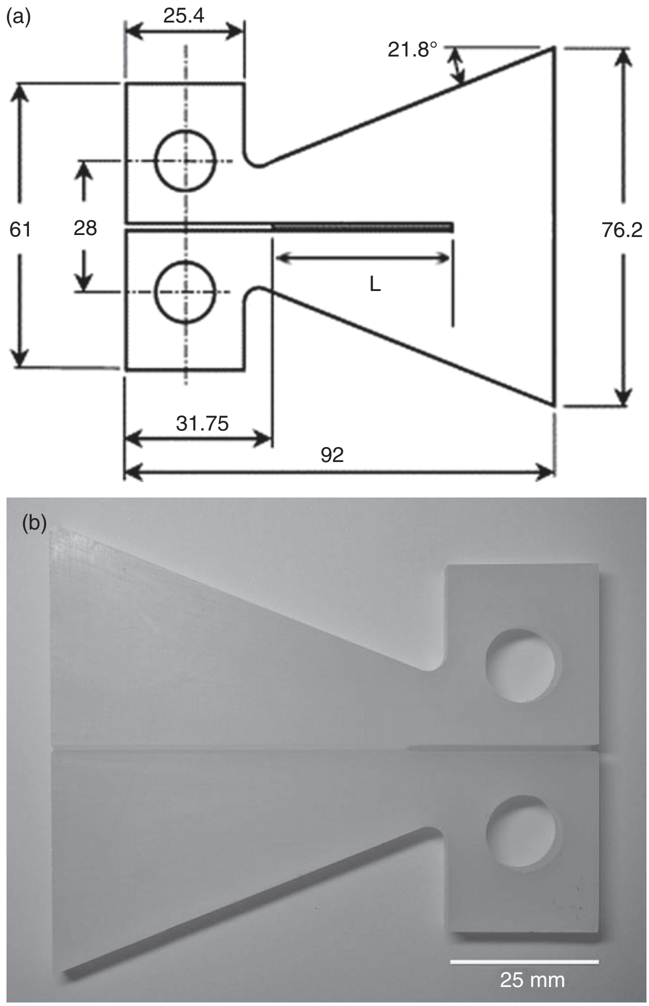


Figure 1.14 Typical TDCB specimen.

in the composites. In a latter work by White et al. [250], it was considered that the method was not feasible as the amine groups did not retain sufficient activity. Zako et al. proposed an intelligent material system using 40% volume fraction unmodified epoxy particles to repair microcracks and delamination damage in a glass/epoxy composite laminate [251]. By heating to 120°C, the embedded epoxy particles (~50 µm) would melt, flow to the crack faces and repair the damage with the help of the excessive amine in the composite. In addition to the poor activity of the amine as mentioned above, manual intervention (i.e. heating) was necessary in this case.

To ensure effective healing in self-healing fiber reinforced polymer composites, Fang and coworkers proposed a strategy as follows [252, 253]. A microencapsulated healing agent (organosilane or organosiloxane that contains Si–H bonds and Si–vinyl bonds) is dispersed in polymer matrix, while a platinum catalyst is supported on the glass fibers. In case a developing crack in the composites ruptures the embedded microcapsules, hydrosilylation of the released healing agent is initiated soon after its contact with the catalyst, and the product of the hydrosilylation rebonds the faces of the crack. The system is somewhat similar to the aforesaid ones [220, 221] (that used DCPD/Grubbs' catalyst pair as the healant) and has some potential merits, including (i) the composites mechanical properties are not compromised by the addition of the catalyst because the catalyst is covalently anchored on the fiber surface and (ii) healing efficiency would be very high as the healing reaction occurs right at the fiber/matrix interface. Nevertheless, performance evaluation of this design has not yet been reported.

For purposes of developing a radical polymerization-based self-healing system, Wilson et al. evaluated the applicability of five peroxide initiators (i.e. benzoyl peroxide, lauroyl peroxide, methyl ethyl ketone peroxide, *tert*-butyl peroxide and *tert*-butyl peroxybenzoate) [254]. Benzoyl peroxide (BPO) was found to be the best one. By dissolving BPO in phenyl acetate (9.9 wt%) and encapsulating the solution, epoxy vinyl ester composites containing 10 wt% of the microcapsules exhibited a healing efficiency of ~80% at ambient temperature, as reflected by the preliminary tests during which a mixture of acrylic monomers and tertiary amine activator was injected into the crack plane after the initial fracture.

In contrast to the conventional self-healing materials with microcapsules, Cho et al. dispersed phase-separated droplets of hydroxyl end-functionalized polydimethylsiloxane (HOPDMS) and polydiethoxysiloxane (PDES) into a vinyl ester matrix, in which the catalyst, di-*n*-butyltin dilaurate (DBTL), contained within polyurethane microcapsules, was pre-embedded (Fig. 1.15) [255]. Polycondensation of HOPDMS with PDES occurred when they met the tin-catalyst from the broken capsules induced by mechanical damage. This system possesses some advantages, including (i) the healing chemistry remains stable in humid or wet environments, (ii) the chemistry is stable to an elevated temperature (>100°C), enabling healing in higher-temperature thermoset systems, (iii) the components are widely available and comparatively low in cost and (iv) the concept of phase separation of the healing agent simplifies processing, as the healing agent can now be simply mixed into the polymer matrix.

