

Design and synthesis of self-healing polymers

ZHANG MingQiu* & RONG MinZhi

Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education; DSAPM Lab, School of Chemistry and Chemical Engineering, Sun Yat-sen (Zhongshan) University, Guangzhou 510275, China

Received October 16, 2011; accepted October 26, 2011; published online March 23, 2012

Self-healing polymers represent a class of materials with built-in capability of rehabilitating damages. The topic has attracted increasingly more attention in the past few years. The on-going research activities clearly indicate that self-healing polymeric materials turn out to be a typical multi-disciplinary area concerning polymer chemistry, organic synthesis, polymer physics, theoretical and experimental mechanics, processing, composites manufacturing, interfacial engineering, etc. The present article briefly reviews the achievements of the groups worldwide, and particularly the work carried out in our own laboratory towards strength recovery for structural applications. To ensure sufficient coverage, thermoplastics and thermosetting polymers, extrinsic and intrinsic self-healing, autonomic and non-autonomic healing approaches are included. Innovative routes that correlate materials chemistry to full capacity restoration are discussed for further development from bioinspired toward biomimetic repair.

self-healing, crack, microcapsules, thermally reversible reaction, photoreversible reaction

1 Introduction

Microcracking would easily be generated in polymers either during manufacturing or in service as a result of mechanical stress or cyclic thermal fatigue. Its propagation and coalescence have to bring about catastrophic failure of the materials and hence significantly deteriorate durability and reliability of the products. Since the tiny damages are mostly difficult to be timely perceived and to repair in particular, the materials had better have the ability of self-healing.

Under inspiration of natural healing in living bodies, healing concepts that offer the ability to restore polymeric materials to their original set of properties have been proposed and successfully applied in recent years [1]. So far, the achievements in this aspect fall into two categories: (i) extrinsic self-healing, which operates taking advantage of the intentionally pre-embedded healing agent, and (ii) intrinsic self-healing, which enables crack healing by the

polymers themselves without the need of additional healing agent.

Meanwhile, a series of review articles that reflect the updated progress of self-healing polymeric materials from different angles (e.g., healing theories [2, 3], healing strategies [4–8], healing systems [9–16], healing chemistry [17–22], stimuli responsible for initiation of healing [23], principles of materials design [24, 25], and specific application [26]) are available now. Regular international forums such as “International Conference on Self-Healing Materials” (Noordwijk aan Zee, Netherlands (2007); Chicago, USA (2009); Bath, UK (2011)) have also been established. Increasingly 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 unrenowned crude oil, ecological concerns, advanced application requirements, miniaturization and integration of products.

In this article, we briefly review the work carried out in different laboratories worldwide and highlight research of the authors' group concerning both thermosetting and ther-

*Corresponding author (email: ceszmq@mail.sysu.edu.cn)

moplastic polymers. Focus is given to the development of novel healing chemistry.

1.1 Extrinsic self-healing

In the case of extrinsic self-healing, the healing agent is stored in some media and incorporated into the materials in advance. As soon as the cracks destroy the fragile reservoirs, the healing agent is released into the crack planes due to capillary effect and re-binds 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. The crack triggered delivery of the healing agent allows autonomic rehabilitation without manual intervention.

The core issue of this technique lies in filling the brittle-walled vessels with polymerizable chemicals, 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 [27–30]. The similar approach was adopted by Motuku *et al.* [31] and Zhao *et al.* [32]. Because the hollow glass capillaries have much larger diameters (on millimeter scale) than those of the reinforcing fibers in composites, they have to act as initiation for composites failure [33]. Instead, Bleay *et al.* [33] 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 [33]. Complete filling of healing agents into the tiny tubes was achieved by vacuum assisted capillary action filling technique.

Accordingly, three types of healing systems were developed [27–43]. (i) Single-part adhesive. All hollow pipettes contained only one kind of resin like epoxy particles (that are 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 separately. (iii) Two-part adhesive. One component was incorporated into hollow tubes and the other in microcapsules.

Trask *et al.* [42] 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 quasi-static 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 systems can be found in ref. [39–41, 43–45].

Toohey *et al.* proposed a self-healing system consisting

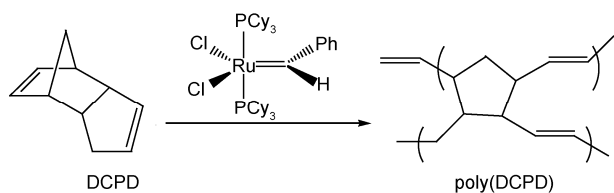
of a three-dimensional microvascular network capable of autonomously repairing repeated damage events [46]. Their work mimicked the architecture of human skin. The 3D microvascular networks were fabricated by deposition of fugitive ink (a mixture of Vaseline/microcrystalline wax (60/40 by weight)) in terms of direct-write assembly [47] through a cylindrical nozzle. Then, the yielded multilayer scaffold was infiltrated with epoxy resin. When the resin was consolidated, a structural matrix was obtained. With the help of heating and 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, fluidic polymerizable healing agent was injected into the networks.

Hansen *et al.* [48] made advancements in direct-write assembly — dual ink deposition and vertical ink writing. They independently deposited two fugitive organic inks to construct a three-dimensional 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.

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 [49, 50]. They firstly worked out glass fiber/epoxy laminates with vascular sandwich core, giving a relatively thin skinned configuration [49]. The healing networks consisted of tubing bonded into the mid-plane 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 [50], a vascular sandwich structure with horizontal supply channels and vertical riser channels in a closed-cell foam core was prepared. Such a network had negligible effect on the baseline static mechanical properties of the composite panel.

Additionally, the researchers in Bristol proposed to construct vascular networks in composites following a biomimetic concept of “ray cell” structure [51, 52], analogous to vasculature in hardwoods. A prototype of this system was introduced within a carbon fiber reinforced epoxy polymer composite laminate [52, 53]. Their results showed that damage morphology is influenced by vascular 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 [52]. 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 transversely. Such a vasculature might offer a self-healing function with minimum mass penalty, without initiating premature failure within a composite structure.

With respect to extrinsic self-healing based on micro



Scheme 1 Ring opening metathesis polymerization of DCPD.

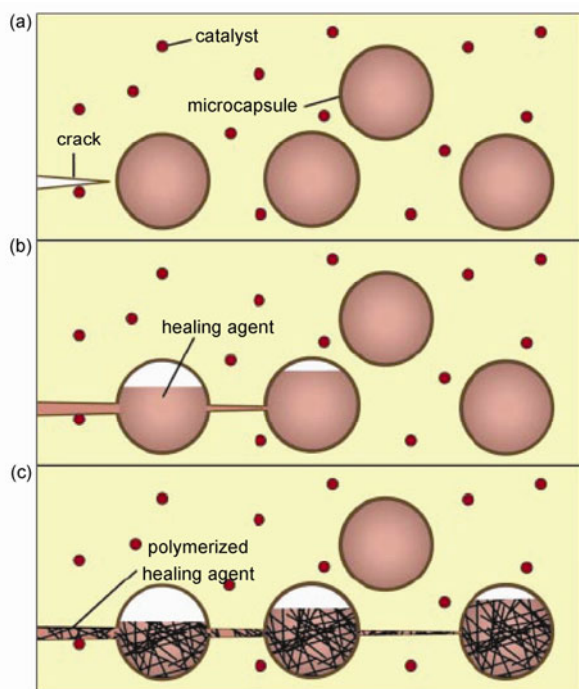


Figure 1 The autonomic healing concept [54]. A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent. (a) Cracks form in the matrix wherever damage occurs; (b) the crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; (c) the healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed.

capsules, the working principle resembles the aforementioned pipelines but the containers for storing healing agents are replaced by fragile microcapsules. The approach developed by White *et al.* in the University of Illinois at Urbana-Champaign [54] plays the role of milestone, which is promising to be developed into a practical technique for mass production and application of the smart materials. They systematically investigated self-healing via ring opening metathesis polymerization (ROMP) of microencapsulated endo-isomer of DCPD and reported a series of important findings [54–66]. When damage in the form of a crack ruptured the microcapsules, DCPD was released into the crack plane where it came in contact and mixed with the pre-embedded Grubbs' catalyst (Scheme 1 and Figure 1). For increasing catalysis efficiency, the catalyst was capsulated by wax and recrystallized, respectively [58, 59]. Delamination [60, 61], low-velocity impact damages [67] and

indentation induced interpenetrating crack networks [68] in fiber reinforced epoxy composites were found to be successfully repaired by the healing agent. Moreover, fatigue crack growth in epoxy [62–64] can also be retarded by the released fluid.

To enhance interfacial bonding between DCPD-loaded capsules and the polymer matrix in composites, Wang *et al.* attached 3-aminopropyltriethoxy silane [69] and γ -glycid-oxypropyltrimethoxy silane [70, 71] to the surface of poly(urea-formaldehyde) (PUF) capsules containing DCPD separately. A chemical bond (Si–O–C) and a 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 [71].

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 [72–79]. 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 products at low temperatures in cracked epoxy materials [78, 79]. 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 [74] or DCPD [75, 76] should be incorporated to improve adhesive properties of the resultant polymer. Towards development of a new healing system, Liu *et al.* [77] synthesized melamine-urea-formaldehyde walled microcapsules containing ENB and its crosslinking agent by *in situ* polymerization in an oil-in-water emulsion. Healing functionality of these capsules in polymer composites yet remains to be characterized.

For purposes of ensuring effective healing in self-healing fiber reinforced polymer composites, Fang *et al.* [80, 81] proposed a strategy as follows. Microencapsulated healing agents (organosilane or organosiloxane that contains Si–H bonds and Si–vinyl bonds) are dispersed in the polymer matrix, while 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 rebounds the faces of the crack.

Wang *et al.* [82] developed a binary self-healing system consisting of epoxy-containing microcapsules and latent curing agent 2-methylimidazoleazine. The latent curing agent was well dispersed in epoxy matrix during composites manufacturing. As a result, self-healing of the cracked sites was achieved through curing of the released epoxy healing

agent.

In contrast to the conventional self-healing materials with microcapsules, Cho *et al.* [83] 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, were pre-embedded. Polycondensation of HOPDMS with PDES occurred when they met the tin-catalyst from the broken capsules induced by mechanical damage.

As for crack repair in elastomer, Sottos *et al.* [84] incorporated PUF walled microcapsules, which contained the constituent resin and initiator, separately, into PDMS. 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. This self-healing material system possesses the unique feature that the healed polymer in the crack plane is the same as the host matrix.