Starting from this siloxane-based materials system, Cho et al. explored self-healing coating approaches [256], where chemical stability and passivating ability are of great importance. The catalyst was microencapsulated, while the siloxanes were present as phase-separated droplets or encapsulated. One of their model systems consisted of an epoxy vinyl ester matrix, 3 wt% $Si[OSn(n\text{-}C_4H_9)_2OOCCH_3]_4$ (TKAS, highly effective for curing PDMS) catalyst-filled PU microcapsules, 14 wt% PDMS healing-agent-containing PUF capsules and 3 wt% methylacryloxy propyl triethoxy silane adhesion promoter. Corrosion-

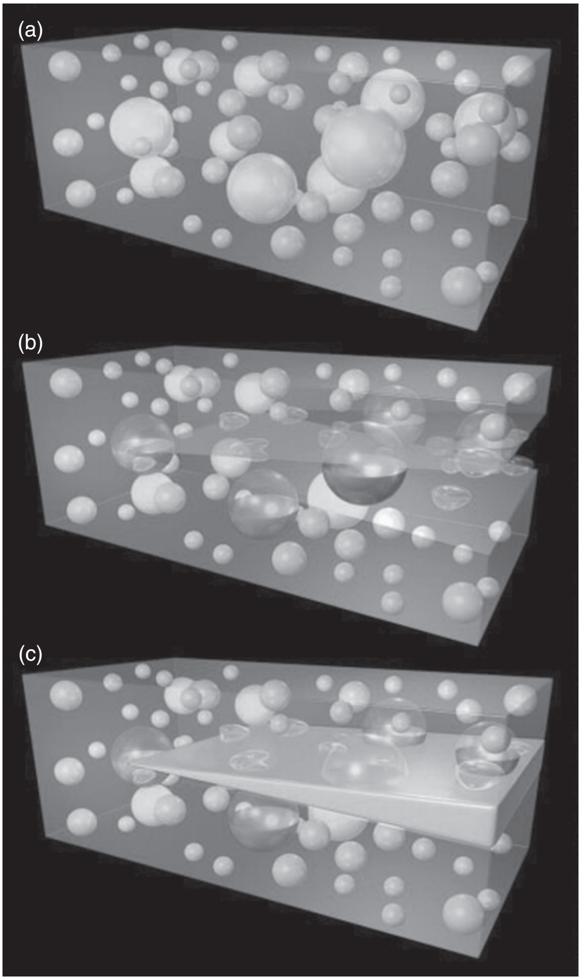


Figure 1.15 Schematic of self-healing process: (a) self-healing composite consisting of microencapsulated catalyst (yellow) and phase-separated healing-agent droplets (white) dispersed in a matrix (green); (b) crack propagating into the matrix releasing catalyst and healing agent into the crack plane; (c) a crack healed by polymerized PDMS (crack width exaggerated) [255]. Reprinted from Cho, S.H., Andersson, H.M., White, S.R., Sottos, N.R., and Braun, P.V. Polydimethylsiloxane-based self-healing materials. *Advanced Materials 18*, 997–1000. Copyright 2006, with permission from Wiley-VCH Verlag GmbH & Co. KGaA. (See color insert.)

test results after scribing and healing for 24 h at room temperature showed the efficacy of the system in protecting the substrate from the environment.

Mangun et al. tried to use PDMS-loaded microcapsules for making high temperature cured self-healing epoxy composites [257]. Their motivation came from the fact that for high performance structural composites processing requirements dictate that a self-healing system must survive elevated temperature for several hours. The epoxy composites were filled with urea-formaldehyde encapsulated PDMS resin and urethane encapsulated organotin catalyst. Healing efficiencies, based on fracture toughness recovery, ranged from 11 to 51% depending on the molecular weight of PDMS resin, quantity of healing agent delivered and use of adhesion promoters. After posttreatment of 4 h at 177°C, fracture tests resulted in a healing efficiency of 28%, which was over 60% retention of self-healing efficiency when compared to the standard cure cycle for the resin system.

As for crack repair in elastomer, Sottos et al. incorporated PUF walled microcapsules, which contained the constituent resin and initiator, respectively, into PDMS [258]. The resin microcapsules were loaded with high-molecular weight vinyl functionalized PDMS and platinum catalyst complexes, while the initiator microcapsules contained a PDMS copolymer with active sites that would link to the vinyl functionalized resin via the action of the platinum catalyst. Damage triggering and healing events took place in an analogous way to the original self-healing epoxy described above. A propagating tear in the PDMS material intersected both resin and initiator microcapsules and ruptured them. The liberated healing fluids then wicked onto the tear plane through capillary action and mix. A crosslinking reaction, the same reaction that polymerized the matrix material, occurred and formed an adhesive polymer layer that rebonded the tear faces. This self-healing material system possesses the unique feature that the healed polymer in the crack plane is the same as the host matrix.

Additionally, Keller et al. investigated performance of the above self-healing PDMS elastomer under torsional fatigue loading by a protocol commonly used in the tire industry [259]. Significant recovery of torsional stiffness was observed. The time of recovery onset correlated with the bulk gel time of the healing chemistry, indicating that the increase in stiffness was generated through self-healing. Total fatigue crack growth in a self-healing specimen was reduced by 24% in comparison to the relevant controls. The retardation of growing fatigue cracks was partly attributed to a sliding-crack-closure mechanism, where the polymerized healing agent shielded the crack tip from the applied far-field stress.