In addition to the polymerizable healing agent, Caruso *et al.* [85] used solvents to heal cracks in thermoset materials. Chlorobenzene was encapsulated by urea-formaldehyde and embedded in epoxy matrix. It is believed that the solvent would induce crosslinking of the incompletely cured resin and heal cracks. Furthermore, they used a mixture of epoxy monomer and solvent instead of pure solvent as core substance of the microspheres [86, 87]. 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. To self-repair macro-length scale damage, on the other hand, Li *et al.* [88–92] showed the effectiveness of confined shape recovery functionality of shape memory polymer (SMP).

1.2 Intrinsic self-healing

The so-called intrinsic self-healing polymers are based on specific molecular structures and performance of the polymers that enable crack healing mostly under certain stimulation. 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.

Previously, intrinsic self-healing of polymers were mostly dedicated to thermoplastic ones. Wool *et al.* [93, 94] systematically studied the theory involved. They pointed out that the healing process goes through five phases: (i) surface

rearrangement, (ii) surface approach, (iii) wetting, (iv) diffusion, and (v) randomization. In addition, Kim and Wool [95] proposed a microscopic model for the last two phases on the basis of reptation model that describes longitudinal chain diffusion responsible for crack healing.

Accordingly, Jud and Kaush [96] 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 [97]. Wool [98] 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.* [99] also performed re-healing 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 $K_{II} \sim t^{1/4}$ predicted by the diffusion model.

It is worth noting that whereas craze healing occurs at temperatures above and below the glass transition temperature [100], crack healing happens only at or above the glass transition temperature [101]. In order to reduce the effective glass transition temperature of PMMA, Lin *et al.* [102] and Wang *et al.* [103] 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 corresponds to the progressive healing due to wetting, while the second is related to diffusion enhancement of the quality of healing behavior.

In fact, internal microcracks in thermoplastics can be healed by localized viscous flow of the polymer. Corten and Urban, for example, well dispersed γ -Fe₂O₃ nanoparticles into PMMA without sacrificing mechanical properties of the latter [104]. When the superparamagnetic filmy nanocomposite was exposed to oscillating magnetic field, the magnetic moment of γ -Fe₂O₃ nanoparticles was 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.

Yamaguchi *et al.* [105, 106] prepared crosslinked polyurethanes (PU) by the reaction between polyester-diol and polyisocyanate with the catalysis of dibutyl-tindilaurate. 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 re-bound at room temperature within 10 min. The autonomic healing of the weakly gelled polymer (with 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.

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 [107–109]. The selected thermoplastic is poly(bisphenol-A-*co*-epichlorohydrin), 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.

Besides simple heating induced healing, thermomechanical healing is valid for some specific polymers, like ionomers. The work by Fall [110] and Kalista *et al.* [111–114] has shown the unique self-healing response in poly(ethylene-*co*-methacrylic acid) (EMAA). EMAA films have been demonstrated 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 rebound and repair damages. By contrast, low speed friction event fails to produce sufficient thermal energy favorable to healing. The combination of elastic flexibility, high melt strength and spontaneous formation of physical crosslinks gives the ionomers a self-healing behavior upon ballistic impact.

Varley and van der Zwaag [115] conducted a careful investigation on the mechanism involved in the self-healing process. 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. In a recent study, 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 plasticisation on the autonomous damage elimination [116]. 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 plasticisation yet were able to reform more rapidly below their melting point. These combined factors create polymer blends with enhanced elastic healing behavior compared with the unmodified ionomer.

In fact, cracks and strength decay are related to structural changes of atoms or molecules, like chain scission. There-

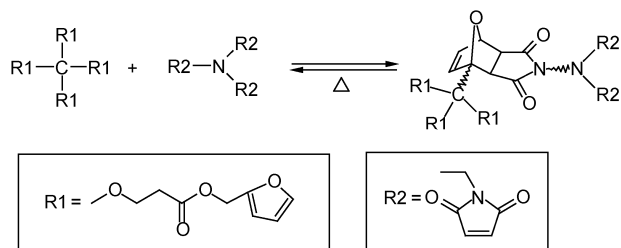
fore, inverse reactions, i.e., recombination of the broken molecules, should be one of the repairing strategies. Such method does not focus on crack healing but on “nanoscopic” deterioration. One example is polycarbonate (PC) synthesized by ester exchange method. The PCs were treated in a steam pressure cabin at 120 °C prior to the repair [117–119]. 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 N₂ 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 ions. The (–ONa) end might attack a carbonate bond at the end of one of the other chains, leading to recombination of these two chains with the elimination of the phenol from PC. The repairing reaction was accelerated by weak alkaline, such as sodium carbonate.

Cracked poly(ether ketone) (PEK) can also be repaired using the same strategy. Two kinds of reactions are involved in this case. One is the ester exchange reaction and the other is the recombination reaction of two macromolecular ends [118, 120].

Ghosh and Urban [121] reported the development of heterogeneous PU networks based on oxetane-substituted derivative of chitosan (OXE-CHI). Upon mechanical damage of the network, four-member oxetane rings open to create two reactive ends. When exposed to ultraviolet light, chitosan chain scission occurs, which forms crosslinks with the reactive oxetane ends, thus repairing the network within one hour.

Reversible polymers share one property in common – reversibility, either in the polymerization process or in the cross-linking process [19, 20]. Such a feature offers versatile possibilities of repeated healing on the molecular scale. For example, thermally reversible crosslinking behavior has been known for a considerably long period of time [122, 123]. Wudl *et al.* combined this with the concept of “self-healing” in making healable polymers [124, 125]. They synthesized highly cross-linked polymeric materials with multi-furan and multi-maleimide via Diels-Alder (DA) reaction (Scheme 2). At temperatures above 120 °C, the “intermonomer” linkages disconnect (corresponding to retro-DA reaction) but then reconnect upon cooling (i.e., DA reaction). This process is fully reversible and can be used to repeatedly restore fractured parts of the polymers without any catalyst (Figure 2).

In the work by Liu and Hsieh [126], 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 com-



Scheme 2 Thermally reversible crosslinking based on Diels-Alder reaction.

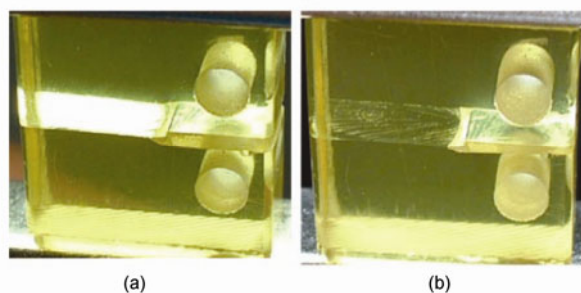


Figure 2 Images of a broken compact tension test specimen (a) before and (b) after thermal treatment, showing disappearance of the crack due to the reversible DA bonds [23].

pounds, so as to incorporate the advantageous characteristics of epoxy resins, including solvent and chemical resistance, thermal and electrical characteristics, and good adherence, to their corresponding cured polymers. Furthermore, Liu and Chen [127] prepared polyamides (PA) possessing furan pendent groups (PA-F) from reacting furfuryl amine with maleimide containing polyamides (PA-MI) via a Michael addition reaction. Thermally reversible cross-linked polyamides were obtained from PA-MI and PA-F polyamides by means of DA and retro-DA reactions. The thermally reversible cross-linked polyamides also exhibited a self-repairing property as well as the ability of mechanical property recovery.

The above-mentioned self-healing polymers based on reversible DA reactions were studied as bulk materials. However, the work by Peterson *et al.* [128] demonstrated another form of application of the polymers. They synthesized a thermally reversible cross-linking 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 conventional epoxy-amine thermosets. Direct application of the reversibly cross-linking 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 cross-linking 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 Diels-Alder reaction, lies in that heating caused the secondary gel phase to liquefy

and flow into the crack surface, and upon cooling cross-links re-formed. Moreover, Peterson *et al.* [129] utilized a *N,N'*-dimethylformamide (DMF)-based BMI solution to manually heal the furan-functionalized epoxy-amine thermosetting materials that was obtained by mixing certain amount of furfuryl glycidyl ether into epoxy resin before curing. 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.

By using Paal-Knorr reaction of polyketones (PK) and furfurylamine, Zhang *et al.* [130] 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. 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 cross-linked and de-cross-linked with BMI under the stimulus of heating. Three-point bending tests showed that the highly cross-linked 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.

Murphy *et al.* [131] simplified the dual monomer route for the synthesis of remendable polymers from DA adducts by replacing the furan-maleimide pair with a single monomer that contained a dicyclopentadiene core unit. The new single-component remendable polymer system utilized the dicyclopentadiene moiety as both diene and dienophile in the thermally reversible Diels-Alder cycloaddition reaction. Additionally, the Staudinger cross-linking 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 healing efficiency of 46 %.

Yoshie *et al.* [132] developed network polymers with recyclability using telechelic prepolymers with reversible reactivity. 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 [133]. The resultant polymer, PEAf2M3, possessed 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.

The group of Lehn screened condensation reactions between various dienes and dienophiles for reversibility [134]. 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) [135]. 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 its volume.

Following the concept dynamic covalent chemistry, Deng *et al.* produced reversible polymer gels with self-healing properties [136]. 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 cross-links was generated. Acylhydrazone bonds are covalent in nature, but acylhydrazone formation displays reversibility under mild conditions with 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 characteristic can be used to reshape a strong chemical gel.

Photoreversibility is an important aspect of reversibility of macromolecules. Chung *et al.* [137] chose photochemical [2+2] cycloaddition of cinnamoyl groups as the healing reaction since the photocycloaddition to form cyclobutane structure [138] and the reversion of cyclobutane to C=C bonds [139] readily occur in solid state. They synthesized a photo-cross-linkable cinnamate monomer, 1,1,1-tris-(cinnamoyloxymethyl)ethane (TCE) by reacting 1,1,1-tris-(hydroxyl-methyl)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 re-cycloaddition 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).

Amamoto *et al.* [140] reported repeatable photoinduced self-healing of covalently cross-linked polymer through

reshuffling of trithiocarbonate units. Healing of cracked parts (i.e., dynamic chain transfer), which were swollen in acetonitrile, was completed with UV light in nitrogen protection under catalysis of 2,2'-azobis(isobutyronitrile). Froimowicz *et al.* [141] introduced anthracene into dendritic macromonomers to generate a photo-reversible material, which was demonstrated to form networks possessing reversible self-healing property under successive UV irradiations at 254 and 366 nm.

Intrinsic self-repair without the aid of healing agents 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 [142]. Nevertheless, Chino and Ashiura [143] synthesized thermally reversible crosslinking rubber having similar mechanical properties to vulcanized one by using supramolecular hydrogen bonding networks. The molecules can be rearranged in the heated state, while the network can be reformed when cooled down. Recently, Leibler *et al.* [144, 145] further demonstrated complete restoration of tensile properties of a thermoplastic elastomer by simply bringing together fractured surfaces. 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 trifunctional 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 significant 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 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 non-associated groups at the interface. The non-associated 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.