On the basis of the above investigations, Sottos and coworkers manufactured a flexible self-healing membrane consisting of a self-healing PDMS composite sandwiched between two layers of PU coated nylon [260]. The autonomic healing response in PDMS was provided through the incorporation of two types of microcapsules. One contained liquid PDMS and PDES, and the other contained a di-n-butyldilauryltin catalyst. Because the self-healing membranes primarily functioned as gas-retention bladders, a new test protocol was developed, in which samples were damaged using a hypodermic needle or a razor blade, and a successful heal was defined as the ability to reseal the damage to withstand a pressure differential across the laminate of 103 kPa (~1 atm). Healing efficiency was a function of microcapsule size, self-healing layer thickness and puncture diameter. The maximum healing success rate occurred in samples with PDMS layer thickness of 1.0 mm, 220 μm microcapsules and a puncture diameter of 0.49 mm. This intelligent laminated structure can be correlated to the work by Carlson et al. reported in an earlier time [261]. They manufactured a skin structure exhibiting flexibility, self-healing and damage sensing. The skin was fabricated on a substrate of copper-clad polyimide sheets in a layer-by-layer technique using polyimide sheets and dot arrays of ultraviolet-curable epoxy (dot size = 2 mm, dot spacing = 2.82 mm). The ultraviolet-curable epoxy acted as both a structural adhesive and as the self-healing fill material. The skin structure was integrated with an array of LC circuits, where each circuit is characterized by a unique resonant frequency. If the skin was damaged, the ultraviolet-curable epoxy was released and cured by ambient sunlight. Tests indicated good performance with respect to self-healing of the skin and fault isolation. By surveying the designs in ref. [260, 261], one might find that a combination of materials chemistry and microelectronics would offer smarter characteristics to end-products with self-healing ability.

In addition to the polymerizable healing agent, Caruso et al. used solvents to heal cracks in thermoset materials [262]. Chlorobenzene was encapsulated by urea-formaldehyde and embedded in an epoxy matrix. It is believed that the solvent would induce crosslinking of the incompletely cured resin and heal cracks. The technique might be an economical, simple and potentially robust alternative to the recovery of virgin properties of a material after crack damage has occurred, as concluded by the authors. Furthermore, they used a mixture of epoxy monomer and solvent instead of pure solvent as core substance of the microspheres [263, 264]. Owing to the residual amine in the partially cured epoxy matrix, epoxy monomer released from the epoxy-solvent microcapsules can be cured and adhered to the original matrix interface. Consequently, healing efficiency was significantly higher than that offered by pure solvent capsules, and complete recovery of fracture toughness was observed.

Comparatively, a one-part and catalyst-free self-healing system, like the above-mentioned solvent microcapsules, is less reported. Cyanoacrylate [162] and poly(vinyl acetate) (PVAc) [167] that had been infiltrated into hollow tubes, for example, have not yet been encapsulated probably due to technical difficulties. Considering its advantage in simplification of self-healing composites manufacturing, Yang et al. prepared microcapsules containing liquid isophorone diisocyanate (IPDI) by interfacial polymerization of a toluene diisocyanate (TDI)-derived polyurethane prepolymer in an oil-in-water emulsion [265]. The capsules were believed to be applicable in an aqueous or moisture-laden environment.

Kumar et al. prepared an anticorrosion coating by incorporating PUF-walled capsules containing several types of film forming compounds (healants) and corrosion inhibitors into commercially available epoxy coatings systems [266]. The encapsulated chemicals included camphor and alkylammonium salt of (2-benzothiazolylthio) succinic acid in xylene for corrosion inhibition and tung oil and spar varnish for the film repair properties. Steel substrates coated with these self-healing systems were scribed and laboratory tested. Growth of coating damage at the scribe was arrested in self-healing coatings with all microcapsule formulations compared to control samples. Subsequently, Suryanarayana et al. embedded PUF microcapsules containing linseed oil in epoxy as a demonstration of a self-healing coating [267]. Cracks in a paint film were rapidly healed within 90 s when linseed oil was released from microcapsules ruptured under simulated mechanical action and dried by oxidation with atmospheric oxygen. This was further confirmed from the corrosion resistance performance of healed films in a salt spray test. In a latter work on the same topic by Jadhav et al. [268], similar conclusions were drawn. He and Shi proposed the concept of self-repairing coating for corrosion protection of aluminum alloys, using cagelike oil core/silica gel shell particles [269]. These micron-scale cagelike microspheres with opened and closed pores encapsulated repairing agent (methyl methacrylate) and catalysts (potassium persulfate and sodium thiosulfate), respectively. Such smart particle composites were prepared based on an interfacial self-assembly process and sol-gel reaction. They were then self-assembled on the AA2024 aluminum alloy surface, followed by the application of a sol-gel film. The hybrid film worked as a primer coating featuring the self-repairing property in response to scratches via polymerization of the released monomer.

Unlike the conventional chemical encapsulation of healing agent, the "physical" encapsulation method was developed by Kirk et al. to prepare "nanoporous silica capsules" [270]. A known amount by weight of the nanosilica (surface area: ~1300 m^2/g, nanopore diameter: 2.5 nm, pore volume: 0.96 cm^3/g) was placed on top of epoxy resin and the hardener. Both substances infiltrated the pores by capillary forces, after which the capsules sank down and accumulated in higher concentration on the bottom of the mixture. The resultant slurries were used for the preparation of the self-healing specimens. It was found that the self-healing capability of the infiltrated silica was not high, as characterized by the recovery of the load-crack opening displacement (COD) stiffness of the specimens. This might be due to the fact that the amount of healing glue inside the long nanochannels was not large enough to heal macrocracks. Accordingly, it would probably be good for the recovery of fatigue damage, by preventing/healing microcracks.

At the end of this subsection, we would like to spend more time on self-healing anticorrosion coatings that are different from the aforesaid ones [266–269] in terms of functioning mechanism, despite the fact that it might slightly go beyond the book's scope.

So far, there have been many corrosion protective coatings, which can be divided into three categories as follows. (i) Sacrificial anodes, such as aluminum, zinc or magnesium, which are the oldest industrial practices to provide longstanding protection. The anode layer on steel continues to corrode when exposed to a corrosion environment, and this protects the underneath surface. (ii) Chemical pretreatment or conversion coating, which is usually formed as an integral part of metal surface due to the interaction between the metal and the treatment solution. Such a coating is constituted by inorganic crystalline or amorphous film that passivates metal surface and improves the adhesion between metal and the organic coating. (iii) Polymeric coatings, which confer an impermeable physical barrier against corrosive species and decorative appearance on metallic substrates.

Sacrificial anodes technique controls the corrosion of a metal surface by making it the cathode of an electrochemical cell, consuming the anode material until eventually it must be replaced. There is no “self-healing” problem for this coating.

The chemical conversion coatings based on chromate compounds are the most popular for the pretreatment of various metallic substrates because they exhibit far better corrosion resistance than any other similar coats derived from phosphating and oxalating processes. Nevertheless, the conversion coats could not provide well enough anticorrosive behavior during the whole service life of the steel. In this context, the concept of active corrosion protection was proposed as an approach of “self-healing” coating. The actively inhibitive components, like chromates, or other environmental-friendly alternatives including molybdates, vanadates, permanganates, tungstates, electroactive conductive polymers, etc. were added to various organic, inorganic and hybrid anticorrosion coatings. These additives are typically anionic inhibitors, which oxidize the surface of the metal to form a thin metal complex on the surface to prevent further oxidation by corrosive chemicals. A protective coating loaded with inhibitor, therefore, not only provides a barrier to the aggressive corrosive species, but also contains a reservoir of inhibitors that can heal the defects in the coating [271–274]. As the coating is broken down locally, the corrosion rate greatly increases in this small region and the inhibitor stored at the outer layers leaches out and migrates to the local damaged area, reacting with the actively corroding metal surface and blocking the corrosion process. In other words, such a coating should release inhibitors only in the case of corrosive attack and prevent them from being leached out or released by ion-exchange processes. To realize this mechanism, a direct addition of a corrosion inhibitor to the coating formulation has been substituted by using nanoscale containers (carriers) loaded with inhibitors. In the latter cases, actively inhibitive compounds are kept in a “trapped state” until the local environment changes or if a corrosion process starts in the coating defect. The nanocontainers respond to this signal and release the immobilized active materials [275, 276]. Today, hundreds of works have been devoted to the attempts of developing self-healing coatings based on the effect of incorporated inorganic or organic corrosion inhibitors [277, 278], in which active anticorrosion coating has achieved practical application for many years.

An organic polymer coating in corrosion protection system is to provide a dense barrier against corrosive species. During its service life, however, the coating would undergo various damages through mechanical abrasion, scratches, impact, etc. resulting in breach points that subsequently propagate and expose the substrate to corrosive agents (moisture, oxygen and aqueous electrolyte solutions). The corrosion processes develop promptly at the defects of the coating films and promote debonding of the paint. Therefore, an effective self-healing of defects in these coatings is necessary to provide long-term protection effect. The works reported in [256, 266–269] belong to this category. In a recent attempt toward self-healing coatings for steel, Kowalski et al. demonstrated the feasibility of an intrinsically conducting polymer film [279]. They prepared a 4.2 μm thick conducting polypyrrole (PPy) coating with a bipolar structure coated on carbon steel, without any additional barrier-type topcoat. The inner layer of the coating was doped with heteropolyanions of $PMo_{12}O_{40}^{3-}$, while the outer layer was doped with dodecylsulfate. The well-designed function of doped ions possessed specific permselective properties, restricting incorporation of aggressive chlorides from corrosive electrolyte. The cation permselective membrane controlled the release of healing ions to the defect zone when artificial defects were formed, efficiently inhibiting corrosion of the underlying metal substrate. As the healing ions reacted with the steel at the damaged zone, an insoluble iron molybdate salt was yielded. This is different from the aforesaid systems where a monomer is released to recreate the coating in the affected region.