Harreld *et al.* [146] synthesized a self-healing non-covalently crosslinked organosiloxane-polypeptide block copolymer. 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 and/or hydrogen bonding) after a disruptive stress incidence.

The group of Meijer and Sijbesma in Eindhoven University of Technology worked out supramolecular ureidopyrimidinone-based polymers containing self-complementary quadruple hydrogen bonding units that give strong and directional secondary interactions [147–149]. Polymeric materials modified with the novel supramolecular polymers show strong temperature dependent properties because of the presence of strong hydrogen bonding interactions: material properties belonging to cross-linked materials at room temperature, and low viscous melts at elevated temperatures. This property allows these materials to be used in self-healing applications in which the temperature can be used as a trigger for the healing process. In this way, no reactive chemicals are needed and no covalent bond formation has to take place, increasing not only the fidelity of the healing process but also the number of times for which healing takes place.

Burnworth *et al.* [150] proposed optically healable metallosupramolecular polymers based on macromolecules with pyridine derivative termini and Zn^{2+} ion complexes. Liquefaction of the polymers due to photo-dissociation of Zn^{2+} motifs and the subsequent re-complex offer the self-healing function. The ultraviolet light–heat conversion rather than photochemical reaction represents another interesting path.

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.* [151, 152]. 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 the ambient. 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 cross-links 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 with great efficiency and simplicity are based on self-assembly [5]. Although such methods in artificial materials have been explored for years, they have not yet become mainstream measures for obtaining self-healing. Tsukruk *et al.* [153] 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. After plastic deformation, the membranes showed autonomous recovery of their properties, which was possible by means of a reversible polymer-nanoparticle self-organization process.

South and Lyon reported self-healing of hydrogel films [154]. They employed spherical, sub-micrometer-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 μ L pipette 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.

In short, despite the fact that the achievements in self-healing polymeric materials are far from satisfactory, the new opportunities found during research and development as mentioned above 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. Hereinafter, efforts made in the authors’ laboratory are discussed.

2 Self-healing based on dual encapsulated healant

2.1 Epoxy/mercaptan system

Epoxy has been widely used in industries as surface coatings, structural adhesives, printed circuit boards, insulation materials for electronic devices, and advanced composite matrices, owing to its superior mechanical and electrical properties, good thermal and dimensional stability, and excellent chemical and corrosion resistance, in addition to

ease of handling and processing. Therefore, we firstly work at self-healing epoxy, as viewed from both academic and engineering points. The healing system consists of dual encapsulated healant, i.e., two types of microcapsules that respectively include epoxy monomer and its hardener.

Considering the specific requirement of self-healing materials, low-viscous highly active epoxy monomer and its hardener should be used as core substances of the healing capsules, separately. To the authors' knowledge, however, epoxy resins have not been applied in the field of self-healing for a long time in the form of microcapsules except that two-part epoxy adhesives had been employed in the aforementioned hollow pipelines strategy [30, 33, 34, 39, 40]. It is mainly due to the difficulty in microencapsulation of suitable hardeners for epoxy, but not in microencapsulation of epoxy itself. The latter can be easily synthesized by *in-situ* polymerization or complex coacervation [155–158], while the conventional amine-type curing agents are amphoteric and highly active, and hence hard to be encapsulated in water or solvents by chemical methods. For example, they cannot be encapsulated by PUF under acidic condition. Although physical extrusion art was used to produce some hardener-loaded capsules [159, 160], such as capsules containing mixture of diethylenetriamine and nonyl phenol with alginate wall and capsules containing diethylamine with thermoplastic wall, they were not suitable for fabricating self-healing composites. The shell wall of the former capsules might suffer from bacterial degradation, while that of the latter was too thick (~100 μm) to be sensitive to propagating cracks. Moreover, special equipments had to be involved.

Polythiol is an effective curing agent for epoxy. Epoxy resin with polythiol as the hardener and strong base as the hardening accelerator is well known for its low-temperature fast curability [161]. Accordingly, microencapsulated epoxy and polythiol might constitute a group of self-healing agent that is able to take effect at or below room temperature. In this context, self-healing can be done free of manual intervention (i.e., heating). It is worth noting that, however, microencapsulation of polythiol is also very difficult by means of the existing techniques like *in-situ* polymerization of urea-formaldehyde or interface polymerization due to the very high activity of the hydrosulfide group of polythiol. Liquid polythiol can be cured by a wide variety of compounds including aldehyde, ketone, peroxides, epoxy resins, isocyanates, acrylic and anhydrides through a number of reaction paths such as oxidation, addition and substitution reactions of hydrosulfide terminal groups [162–164]. In most cases, hollow spheres with very thick wall rather than the desired capsules have to be obtained.

To solve the problem, we use an improved *in-situ* polymerization of melamine-formaldehyde, which is inert towards mercaptan, in an oil-in-water emulsion [165]. *In situ* polymerization with poly(melamine-formaldehyde) (PMF) or methanol etherified PMF has been applied to en-

capsulate liquids such as dye solution [166], dicyclopentadiene [167], lauryl alcohol [168], fragrant oil [169, 170] and methylparathion [171]. To obtain microcapsules with sufficient strength, the encapsulation process was usually conducted at higher pH value of 3.5–6.5 and higher temperature of 60–80 °C or longer reaction time of 3–8 h. Although these rigorous processing parameters had little effect on the aforementioned inert core materials, they may lead to failure of microencapsulation or excessive consumption of the active core material, e.g., polythiol in the present work. Therefore, it is necessary to explore the suitable reaction conditions.

As for the epoxy-loaded microcapsules, PMF also plays the role of their shell wall [172]. This is necessary for homogeneous dispersion of the capsules, which respectively contain epoxy and polythiol, in the composites.

The protocol proposed by White *et al.* was used to evaluate self-healing ability of the materials, which carried out fracture tests on tapered double cantilever beam (TDCB) specimens [54, 173]. The efficiency of healing, η , is defined as the ratio of fracture toughness, K_{IC} , of healed (i.e., K_{IC}^{Healed}) and virgin (i.e., K_{IC}^{Virgin}) materials:

$$\eta = \frac{K_{IC}^{\text{Healed}}}{K_{IC}^{\text{Virgin}}} \quad (1)$$

The self-healing epoxy composites with the encapsulated healing agent are prepared according to the procedures described previously [174].

The optical microscopic photo in Figure 3 shows the dispersion of both epoxy- and mercaptan-loaded microcapsules in epoxy matrix. The volume mean diameters of the microcapsules are estimated to be 93.9 and 92.8 μm, respectively. Besides, their densities are found to be 1.24 and 1.26 g/cm³, respectively, as indicated by the separated pyc-

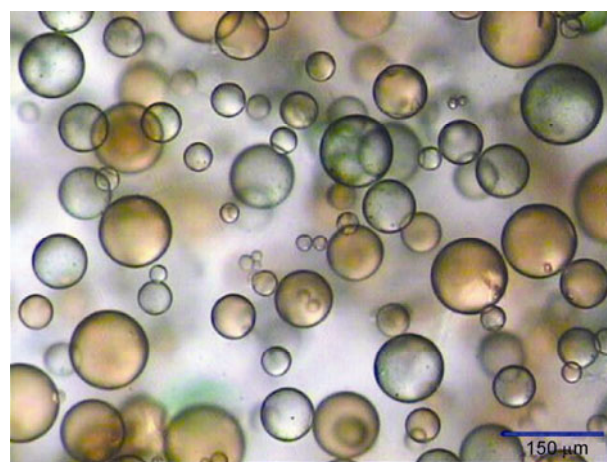


Figure 3 Optical microscopic photo taken from a self-healing TDCB specimen, which contains 5 wt% epoxy-loaded capsules (light red) and 5 wt% hardener-loaded capsules (light green). To differentiate the two types of microcapsules for visual inspection, the core materials have been mixed with 0.1 % red and green dyestuff before microencapsulation, separately.

nometer tests. The similarity in their surface feature, physical properties and geometry certainly benefits uniform distribution of the microcapsules in the composite. As a result, the contact probability between the released epoxy and curing agent is increased after damage-induced breakage of the capsules. Furthermore, since the two types of core materials possess good intersolubility, their interdiffusion and homogenization in the subsequent polymerization are favored.

In fact, the microcapsules can form hydrogen bonding with the matrix due to the polar groups (like amine and hydroxyl) on their melamine-formaldehyde shells. The strong interaction between the microcapsules and the matrix ensures timely penetration of cracks through the encapsulated healing agent.

Healing efficiency of the specimens measured at different temperatures is shown in Figure 4. The healing is very fast at temperatures from 10 to 30 °C as expected. The healing efficiency attains 82%–88 % after 3 h at 20 and 30 °C, and exceeds 100 % only after 12 h. Although the self-repair process is slowed down with decreasing temperature, an 86 % recovery at –10 °C is observed after 36 h. The data are quite satisfactory and demonstrate that our technical route works.

The reaction between epoxy and mercaptan belongs to addition polymerization. Accordingly, stoichiometric ratio of epoxy/mercaptan and uniform mixing at the molecule level are critical for a perfect cure [161, 174]. Because the capsule size corresponds to the amount of releasable healing agent and spreading area of the healing agent delivered into cracked planes, the embedded epoxy- and hardener-loaded microcapsules with mismatched sizes may lead to localized excess of one ingredient and deviation from the required stoichiometric ratio [175]. Similarly, mismatched fractions of the microcapsules would also bring about the same result.

In addition to the ability to repair the cracks generated by monotonic fracture, the epoxy/mercaptan healing system should also be able to suppress and rehabilitate fatigue

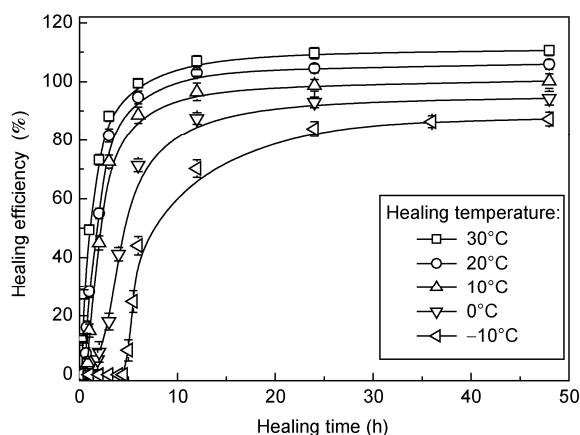


Figure 4 Time dependence of healing efficiency at different temperatures [174]. The self-healing composite contains 2.5 wt% epoxy-loaded capsules and 2.5 wt% hardener-loaded capsules.

crack. This is because most polymeric materials including epoxy suffer from poor fatigue resistance and would fail at stress levels much lower than the critical stress intensity.

It is worth noting that under cyclic loading condition, the forces required to squeeze the fluidic healing agent (released from the broken capsules) out of the crack during unloading and to draw the fluid into the crack during loading would shield the crack tip [176]. This hydrodynamic pressure crack tip shielding mechanism can also improve the resistance to fatigue crack propagation. The effect has to be firstly revealed by manually injecting the mixture of epoxy prepolymer and polythiol at the stoichiometric ratio of 1.2:1 by weight (which is the same as the healing agent formulation except that the amine catalyst is excluded) into the crack plane of neat epoxy specimen without interrupting the fatigue experiment (Figure 5). The infiltrated liquid mixture can be considered to be chemically stable because epoxy-polythiol would hardly react with each other without proper catalysis. As a result, the subsequent crack propagation keeps steadiness on the whole like the case of submerged specimens [179]. Compared with the neat epoxy specimen, the infiltration greatly decreases the crack growth rate from 1.8×10^{-3} mm/cycle to 4.0×10^{-4} mm/cycle and increases the fatigue life by ~207 % (cf. curves a and b in Figure 5). The results agree with those observed in the case of infiltration of epoxy prepolymer (or the hardener) alone [178]. Secondly, the dependence of crack length on fatigue cycle of the control specimen with 10 wt% epoxy-loaded capsules and 10 wt% polythiol-loaded capsules (no tertiary amine catalyst is included) was measured (curve c in Figure 5). The crack growth rate is further reduced to 1.3×10^{-4} mm/cycle, and the fatigue life extension increases by ~1161 % compared with that of neat epoxy specimen. It means that both microcapsules induced-toughening [180] and hydrodynamic pressure crack tip shielding mechanisms

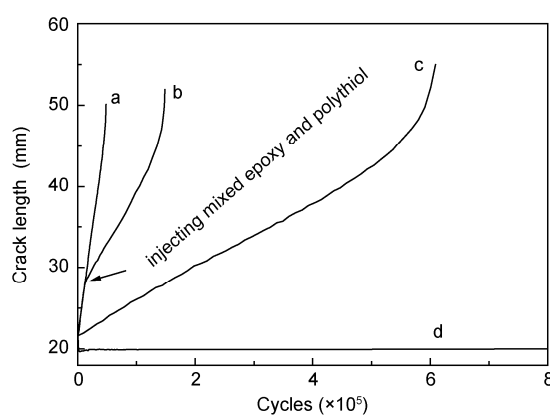


Figure 5 Crack length vs. fatigue cycle of (a) neat epoxy specimen, (b) manual infiltration specimen, (c) control specimen and (d) self-healing specimen [177]. The manual injection specimen was injected by the stoichiometric mixture of epoxy and polythiol excluding the amine catalyst in dynamic infiltration fashion [178]. The testing parameters are $\Delta K_I = 0.504$ MPa $m^{1/2}$, $K_{max} = 0.560$ MPa $m^{1/2}$, $K_{min} = 0.056$ MPa $m^{1/2}$, $R = 0.1$ and $f = 5$ Hz.

have taken effect, while the former makes more contribution to retardation of fatigue crack than the latter.

When the healing agent flowing out of the broken microcapsules contains catalyst and could rapidly react, polymeric wedge and adhesive bonding mechanisms [177, 178] are involved, which can greatly extend fatigue life of the material (see curve d in Figure 5). Accordingly, the healing efficiency is infinite.

Although the epoxy-mercaptan healing agent has demonstrated its applicability in self-repair of cured epoxy without manual intervention, whether it works for fiber reinforced composites still remains open. In this context, woven glass fabric/epoxy composites containing the epoxy-mercaptan based self-healing agent were manufactured and characterized to examine their ability of autonomic repair of impact damage as follows.

The composite laminates were firstly impacted and then healed at room temperature. The healing capability was mainly assessed by the change in damage area using scanning acoustic microscope (SAM) through-scan mode (T-Scan Mode) [181].

Figure 6 shows that when the laminates have been impacted by 1.5 J, the impact damage areas are gradually reduced. Clearly, the impact damage zones are filled by the epoxy healing agent, which is polymerized with time. The rate of damage area reduction attains 18% after 30 min, exceeds 85% only after 6 h, and approximately reaches the equilibrium at 97% after 12 h. By contrast, for the control laminates only containing epoxy-capsules but excluding the hardener-capsules, the damage areas nearly do not change

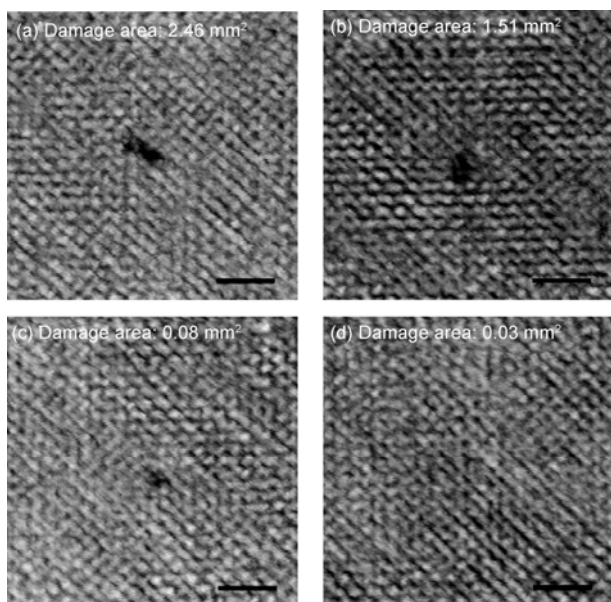


Figure 6 T-scan ultrasonic images of the impacted self-healing laminates containing 11.9 wt% dual-capsules, showing variation of damage areas with time at room temperature without manual intervention including lateral pressure [181]. Impact energy 1.5 J. Healing times: (a) 0, (b) 1 h, (c) 12 h, and (d) 24 h. The attached scale bars represent 10 mm in length.

with time under otherwise identical conditions. When the control laminates only contained the hardener-capsules but excluded epoxy-capsules, the same results were observed. In association with the investigation of reactivity of the healing agent at room temperature and the recovery of compressive strength after impact as well, the acoustic images are demonstrated to be able to reflect the effect of damage healing in the laminates.

2.2 Epoxy/ $(C_2H_5)_2O \cdot BF_3$ system

The *in situ* self-healing of fatigue cracks discussed in the last sub-section has shown the importance of chemical kinetics of healing action. In polymeric materials subjected to either fatigue or low-velocity impact, sub-micron cracks (0.009–0.3 μm) would quickly appear and then coalesce to form macroscopic damages. Therefore, a fast healing reaction is critical for practical application so that cracks can be eliminated soon after its emergence to avoid possible propagation.

For epoxy based healing system being able to operate at or below room temperature, acceleration of its rate of crack healing can be achieved by selection of proper curing agents. Comparatively, boron-containing compounds might act as qualified candidates in this regard.

As a typical boron-containing compounds, boron trifluoride diethyl etherate ($(C_2H_5)_2O \cdot BF_3$) has been commercially used as a hardener for low temperature fast cure epoxy adhesives. The curing reaction of epoxy catalyzed by $(C_2H_5)_2O \cdot BF_3$ proceeds so fast at ambient temperature that tremendous exotherm is produced [182]; therefore it is quite suitable for triggering polymerization of epoxy monomer in a cold environment. Another interesting advantage of $(C_2H_5)_2O \cdot BF_3$ lies in that the epoxy- BF_3 cure is dominated by cationic chain polymerization mechanism. $(C_2H_5)_2O \cdot BF_3$ plays the role of catalytic curing agent that does not build itself into the thermoset structure, which is apparently different from reactive curing agents represented by amines and anhydrides. Owing to the different curing mechanisms, structures and properties of the cured epoxy are also different accordingly. In the case of reactive curing, the sites where the curing agents are located serve as the reactive loci, and the curing reaction develops radially outwardly. As a result, a microscopically heterogeneously consolidated product is obtained, in which crosslinking density near the reactive loci is higher than that away from the reactive loci. Partially reacted or even completely unreacted epoxy monomers might be presented adjacent to the reactive loci. By contrast, for catalytic curing, ring-opening of epoxide groups simultaneously takes place throughout the resin. In the vicinity of the reactive sites, curing reaction proceeds very fast leading to higher crosslinking degree. With the lapse of time, the rate of curing reaction decreases and the crosslinking degree of the post-crosslinking portions has to be lower. The cured epoxy is eventually composed of alter-

nating structures with high and low crosslinking degrees. Therefore, an increase in the concentration of reactive curing agent would increase the number of reactive loci of curing and crosslinking degree of the resultant, while a higher dosage of catalytic curing agent may result in a higher rate of curing reactions, lower amount of the post-crosslinking portions, and higher crosslinking degree of the cured resin. Owing to these characteristics, the strict stoichiometric ratio of epoxide/hardener required by addition polymerization (for example, the epoxy-mercaptan cure [174, 175, 177] mentioned above) is no longer necessary for the epoxy-BF₃ cure. In this context, when (C₂H₅)₂O·BF₃ is introduced as the partner of epoxy to prepare two-component self-healing agent, uniform distribution of alternate epoxy- and hardener-loaded capsules is not a must for manufacturing self-healing epoxy composites. Curing of epoxy released from the broken microcapsules would be ignited and spread out quickly so long as the epoxy fluid meets (C₂H₅)₂O·BF₃ [183]. Only a small amount of (C₂H₅)₂O·BF₃ (1–5 wt% relative to the quantity of epoxy) is sufficient for initiating the reaction. Evidently, the processing and working windows of self-healing materials would thus become much wider.

(C₂H₅)₂O·BF₃ is highly active and hygroscopic. Its activity would easily be lost if conventional encapsulation approaches are applied. Since it should be properly shielded from the composite manufacturing to avoid any possible deactivation effect, a specific approach is developed in our laboratory. It differs from the conventional way of microencapsulation, and infiltrates the fluidic (C₂H₅)₂O·BF₃ into polymeric hollow microcapsules instead [184].

The self-healing epoxy composites contain epoxy- [185] and (C₂H₅)₂O·BF₃-loaded capsules were assessed by the protocol suggested by Jones *et al.* in terms of impact test [108]. The healing efficiency is defined as the ratio of impact strength of healed and virgin materials. Izod notched tests were conducted at 20 °C. After testing, the specimens that had been broken into two pieces were kept in alignment and intimate contact for healing at 20 °C for different times. Then, the healed specimens were tested again following the above procedure to check the effect of healing.