1.4 INSIGHTS FOR FUTURE WORK

Owing to their smart nature, self-healing materials might solve technical problems that are hard to be solved or simply cannot be solved by traditional approaches. They have opened up broad prospects for key engineering communities and cutting-edge technologies. For example, aviation and automobile industries treat self-healing materials as an advanced means of upgrade. Materials capable of stopping possible crack formation and extending fatigue longevity are certainly attractive for every aspect of modern industries. However, the structural materials applied in practice have to withstand extremes of temperature, pressure and acceleration, as well as unexpected impacts. There is still a long way to prove the feasibility of the self-help concept. On the whole, research in this field is still in the infancy. As concluded by Trask et al. [29], most of the self-healing work to date has been bioinspired and not biomimetic, although this is slowly changing. According to their opinion, biomimetic self-healing must mimic self-healing to a higher degree but the distinction is very difficult to define because in practice exact replication of natural systems is very challenging.

Despite the fact that the achievements in self-healing polymers and polymer composites are far from satisfactory, the new opportunities found during researches and development have demonstrated that it is feasible to either invent new polymers with inherent crack repair capability or integrate existing materials with novel healing systems. Interdisciplinary studies based on tight collaboration among scientists and engineers are prerequisites for overcoming the difficulties. The related works and outcomes have broadened the application possibility of polymeric materials. Also, the extended service life of components made from these intelligent materials would contribute to reduce waste disposal. It is undoubtedly important for building up a sustainable society.

Comparatively, extrinsic self-healing techniques might be easier to be commercialized for large-scale usage within a relatively short period of time. This is not only because incorporation of a healing agent into a target material approaches to conventional compounding techniques used in polymer engineering, but also because of the emergence of new specific research and development tools and techniques. X-ray microtomography, for example, has allowed quantitative analysis of the fracture and release processes in a microcapsule-based self-healing polymer [280]. Visualization of the release of the healing agent from ruptured capsules was accomplished using a profluorophore [281], which was converted by the librated tetra-functional thiol into rhodamine leading to strong fluorescence without the necessity for UV illumination [173].

Besides the methodologies described in the above subsections, the ongoing attempts are continuously presenting new concepts. For example, Lee et al. considered solid-state devices that integrate ductile polymeric layers and brittle semiconductor or metal films [37]. Using computer simulations, they showed that adding nanoparticles to the polymers yielded materials in which the particles became localized at nanoscale cracks and effectively form "patches" to repair the damaged regions (for more details, refer to Chapter 2). Interestingly, the strategy presented by Liu et al. shows a possible route to carry out self-healing with nanoparticles in reality [282]. They demonstrated delivery of inorganic nanoparticles to induced cracks on multilayer barrier films through the incorporation of a reactive metal oxide precursor within electrospun water-degradable polymer fibers. Cracks allowed the influx of moisture and subsequent hydrolysis of the polymer. The metal oxide precursor was then released and hydrolyzed to form nanoparticles that sealed the crack. Alessandri also showed that the holes made by laser irradiation in the composites of gold nanoparticles/conductive pressure sensitive adhesives were self-healed due to chemocapillary flow induced by surface compositional gradients [283]. In addition, Trau et al. proposed healing under electric field in terms of electrohydrodynamic aggregation of colloidal dielectric particles [284]. To self-repair macro-length scale damage, on the other hand, Li et al. showed the effectiveness of confined shape recovery functionality of shape memory polymer (SMP) [285–289]. By creating a semi-interpenetrating network composed of a crosslinked thermoset and a thermoplastic, Karger-Kocsis considered that both shape memory and self-healing functions can be combined [290]. In such an intelligent material, the thermoplastic polymer (amorphous or semicrystalline) offers "switching" and "healing" effects, whereas the crosslinked thermoset acts as the fixing phase. Xiao et al. further demonstrated that thermal healing capability of epoxy SMP can be greatly improved by the addition of a small amount of grapheme [291].

In fact, the progress in development of novel self-healable polymers and polymer composites relies on the application of existing techniques and, more importantly, the innovation in the related sciences and technologies. It is the latter that might eventually lead to biomimetic self-healing in real meaning.

Carbon nanotubes, which have been extensively studied as a next generation material in the past decade, for example, have shown the potential in this aspect. Thostenson and Chou revealed that the electrically conductive networks of carbon nanotubes in traditional fiber reinforced polymer composites can act as sensors of distributed strain [292]. Accordingly, damage progression was in situ monitored and crack healing effectiveness was also evaluated. Similar conclusions were drawn by Koratkar and coworkers [293, 294]. In addition, localized fast heating of the crack interface with the help of carbon nanotubes activated the heating-curing additive, resulting in up to 70% recovery of strength of the composites [293]. Meanwhile, Lanzara et al. performed a molecular dynamics study to investigate the use of single-wall carbon nanotubes as nanoreservoirs for self-healing [295]. The organic molecules, which served as a healing agent and were stored inside the nanotubes, escaped into space in a few picoseconds. The simulation results suggested the possibility of using carbon nanotubes as a reinforcing self-healing device that has the capability to slow down fracture propagation in a hosting matrix, automatically heal the crack, self-repair and reinforce the material prior and after the repairing process. Evidently, the multifunctionality of carbon nanotubes demonstrated by the above three groups implies that the tasks of diagnosis, detection, healing and reinforcing can be fulfilled by carbon nanotubes alone. No additional components are required. This resembles the situation of biological systems to a certain extent.

In a recent report by Odom et al. [296], the healing strategy based on microcapsules has extended into conductivity restoration. Solutions of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) in various solvents were separately incorporated into PUF microcapsules. Rupture of a mixture of TTF-containing microcapsules and TCNQ-containing microcapsules resulted in the formation of the crystalline conductive TTF-TCNQ charge-transfer salt. Preliminary measurements demonstrated the partial restoration of conductivity of severed gold electrodes in the presence of TTF-TCNQ derived in situ, which might be applicable to electronic devices.