As mentioned earlier, weight ratios of (C₂H₅)₂O·BF₃/epoxy ranging from 1 wt% to 5 wt% are sufficient for curing epoxy. However, healing of cracks in composites depends on the curing reaction of the crack-released epoxy with the bled (C₂H₅)₂O·BF₃. That means, exact proportions of the two types of capsules taking part in the reaction can hardly be predicted for this specific case. The suitable recipe has to be determined from actual tests. For this reason, a series of epoxy composites filled with various contents of epoxy- and (C₂H₅)₂O·BF₃-loaded capsules at different ratios were prepared and evaluated.

As exhibited in Figure 7, healing of cracks is available only when both epoxy- and (C₂H₅)₂O·BF₃-loaded capsules are added to the composites. The system filled with only a

single component of the healing agent cannot offer any healing functionality. When the dosage of (C₂H₅)₂O·BF₃-loaded capsules is fixed, healing efficiency of the epoxy composites increases with the content of epoxy-loaded capsules up to 5 wt%, and then tends to level off (Figure 7(a)). The maximum healing efficiency is about 88%. At lower content of epoxy-loaded capsules, the released epoxy fluid would be insufficient to cover the broken surface, and hence poor healing effect is detected. This deduction can be evidenced from another angle by the data in Figure 7(b), in which similarly high healing efficiencies are perceived for all of the epoxy composites containing epoxy-loaded capsules over 5 wt% and (C₂H₅)₂O·BF₃-loaded capsules over 1 wt%. By contrast, the composite with 2.5 wt% epoxy-loaded capsules only shows a healing efficiency of ~30% regardless of the content of (C₂H₅)₂O·BF₃-loaded capsules.

Figure 7 also illustrates the importance of the content of (C₂H₅)₂O·BF₃-loaded capsules. Healing efficiency of the composites increases with a rise in (C₂H₅)₂O·BF₃-loaded capsules addition within low content regime, but it becomes nearly independent of the content of (C₂H₅)₂O·BF₃-loaded capsules at 1 wt% and above.

Supposing that the dual capsules are homogeneously dis-

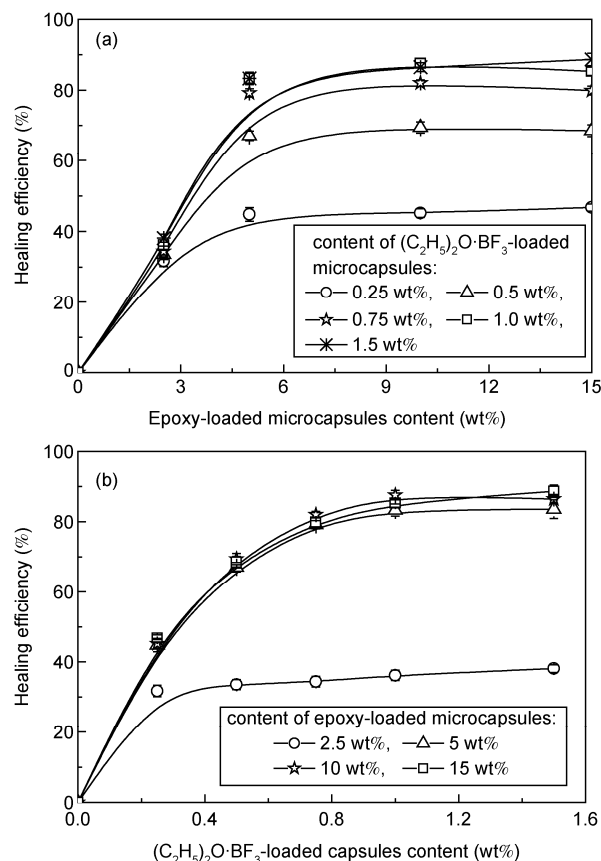


Figure 7 Dependence of healing efficiency of the self-healing epoxy composites on content of the healing agent [186]. Epoxy-loaded microcapsules: core content = 70 wt%, average diameter = 30 μm. (C₂H₅)₂O·BF₃-loaded microcapsules: core content = 20 wt%, average diameter = 10 μm. Healing of the fractured specimens was conducted at 20 °C for 2 h.

tributed throughout the composites, and all the capsules at the crack surfaces can be fractured, the corresponding $(C_2H_5)_2O \cdot BF_3$ /epoxy weight ratio of the released healant can be estimated [186]. It is found that, for the low content epoxy-loaded capsules (i.e., 2.5 wt%), $(C_2H_5)_2O \cdot BF_3$ -loaded capsules with contents from 0.25 to 1.5 wt% are sufficient, because the estimated $(C_2H_5)_2O \cdot BF_3$ /epoxy weight ratios range between 2.9 and 17.1 wt%, agreeing with the standard proportions of 1–5 wt%. Therefore, the aforementioned low healing efficiency of the composites filled with 2.5 wt% epoxy-loaded capsules has to result from the insufficient supply of the released epoxy. On the other hand, 0.25 wt% $(C_2H_5)_2O \cdot BF_3$ -loaded capsules are too little to induce a complete cure of epoxy healing agent for the composites containing 10–20 wt% epoxy-loaded capsules, since the estimated $(C_2H_5)_2O \cdot BF_3$ /epoxy weight ratios are only 0.4–0.7 wt%, lower than the lower limit of the recipe (i.e., 1 wt%). The analysis explains the poor healing ability of the composites with low content $(C_2H_5)_2O \cdot BF_3$ -loaded capsules (Figure 7).

To reveal influence of the two types of microcapsules on mechanical performance of epoxy matrix, Figure 8 depicts tensile and flexural properties of the composites with a constant content of epoxy-loaded capsules of 5 wt%, which is chosen because the above healing tests indicate it is the critical value for having a high healing efficiency. Similar to

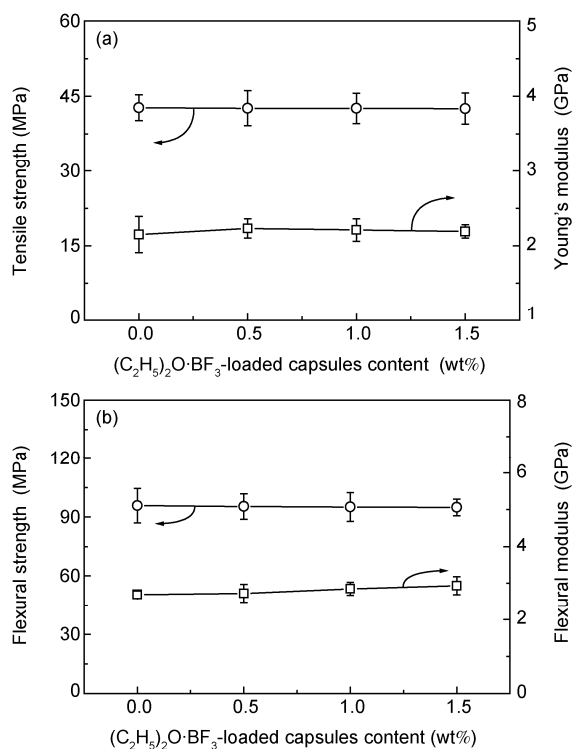


Figure 8 Influence of content of $(C_2H_5)_2O \cdot BF_3$ -loaded capsules on (a) tensile and (b) flexural properties of the self-healing epoxy composites containing 5 wt% epoxy-loaded capsules [185]. Epoxy-loaded microcapsules: core content = 70 wt%, average diameter = 30 μm . $(C_2H_5)_2O \cdot BF_3$ -loaded microcapsules: core content = 20 wt%, average diameter = 10 μm .

the results of addition of individual type of the capsules, incorporation of both types of the capsules still does not lead to remarkable variation in the static mechanical properties. Nevertheless, addition of the dual capsules can arouse evident decrease in impact strength of the composites. The trend of embrittlement is more apparent at lower content of epoxy-loaded capsules. For the composite containing 5 wt% epoxy-loaded capsules and 1 wt% $(C_2H_5)_2O \cdot BF_3$ -loaded capsules, its impact strength is about 81% of that of unfilled epoxy.

We have further examined impact performance of the composites as a function of epoxy-loaded capsules' size to understand its effect at constant filling concentrations. Because the capsules cannot arrest the development of cracks, the larger capsules would definitely cause higher stress concentration [187, 188] and greater extent of reduction in impact strength. On the whole, the decay in impact strength is not severe, and can be limited to a marginal range so long as the amounts of the embedded capsules are not high.

3 Self-healing based on single encapsulated healant

3.1 Epoxy/imidazole latent hardener system

It is known that the epoxy materials for advanced engineering applications should be cured by higher temperature curing agents, besides molecular modification or introduction of the secondary components. Similarly, when imparting self-healing functionality to these epoxy materials, the corresponding epoxy based healing agent also had better be cured at higher temperature after triggering to provide the repaired damage sites with comparable properties.

Based on the above consideration, we propose making a new two-component healant consisting of epoxy-loaded microcapsules and a latent curing agent. The recipe is different from those reported previously. Epoxy is microencapsulated as polymerizable healing resin in hopes of guaranteeing miscibility between the healing agent and the epoxy based composites. Additionally, the complex of $CuBr_2$ and 2-methylimidazole ($CuBr_2(2-MeIm)_4$) is synthesized as the latent hardener of the epoxy healing agent. The complex possesses long-term stability, and would be dissociated into $CuBr_2$ and 2-methylimidazole again at around 130–170 $^{\circ}C$ [189–191]. Taking advantage of this habit, anionic polymerization of the released epoxy healing agent catalyzed by 2-methylimidazole (i.e., cracks healing) can be triggered at the dissociation temperature of $CuBr_2(2-MeIm)_4$, which is higher than the curing temperature for making the composites. Another advantage of $CuBr_2(2-MeIm)_4$ lies in its dissolubility in uncured epoxy. As a result, the latent curing agent can be homogeneously pre-dispersed (dissolved) in the composites' matrix on the molecular scale. It is believed that this might increase the probability of contact between the epoxy resin from the ruptured microcapsules

and the dissociated imidazole. That is, the released epoxy healing agent can be activated wherever it is. Consequently, higher adhesion strength and better repair effect can be expected.

Previously, we tried to fabricate self-healing epoxy with both encapsulated epoxy and imidazole particles [192]. The latter has a smaller size ($\leq 10 \mu\text{m}$) and higher softening point (95–115 °C). The included imidazole granules are flowable at a temperature higher than their softening point and then catalyze consolidation of the counterpart epoxy. Although full recovery of fracture toughness was observed after healing at 120–140 °C, the encapsulated imidazole particulates with irregularly angular appearances were the sources of defects or stress concentration in the composite matrix after all. Therefore, utilization of the above $\text{CuBr}_2(2\text{-MeIm})_4$ as latent hardeners might be an interesting progress, which excludes the shortcoming of the solid imidazole particles, while still bringing the higher temperature curing characteristics of imidazole into play.