From a long-term point of view, synthesis of new polymers accompanied by intrinsic self-healing function through molecular design would be a reasonable solution. Recent exploration has shown the prospects of this trend, but the automatic trigger mechanism remains open. Working out the solutions would certainly push polymer sciences and engineering forward.

Interesting new attempts toward this target are related to mechanochemistry [297–300]. Piermattei et al. [297] designed latent catalysts that combine a metal with polymer-functionalized ligands, producing a long chain with a single coordination complex in the center. In these latent catalysts, selective scission of a coordination bond, which is weak compared with the covalent bonds in the polymer, results in either a catalytically active ligand or a catalytically active metal site (Fig. 1.16). They found that silver(I) complexes of polymer-functionalized N-heterocyclic carbenes catalyzed a transesterification reaction when exposed to ultrasound in solution. Furthermore, ultrasonic acti-

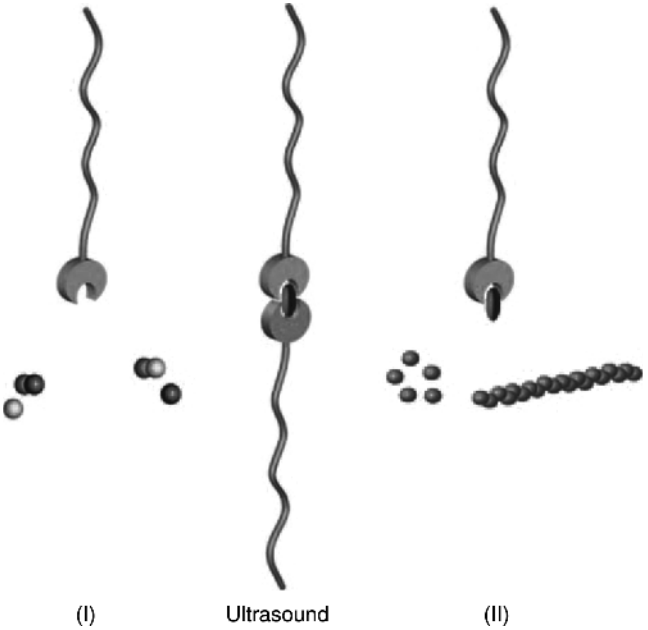


Figure 1.16 Cartoon depicting the ultrasound-induced mechanochemical scission of a metal complex with polymeric ligands, resulting in the activation of a catalyst [297]. In (i), the active ligand catalyses transesterification and in (ii) the metal centre catalyses polymerization. Copyright 2009, reprinted with permission from Macmillan Publishers Ltd: Nature Chemistry. (See color insert.)

vation of a ruthenium biscarbene complex with appended polymer chains led to catalysis of olefin metathesis reactions. In each case, the catalytic activity originating from ligand dissociation brought about by transfer of mechanical forces from the polymeric substituents to the coordination bond. Such mechanochemical catalyst activation has potential applications not only in transduction and amplification of mechanical signals, but also in mechanically initiated polymerizations for self-healing materials by restoring the original molecular weight of the target polymer [298]. Similarly, Kersey et al. suggested inclusion of reversible interactions in a material for engineering repair without an external stimulus [299]. They described a family of hybrid polymer gels, in which covalent crosslinks created a permanent, stiff scaffold onto which reversible metal–ligand coordinative crosslinks were added. In this way, the reversible component would relieve stress from the permanent network, break preferentially under significant load and reform once that stress was removed to restore strength to the material [63, 64]. On the other hand, Davis et al. created mechanoresponsive polymeric materials by directly linking force-activated mechanophores into the polymer chains of bulk polymers or by using the mechanophores as crosslinks [300]. Under tensile stress, covalent bond scission in mechanophore resulted in an electrocyclic ring-opening. The colorless spiropyran, used as a mechanophore, underwent a well-characterized color change on ring-opening, which allowed the reaction to be visualized as plastic deformation occurred. The position of mechanical stress was therefore visible, so these materials acted as molecular force sensors and had potential applications in damage sensing. In other words, the force activation of covalent bonds can serve as a general strategy for the development of new mechanophore building blocks that impart polymeric materials with desirable functionalities ranging from damage sensing to fully regenerative self-healing.

Evidently, these works foreshow the possibility that conventional mechanical force might automatically trigger the start of the intrinsic repair process. The challenges lie in that (i) the strength of the mechanosensitive bonds should be high enough to provide the polymeric materials with adequate load bearing capability (which is of particular importance for structural materials) and (ii) the resources of monomer supply should also be simultaneously activated, which is critical for the healing in the glassy state.