Figure 9 shows the curing processes of $\text{CuBr}_2(2\text{-MeIm})_4$ /epoxy system in terms of conversion versus temperature estimated from the non-isothermal differential scanning calorimetry (DSC) scans [193]. It is observed that curing of epoxy occurred at about 130 °C. The exothermic peaks appear at 141–176 °C, while the corresponding conversions are still lower than 50%. It means that $\text{CuBr}_2(2\text{-MeIm})_4$ is a mild curing agent. Clearly, the curing reaction proceeds very slowly at lower temperature (e.g., 120 °C). This is convinced by the isothermal DSC scans of the system. At a constant temperature of 120 °C, there is no detectable exothermic peak within 90 min, implying nearly no curing takes place. In accordance with this finding, the curing temperature for preparing self-healing composites should be lower than the healing temperature, so as to avoid any change in the healing agent and the latent hardener when the composites were cured. In other words, the developed healing system proves to be durable for long-term application under moderate temperature.

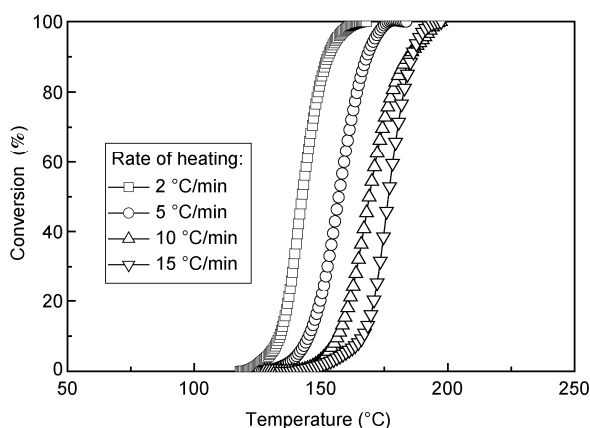


Figure 9 Temperature dependence of conversion of curing reaction of epoxy activated by $\text{CuBr}_2(2\text{-MeIm})_4$ (1 wt%) at different heating rates [193].

The self-healing epoxy material was prepared according to the following procedures. A certain amount of $\text{CuBr}_2(2\text{-MeIm})_4$ latent hardener was mixed with EPON 828 at 60 °C with stirring. Then the mixture was cooled down to 40 °C and compounded with a given proportion of the urea-formaldehyde resin encapsulated epoxy monomer as the healing agent. Under ultrasonic agitation, the compound was mixed with 15.2 phr tetraethylenepentamine (TEPA) curing agent and degassed. Eventually, the mixture was cast and cured for 2 h at 60 °C, followed by 2 h at 80 °C and 2 h at 100 °C.

Figure 10(a) shows the dependence of fracture toughness of the healed specimen, $K_{\text{IC}}^{\text{Healed}}$, on the content of the latent hardener. The healing efficiency, η , is estimated according to Eq. (1). When the epoxy-loaded microcapsules' content is 5 wt%, the values of $K_{\text{IC}}^{\text{Healed}}$ are relatively low within the entire loading range of the latent curing agent. It results from the insufficient dosage of the epoxy-loaded microcapsules, leading to insufficient quantity of the released epoxy monomer for covering the broken surface. Therefore, some cracked portions have to be left unhealed and the apparent fracture toughness is not as high as expected. In the case of 10 wt% of the epoxy-loaded microcapsules and 2 wt%

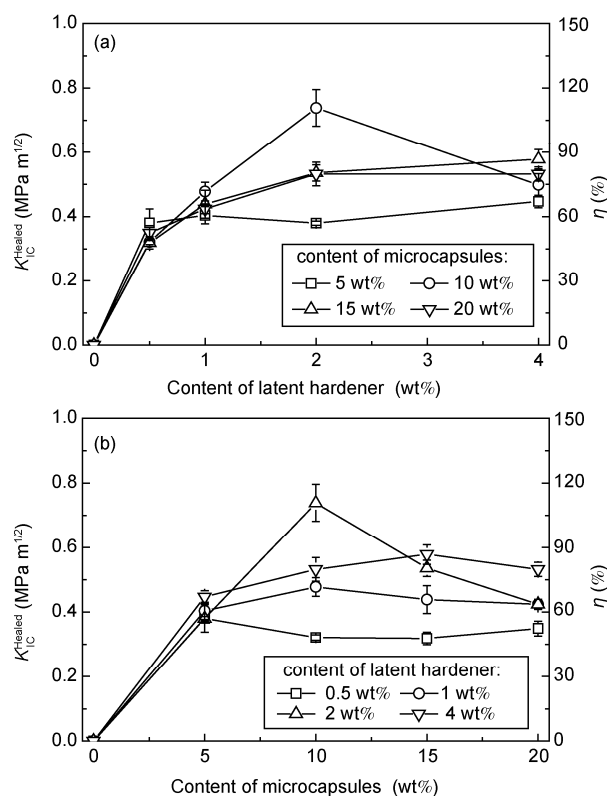


Figure 10 Influence of (a) latent hardener's content and (b) epoxy-loaded microcapsules' content on self-healing ability of epoxy measured by single-edge notched bending (SENB) tests [193]. Average diameter of the epoxy-loaded microcapsules: 37–42 μm ; content of the epoxy monomer inside the microcapsules: 63%–68%. Healing was conducted at 130 °C for 1 h.

of the latent hardener, the highest K_{IC}^{Healed} and η are observed, meaning the optimum proportion has been reached. Further increase in the content of the latent hardener could not ensure the best crosslinking degree, and the effect of repair has to be lower accordingly. For the system containing 15 wt% and 20 wt% epoxy-loaded microcapsules, the areas of the cracked planes that can be healed are reduced accordingly. The amount of the latent hardener that might contact the released epoxy becomes insufficient, which also leads to lower repair efficiencies than the maximum. It is interesting to note that the aforementioned highest healing efficiency is 111 %, which implies that the fracture toughness of the healed sample is higher than that of the virgin one. For understanding the cause, fracture toughness of epoxy cured only by $CuBr_2(2-MeIm)_4$ (5 wt%) was measured. The value $0.81 \text{ MPa m}^{1/2}$ is 1.23 times higher than that of bulk epoxy, which was cured by TEPA. Therefore, the bonding material not only healed the cracks but also provided the damaged sites with higher fracture toughness. The phenomenon resembles the outcome of dual capsules of the epoxy- mercaptan system (Figure 4).

Figure 10(b) shows the influence of epoxy-loaded microcapsules' content at a certain dosage of the latent hardener. With increasing the content of epoxy-loaded microcapsules, K_{IC}^{Healed} increases first, and then decreases. Besides, the content of the epoxy-loaded microcapsules corresponding to the maximum K_{IC}^{Healed} increases with the latent hardener content. It demonstrates that the highest healing efficiency can be obtained only at the optimum microcapsule/latent hardener ratio, as found in Figure 10(a).

On the basis of the above investigation, the applicability of epoxy/imidazole latent hardener system to the healing of interlaminar failure in woven glass fabric composites is studied [194]. Here EPON 828 acts as the matrix of the composite laminates as before. Meanwhile, one of the most common woven materials, 0/90 woven glass roving (C-glass, 13×12 plain weave, 0.2 mm thick, 1000 tows, 200 g/m^2), is selected to reinforce the composites. The specimens for the investigation are 12-ply laminates with 27 vol% glass fiber, in which the epoxy-loaded microcapsules (with an average diameter of 37–42 μm , and core content of 63%–68 %) were embedded and the latent hardener ($CuBr_2(2-MeIm)_4$) was dissolved in advance. Double cantilever beam (DCB) tests are conducted to measure interlaminar fracture toughness and healing efficiency. The experimental results indicate that a healing efficiency over 70% relative to the fracture toughness of virgin composites was obtained in the case of 30 wt% epoxy-loaded microcapsules and 2 wt% latent hardener. Due to the specific structure of the laminates, it is hard for the released healing resin to fully impregnate the fiber-rich region and the broken fibers cannot be joined as the original versions. Therefore, complete recovery of the virgin interlaminar fracture toughness of the

composites needs additional measures.

In view of practical application, self-healing function of composite materials should be persistent. A careful observation reveals that healing efficiency of the above laminates firstly decreases with storage time at room temperature, and then levels off for over two months. By means of a systematic investigation and particularly verification tests with dynamic mechanical analysis (DMA), diffusion of epoxy monomer from the microcapsules due to volumetric contraction of the composites during manufacturing is found to be the probable cause [195]. The diffusing sites on the microcapsules are eventually blocked because the penetrated resin is gradually cured by the remnant amine curing agent in the composites' matrix, and eventually the healing ability is no longer reduced after a longer storage time. On the basis of these findings, it is understood that enhancement of the compactness of the microcapsules containing epoxy would be critical for improving the stability of the self-healing composites.

As a continuation of the above work, healing of impact damage in the self-healing epoxy/woven glass fabric composites with embedded epoxy-loaded microcapsules and latent hardener is also evaluated [196]. Accordingly, compression after impact (CAI) [197], a measure of damage tolerance of composite laminates, is employed as the main characterization means.

It is found that failure modes of the CAI specimens are greatly affected by the healing. As illustrated in Figure 11(a), failure of the impacted composite laminates is primarily caused by the crack propagating from the existing damage on the back face [198]. The fracture plane is approximately perpendicular to the compression direction (Figure 11(b)). When the impacted specimen is healed and then subjected to compression, however, shear buckling takes place like conventional laminates [199]. The fracture plane makes an angle of about 45° with the loading direction and the broken parts becoming non-coplanar (Figure 11(c) and (d)), implying that the compression failure starts with the kink zone formation [200] that propagates into the fracture. It manifests that the impact damage must have been recovered to a great extent prior to the compression test. In addition, Figure 11(c) indicates that the compression failure site is not located in the original impact damage zone (i.e., the central region) of the healed specimen, which is different from the case of Figure 11(a). The mechanism is unclear. As the average fracture toughness of the bulk epoxy cured by 2-ethyl-4-methylimidazole (i.e., the cured matrix of the laminates) is $0.46 \text{ MPa m}^{1/2}$, which is only 57 % of the bulk epoxy cured by $CuBr_2(2-MeIm)_4$ (i.e., the cured healing agent), it might be inferred that the higher fracture toughness of the healed portion than that of the matrix leads to higher resistance to compressive failure of the former. Consequently, the ultimate compression failure has to occur in a place other than the healed portion.