To create relatively weak bonds in polymers for possibly self-healing, Kamada et al. made use of thiol-disulfide exchange reactions [301]. The basic idea lies in that thiolate anion (formed from the thiol group) attacks a sulfur atom of a disulfide bond (S-S). The original disulfide bond is broken, and another sulfur atom is released as a new thiolate. On the other hand, a new disulfide bond forms between the attacking thiolate and the original sulfur atom. In this reaction, the S-S bonds are reshuffled by the exchange. If a material crosslinked with these labile S-S bonds was stressed and deformed, the crosslinks would be broken, allowing the building blocks to slip and slide and then rebond with new neighbors to reform a continuous film. This structural rearrangement should preserve the mechanical uniformity of the network and prevent catastrophic failure. In the preliminary work, Kamada et al. synthesized a poly(n-butyl acrylate)-based star polymer by atom transfer radical polymerization [301]. Disulfide functionality was introduced into the periphery of star polymers by using a disulfide crosslinking agent. Dynamic mechanical property measurements showed that the S-S-functionalized star polymers responded to reduction-oxidation conditions, indicating that the disulfide bonds did cleave and reform. Mechanochemistry of the material has not yet been reported.

What deserves to be mentioned is that Lenhardt et al. provided a possible solution for mechanochemistry-aided intrinsic self-healing at a different angle [302]. They found a polymer molecule that was so springy it snapped back from stretching, much smaller than it was before. In this context, self-healing polymeric materials can be developed in which the macromolecules near cracked portions would be able to jump into action and perform new chemistry to build bridges across the cracks.

In conclusion, the main concern at present should be focused on proof-of principle experiments for developing as many ways as possible the introduction of self-healing mechanisms into various types of polymers and polymer composites (Table 1.1). This is absolutely necessary prior to the screening and

TABLE 1.1 Examples of Self-Healing Polymers and Polymer Composites Toward Restoration of Mechanical Properties*

Category of material to be repaired	Material to be repaired	Healing system	Trigger mechanism	Healing mechanism	Assessment of healing effect	Ref.
Thermoplastic	PMMA, MMA-MEA copolymer, PC	Bulk	Heating or solvent induced	Chain interdiffusion and entanglements	CT test and photography	[73, 79–84]
Thermoplastic	EMAA	Bulk	Thermomechanically induced local melting	Chain interdiffusion and entanglements	Visual inspection after sawing, cutting and puncture; modified adhesive peel test, and quasistatic test method	[105–111]
Thermoplastic	PC	Bulk (weak alkali/hydrolyzed chains)	Steam	Weak alkali catalyzed polymerization	Molecular weight and mechanical strength	[113]
Thermoplastic	PPE	Bulk (copper ion/oxygen/scission chains)	Heating	Copper ion catalyzed polymerization	Molecular weight	[114]
Thermoplastic	PMMA	Bulk (γ-Fe_2O_3 nanoparticles)	Oscillating magnetic field	Oscillation of γ-Fe_2O_3 particles induced localized amorphous flow	Modulus (nanoindentation, tensile test), failure strain	[86]

(*Continued*)

TABLE 1.1 (*Continued*)

Category of material to be repaired	Material to be repaired	Healing system	Trigger mechanism	Healing mechanism	Assessment of healing effect	Ref.
Thermoplastic	PMMA	Encapsulated glycidyl methacrylate (GMA)	Crack induced rupture of microencapsulated GMA	Living polymerization	Impact test	[303]
Thermoset	Epoxy	Bulk	Heating	Postcuring of residual functional groups	Impact test	[87, 81–88]
Thermoset	Epoxy, fibers/unsaturated polyester, and fibers/epoxy	Cyanoacrylate, epoxy monomer, unsaturated polyester, etc. stored in hollow tubes	Crack induced breakage of hollow tubes containing healant	Curing of healant	Tensile, flexural and impact tests; photography; ultrasonic C-scan	[162–178]
Thermoset	Epoxy, fibers/unsaturated polyester and fiber/epoxy	Encapsulated DCPD and particulate Grubbs' catalyst dispersed in matrix	Crack induced rupture of microencapsulated DCPD	Ring-opening metathesis polymerization of DCPD	TDCB, DCB and fatigue tests	[35, 205–217]
Thermoset	Epoxy	Encapsulated exo-DCPD and particulate WCl_6	Crack induced rupture of microencapsulated DCPD	Ring-opening metathesis polymerization of DCPD	TDCB	[243]

Thermoset	Epoxy	DCPD stored in 3D microvascular networks and particulate Grubbs' catalyst dispersed in matrix	Crack induced damage of 3D microvascular networks, releasing healant	Ring-opening metathesis polymerization of DCPD	Four-point bending	[38]
Thermoset	Epoxy	Epoxy and aliphatic amidoamine hardener respectively stored in microchannels	Crack induced damage of 3D microvascular networks, releasing healant	Curing of healant	DCDC	[196]
Thermoset	Epoxy and woven glass fibers/epoxy	Encapsulated epoxy monomer and latent hardener predissolved in matrix	Crack induced rupture of microencapsulated epoxy monomer	Curing of healant	SENB, DCB and CAI tests	[304–306]
Thermoset	Epoxy, woven glass fibers/epoxy	Encapsulated epoxy monomer and encapsulated mercaptan	Crack induced rupture of microencapsulated healant	Addition polymerization	TDCB, fatigue and CAI tests	[307–310]

(*Continued*)

TABLE 1.1 (*Continued*)