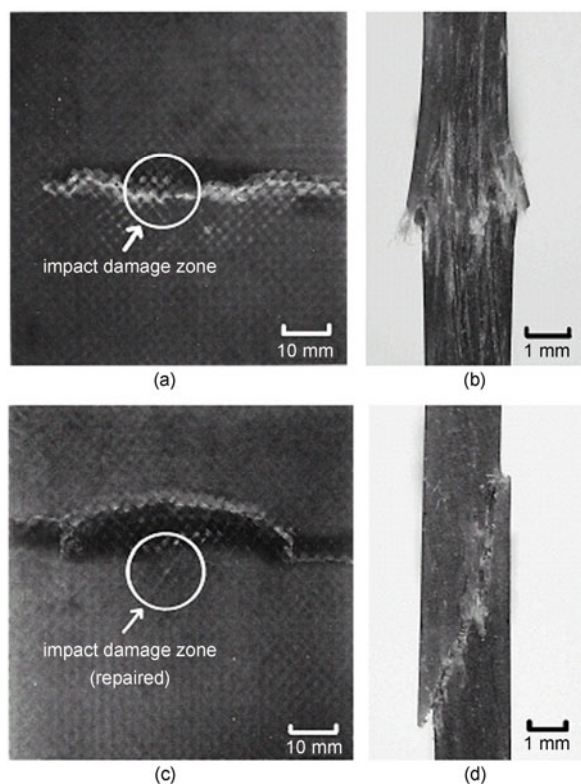


Figure 11 Photographs of (a, b) composite laminates that were impacted at 2.0 J and then compressed to failure, and (c, d) composite laminates that were impacted at 2.0 J, repaired in a hot press under 60 kPa at 140 °C for 0.5 h and then compressed to failure [196]. (a, c): front views; (b, d): side views. Content and size of the microencapsulated epoxy: 10 wt% and 40 μm . Content of $\text{CuBr}_2(2\text{-MeIm})_4$: 2 wt%.

3.2 Living polymerization system

The above healing strategies are devoted to cure epoxy based materials. However, the healing agent cannot react with thermoplastics at room temperature. Moreover, there are few published attempts allowing autonomic self-healing of damaged thermoplastic polymers. In this context, new concepts towards manufacturing of self-healing thermoplastics need to be proposed.

Living polymerization is a process in which chain transfer and termination are removed [201]. It proves to be very useful in obtaining various types of tailor-made polymers with finely controlled molecular weight and molecular weight distribution. Because the resultant polymer carries living ends, chain growth is always allowed so long as the monomer is available. It is therefore a widely used method for synthesizing block copolymers since the polymer can be prepared in stages, each of which contains a different monomer. Being enlightened by this interesting characteristic, we suggest mixing microencapsulated glycidyl methacrylate (GMA) monomer (serving as a healing agent) with a living PMMA as the matrix [202]. Owing to the infinitely long lives of the molecules' ends of the matrix, as long as the monomer is released from the spheres as a result of

crack initiation or propagation, the polymerization process of the healing agent will be started at ambient temperature wherever the monomer meets the matrix. Then, the newly formed macromolecules, which are covalently attached to the interface, would fill the interstitial space of cracks and fuse with the matrix into one. In this way, the inert matrix that is passively healed in the case of thermosetting polymers turns to play an active role, simply as part of the healing agent (initiator). In other words, covalent bonding can be established between the separated parts during the healing process. Since no catalyst is required for resuming chain growth in this system, naturally there is no question about catalyst deactivation. In addition, repeated (or multiple) healing might be feasible in case of sufficient monomer supply because the matrix and the repaired portions still contain living terminals.

According to the above-mentioned idea, atom transfer radical polymerization (ATRP), one of the most powerful control/living radical polymerization techniques [203–205], is selected as the healing reaction. It has been known that polymers prepared by ATRP are highly chain end-functionalized and can participate in various post-polymerization modifications [206]. The control of the polymerization afforded by ATRP is a result of the formation of radicals that can grow, but are reversibly deactivated to form dormant species. Reactivation of the dormant species allows for the polymer chains to grow again, only to be deactivated later. Such a process results in a polymer chain that slowly, but steadily, grows and has a well-defined end group. In general, the initiator is a simple, commercially available alkyl halide. The catalyst is a transition metal that is complexed by one or more ligands. The catalyst does not need to be used in a one-to-one ratio with the initiator but can be used in much smaller amounts. The deactivator can be formed in situ, or for better control, a small amount (relative to the catalyst) can be added. Additionally, the catalyst is tolerant of water and trace amounts of oxygen.

So far, a variety of methacrylate monomers possessing carbon to carbon double bonds have been successfully homopolymerized in ATRP systems at ambient temperature, including methyl methacrylate (MMA) [207], benzyl methacrylate (BMA) [208], and GMA [209]. Moreover, copolymerization of GMA with methyl acrylate can also proceed by ATRP at ambient temperature [210]. Considering the need of autonomic self-healing without manual intervention, therefore, we choose PMMA made by ATRP as the matrix polymer, in which microencapsulated GMA is dispersed as one-component healant in a way similar to that applied in making self-healing epoxy composites with GMA-loaded microcapsules [211]. Compared with MMA, GMA is easier to be encapsulated via *in-situ* interfacial polymerization because of its high boiling point (189 °C), low volatility, and low solubility in water. The similar polarity of PMMA and GMA facilitates wetting of GMA monomer on the surface of PMMA matrix and hence the subsequent copoly-

merization.

As mentioned earlier, it is expected that the fluidic healing agent (i.e., monomer) issued from the broken capsules is able to polymerize with the living matrix on its fracture surface so as to mend cracks. Therefore, the initiating activity of the resultant matrix should be verified prior to authentic healing experiments. For this purpose, two verification tests were carried out separately.

Firstly, fresh MMA monomers were polymerized using PMMA-Br as the macroinitiator under bulk polymerization conditions at ambient temperature as established above. Specifically, the experiment was carried out as follows. Living PMMA ($M_n = 2.3 \times 10^4$, $M_w/M_n = 1.15$, 27.7 g, 1.2 mmol), tetrabutylammonium bromide (Bu_4NBr) (3.093 g, 9.6 mmol), MMA (6.0 g, 0.06 mmol) and acetone (300 mL) were incorporated into a flask. Under mechanical agitation, both PMMA and Bu_4NBr were completely dissolved and then argon was introduced for 30 min. Afterwards, CuBr

(0.171 g, 1.2 mmol) was quickly added to the system with stirring for 10 min, and finally N,N,N',N',N'' -pentamethyldiethylenetriamine (PMDETA) (0.207 g, 1.2 mmol) was injected into the flask. Having been reacted for 12 h, the polymerized fluidic product was taken out, dissolved in tetrahydrofuran (THF), precipitated in excessive methanol, and dried. Gel permeation chromatography (GPC) measurement of the chain-extended product indicates PMMA with a higher molecule weight has been yielded ($M_n = 2.8 \times 10^4$, $M_w/M_n = 1.10$, refer to Figure 12(a)). It proves the living nature of the PMMA as well as the existence of terminal bromine at PMMA chains.

Secondly, a visual inspection was conducted. Bulk PMMA was firstly prepared by ATRP in a tube. Then, several acrylate monomers were poured onto it in random sequence. The typical procedures are described as follows. Ethyl methacrylate (EMA) was firstly added onto the aforementioned bulk PMMA, allowing polymerization of the monomer at 25 °C. Similarly, MMA was subsequently added onto the surface of solidified poly(ethyl methacrylate) (PEMA). The procedure was repeated for several times by using EMA, MMA and GMA monomers. Eventually, a rod with a multilayer sandwich structure was obtained (Figure 12(b)). This experiment simulates the situation when the released healing monomer meets the matrix, and evidences that the macromolecules in either the base PMMA or the resultant polymers (like PEMA, PMMA and PGMA shown in Figure 12(b)) remain active. The obscure interfaces between layers are indicative of diffusion of monomers and formation of copolymers. Clearly, the PMMA derived from ATRP can initiate polymerization of proper monomers whenever the monomers come into contact with the living polymer. It satisfies the requirement of the proposed self-healing via living polymerization.

To assess the healing ability of the materials, GMA-loaded capsules were embedded in the living PMMA, and the method proposed by Jones *et al.* [108] was employed as follows. The healing efficiency is defined as the ratio of impact strength of healed and virgin materials. Izod notched impact tests were conducted at 25 °C. After testing, the specimens that had been broken into two pieces were placed into a desiccator with argon, and kept in alignment and intimate contact for healing at 25 °C for 24 h. Then, the healed specimens were tested again following the above procedure to check the effect of healing. Figure 13(a) indicates that our technical route works as planned. Initially, the healing efficiency increases rapidly with increasing healing time, attains ~89 % after 12 h, and reaches the equilibrium at about 100 % after 21 h. Therefore, a conservative healing period of 24 h was used for the rest of the tests to ensure full healing under room temperature circumstances (Figure 13(b)).

To have more information about the feasibility of achieving *in-situ* self-healing, four groups of self-healing PMMA specimens were manufactured with varying con-

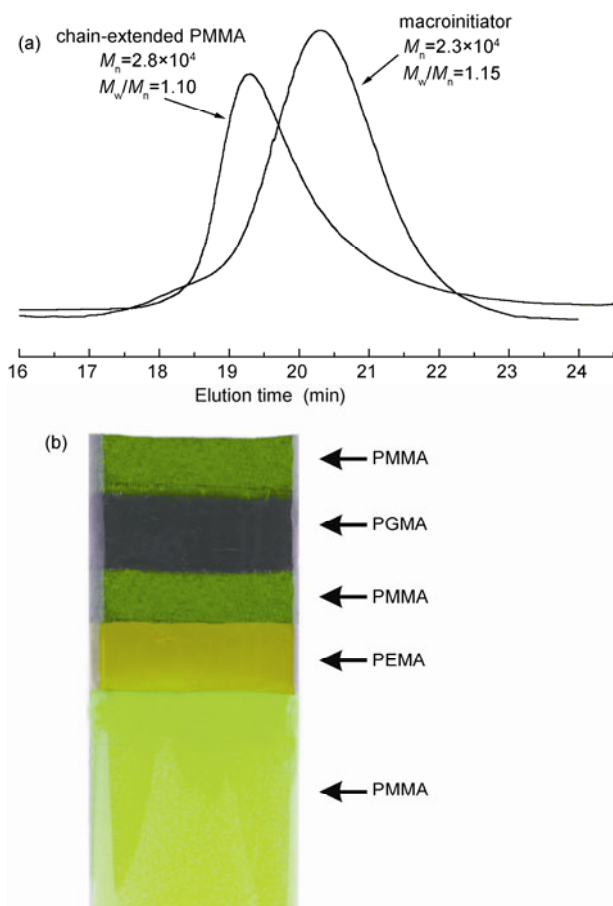


Figure 12 (a) GPC curves of PMMA before and after chain extension reaction via ATRP process. Reaction conditions: $[\text{MMA}]_0 / [\text{macroinitiator}]_0 / [\text{CuBr}]_0 / [\text{PMDETA}]_0 / [\text{Bu}_4\text{NBr}] = 50 / 1 / 1 / 1 / 8$ (molar ratio), 25 °C, 12 h. (b) Multilayer sandwich structure formed by successively adding acrylate monomers onto living PMMA [202]. Carbon black and yellow dye were respectively incorporated into the layers of PGMA and PEMA for coloring.

centrations of GMA-loaded microcapsules from 5 to 20 wt% by weight. Relatively large microcapsules with an average diameter of 283 μm were employed to maximize the delivery of the healing agent for best healing performance. As exhibited in Figure 13(b), the healing efficiency drastically increases with the capsule concentration from 0 to 10 wt% and then slowly increases within the capsule content range from 10 wt% to 20 wt%. It suggests that the self-healing performance of the present system is determined by the amount of the healing agent provided by the broken microcapsules on the fracture planes.