Category of material to be repaired	Material to be repaired	Healing system	Trigger mechanism	Healing mechanism	Assessment of healing effect	Ref.
Thermoset	Epoxy	Encapsulated epoxy monomer and encapsulated boron-containing hardener (or boron-containing hardener loaded-porous media)	Crack induced rupture of microencapsulated epoxy monomer	Cationic polymerization	Impact test	[311, 312]
Thermoset	Epoxy	Encapsulated PDMS and encapsulated organotin catalyst	Crack induced rupture of microencapsulated healant	Polycondensation of polysiloxanes	TDCB	[257]
Thermoset	Epoxy	Encapsulated styrene and encapsulated BPO	Crack induced rupture of microencapsulated healant	Free radical polymerization	Impact test	[313]
Thermoset	Glass fibers/epoxy	Epoxy granules	Heating	Curing of healant with excessive amine in the matrix	Three-point bending and tensile fatigue	[251]

Thermoset	Epoxy	Percolating PCL	Heating	Heating induced bleeding, wetting and mending	SENB	[96]
Thermoset	Epoxy and woven carbon fibers/epoxy	EMAA particles or fibers	Heating	Thermal adhesion	SENB, TDCB and DCB	[97, 99]
Thermoset	Epoxy	Thermally reversible crosslinking gel from furfurylamine and bismaleimide	Thermal treatment	DA reaction induced liquefaction, flow and recrosslinking of the gel	CT	[148]
Thermoset	Epoxy	Encapsulated solvent (chlorobenzene)	Crack induced rupture of microencapsulated solvent	Solvent induced crosslinking of incompletely cured resin	TDCB	[261]
Thermoset	Epoxy	Encapsulated GMA	Crack induced rupture of microencapsulated GMA	Nucleophilic addition and ring-opening reactions	TDCB	[314]
Thermoset	Unsaturated polyester	Styrene or epoxy monomer	Crack induced rupture of microencapsulated healant	Polymerization or curing of healant triggered by functional sites or embedded amine in matrix	Mechanical strength and visual inspection	[249]

(*Continued*)

TABLE 1.1 (*Continued*)

Category of material to be repaired	Material to be repaired	Healing system	Trigger mechanism	Healing mechanism	Assessment of healing effect	Ref.
Thermoset	Unsaturated polyester	Phase-separated polysiloxane droplets/tin catalyst	Crack induced rupture of microencapsulated catalyst	Polycondensation of polysiloxanes	TDCB	[255]
Thermoplastic/thermoset semi-interpenetrating network	Poly(bisphenol-A-co-epichlorohydrin)/epoxy	Bulk	Heating	Chain interdiffusion and entanglements	CT and impact tests, photography	[93, 94]
Thermoset with thermally reversible crosslinked networks	Crosslinked multifuran/multimaleimide	Bulk	Thermal treatment	DA reaction	CT and DCDC tests	[120, 121, 146]
Thermoset with thermally reversible crosslinked networks	Carbon fibers/crosslinked multifuran/multimaleimide	Bulk	Resistive heating	DA reaction	Short span three-point bending	[126]
Thermoset with thermally reversible crosslinked networks	Crosslinked polymer from dicyclopentadiene-based monomer	Bulk	Thermal treatment	DA reaction	Compression and SENB tests	[132]
Thermoset with thermally reversible crosslinked networks	Epoxy	Bulk	Thermal treatment	DA reaction	Visual inspection after impact, and DCDC test	[315–317]

Thermoplastic with thermally reversible crosslinked networks	PA crosslinked with thermally reversible bonds	Bulk	Thermal treatment	DA reaction	Tensile test and photography	[129]
Thermoplastic with thermally reversible crosslinked networks	PK crosslinked with thermally reversible bonds	Bulk	Thermal treatment	DA reaction	Three-point bending (the failed samples were remolded by hot compression and then tested offering recovered strength)	[131]
Elastomer	Silicone rubber	Encapsulated polysiloxane/ platinum catalyst/initiator	Crack induced rupture of microencapsulated healant and initiator	Polycondensation of polysiloxanes	Tear strength and torsion fatigue	[258, 259]
Elastomer with thermally reversible crosslinked networks	PEA crosslinked with thermally reversible bonds	Bulk	Thermal treatment	DA reaction	Tensile test	[138]
Thermoplastic elastomer	Supramolecular rubbers from fatty acid derivatives, diethylene triamine and urea	Bulk	Rupture induced nonassociated hydrogen-bonding groups	Reassociation of nonassociated hydrogen bonds	Tensile test	[153]

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*This table includes some materials developed in the authors' laboratory. More details of them are available in Chapters 3–7. Besides, the original forms of the abbreviated nomenclatures can be found in the Appendix.

use of the potential of such a smart functionality in practical products. Other closely related topics that merit adequate attention lie in (i) durability and stability of the self-healing performance and (ii) processing and manufacturing. Because physical and chemical aging of polymeric structures is inevitable when exposed to different environments, it is unreasonable to expect that the self-healing mechanism has an infinitely long life. Nevertheless, the performance decay should not proceed too fast after all. In this context, design, characterization and prediction of long-term self-healing capability as a function of environmental factors (including temperature, moisture, corrosive liquid, irradiation, etc.) have to be always born in mind. Reliability improvement is of equal importance as remendability improvement. Otherwise, the developed healing system would be meaningless. Additionally, many of the current research works deal with prototype formulations and structures. Processability and processing parameters of target end-products made from self-healing materials have not yet become a hot branch. With the deepening of the understanding based on trial and error, the problem would be placed on the docket sooner or later like all of the newly synthesized polymers. Only at that time one could begin to talk about the availability of self-healing materials for daily use.

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