Although full recovery of impact strength of the material at room temperature is observed in the above work, it is worth noting that plenty of catalysts are needed for ATRP, which have to remain in the resultant polymer and are difficult to be removed. Since transition metal ions are the chief constituents of ATRP catalysts, they are unstable in air and would accelerate hot-oxygen ageing of the polymer [212, 213]. Additionally, short-term exposure of ATRP product to air would lead to oxidation of the lower oxidation state copper Cu(I) in ATRP catalysts to Cu(II), and polymerization cannot be resumed as a result. That means the living polymerization-aided self-healing process could no longer proceed if the fractured surface met air. These disadvantages would certainly limit practical application of

the self-healing materials based on ATRP living polymerization.

To circumvent the weaknesses of ATRP and to give full play to living polymerization, reversible addition-fragmentation chain transfer (RAFT) polymerization [214] is introduced to prepare the living polymer matrix instead [215, 216]. Thioester is incorporated to achieve a successful RAFT polymerization without detriment to ageing-resistance of the resultant polymer. Furthermore, oxygen only plays the role of the inhibitor at room temperature, which does not destroy reactivity of the polymer but suspend it. Once oxygen is expelled, the polymerization can go on again. In fact, there exists reversible dynamic balance between the living species and dormant species. For crack remending, only the polymerization of monomers right at the top surface in contact with air has to be inhibited by oxygen, while curing of monomers inside the crack would not be affected. In fact, RAFT polymerization is considerably more versatile than other forms of living radical polymerization in that it is compatible with a wider range of monomers and reaction conditions [217]. Some monomers might be hardly polymerized in the presence of ATRP catalysts. Besides, the components of ATRP catalysts are toxic, which is unfavorable for commercialization of ATRP based products.

To verify the feasibility of this consideration, living PMMA prepared via ambient temperature RAFT polymerization with cumyl phenyldithioacetate as the RAFT agent [218] acts as the polymer matrix, and GMA-loaded poly(melamine formaldehyde) (PMF) microcapsules are added into the living PMMA to supply fluidic healing agent.

Experimental results [216] show that upon mechanical damage of the composites, the monomer released from broken microcapsules can also resume polymerization with the living matrix, establishing chemical bonding between the cracked planes. As a result, full recovery of mechanical strength was achieved at room temperature without manual intervention. More importantly, control experiments were carried out to evaluate the sensitivity of living PMMA to air as follows. The living PMMA specimens containing GMA-loaded microcapsules were firstly impacted to failure, and then exposed to air for a period of time. Afterwards, the broken specimens were brought into contact and healed in argon at 25 $^{\circ}\text{C}$ for 72 h. The data in Table 1 indicate that exposure to air for several days has no remarkable influence on the living property of PMMA. The reduction in healing efficiency is probably due to moisture absorption at the fracture surfaces, which partly hinders the polymerization of GMA. The results evidence the advantage of self-healing via RAFT polymerization over ATRP. Clearly, the present healing system is more feasible for practical application.

Because RAFT polymerization can be initiated by heating in the presence of oxygen [219] or by γ -ray [220] and ultraviolet irradiation [221], applicability of the corresponding self-healing material might thus be broadened,

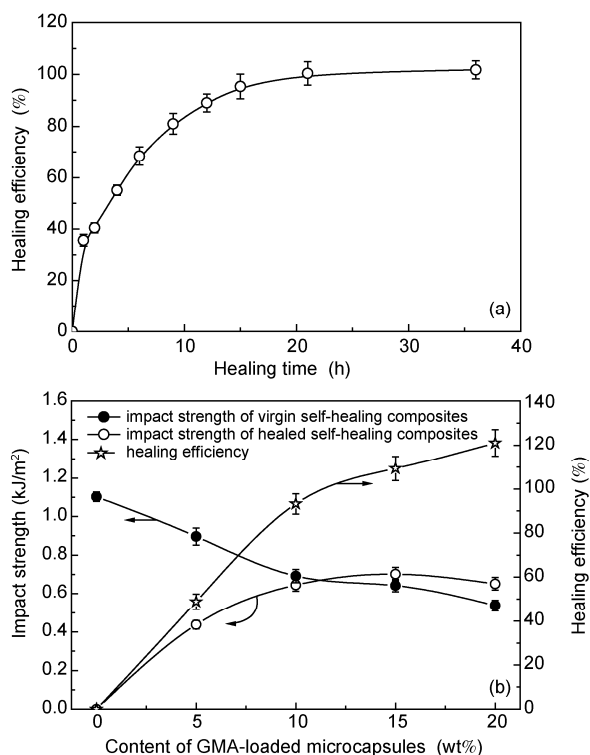


Figure 13 (a) Healing efficiency of PMMA composites containing 15 wt% GMA-loaded microcapsules as a function of healing time at 25 $^{\circ}\text{C}$ [202]. (b) Influence of content of GMA-loaded microcapsules on impact strengths of virgin and healed composites and healing efficiency. Healing of the fractured specimens was conducted at 25 $^{\circ}\text{C}$ for 24 h. The average diameter of the microcapsules is 283 μm .

Table 1 Control tests showing sensitivity of living PMMA to air [216]

Time of air exposure (day)	0	1	2	3	4	5
Healing efficiency (%)	96.50	90.33	93.07	88.09	87.61	89.18

promoting development of self-healing products capable of operating under Joule heat build-up or sunlight stimulus.

On the whole, room temperature living polymerization proves to be an effective way to impart autonomic self-healing capability to thermoplastic polymers. An additional potential advantage lies in the fact that the living matrix itself might allow self-healing of radiation (like ionizing, UV and electromagnetic radiation) induced degradation because of recombination between the new free radicals and the macromolecular radicals on the matrix chain ends [222]. Consequently, multi-scale self-healing at both micron and molecular levels that is critical for space applications could possibly be developed.

4 Self-healing based on thermally reversible reactions

Extrinsic self-healing with the help of embedded healing agent, which was developed in our laboratory, has been discussed in Sections 2 and 3. In spite of the fact that the healing efficiency, healing speed and healing conditions can be conveniently tailored and tuned by choosing proper healing chemistry, the most apparent challenge lies in the strategy itself—additional healing agent has to be incorporated. The complexity of materials manufacturing might thus be increased, in case the function of self-healing is planned to be integrated. In this context, synthesis of intrinsic self-healing materials seems to be a promising solution, besides further optimization and improvement of the healing agent for extrinsic self-healing.

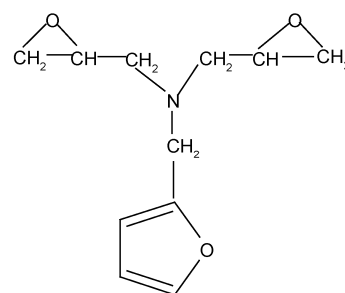
As reviewed in the Introduction part, the group of Wudl produced a DA crosslinked polymer consisting of furan- and maleimide-based monomers [124]. The appearance of DA bonds on the polymer backbone brings thermal reversibility that enables healing of fractured surface after being heated to 120 °C and then cooled down to room temperature. Following the concept of DA chemistry, we developed a novel epoxy with intrinsic (thermally responsive) self-healing ability. The polymer might not only become a new member of the epoxy family but also help to enrich the database of design of the relevant molecules.

So far, there are two types of intrinsic self-healing polymers made of maleimide and furan compounds [23]. One is the macromolecular network constructed directly by the copolymerization of multi-furan and multi-maleimide [124]. The polymer is characterized by high density of DA bonds and high healing efficiency. In the case of low-melting point bismaleimide, the synthesis can be conducted without the aid of any solvent. Because the entire

polymeric network is composed of DA bonds, however, glass transition temperature and service temperature of the material could not be high. In addition, the components made from this polymer might be easily deformed during crack healing as its healing temperature is higher than the glass transition temperature. The other type of intrinsic self-healing polymers from maleimide and furan is made through DA reactions among the maleimide and furan in the side chains [126, 127]. The skeletons are responsible for mechanical strengths, heat resistance and higher glass transition temperatures. Due to the presence of macromolecular main chains, such a self-healing system has poorer processability, and strong polar solvents have to be used to dissolve the monomers. On the other hand, the low amount of maleimide and furan in the side chains would result in limited healing efficiency.

To obtain intrinsic thermally responsive self-healing polymer with improved healing efficiency, operating temperature and processability, we proposed to synthesize an epoxy monomer, *N,N*-diglycidyl-furfurylamine (DGFA, Scheme 3) [223]. Consequently, epoxide groups are combined with furan in one molecule. The epoxide groups can react with conventional curing agent of epoxy resin (anhydride, for example) to form an irreversible epoxy network, providing the material with outstanding mechanical properties and thermal resistance as usual. Meanwhile, the furan groups can react with maleimide to introduce thermally reversible DA bonds into the epoxy network, so that the self-healing function is implanted. Eventually, the molecular networks in the cured material are composed of two types of intermonomer linkage. In this context, advantages of epoxy and intrinsic self-healing ability join together. By optimizing the curing conditions, the epoxy material possesses thermal remendability under its glass transition temperature.

Having been synthesized according to a two-step reaction mechanism [223], DGFA was cured by methylhexahydrophthalic anhydride (MHHPA) and *N,N'*-(4,4'-diphenylmethane) bismaleimide (DPMBMI) to construct cross-

**Scheme 3** Molecular structure of DGFA.

linked polymers. Its reversibility was studied by applying cyclic retro-DA (heat treatment at 140 °C for 20 min to attain a retro-DA sample) and DA (heat treatment at 80 °C for 72 h to attain a DA sample) reactions up to four times, which was monitored by differential scanning calorimetry (DSC). The higher heating temperatures for both retro-DA and DA reactions were chosen to increase the reaction efficiency. As shown in Figure 14, the original cured DGFA (DA0) gives an endothermic peak of retro-DA reaction at 126 °C, while the rDA1 only shows a glass transition at 128.5 °C. This implies that the retro-DA reaction has already been completed during the heat treatment at 140 °C for 20 min. Subsequently, the rDA1 is allowed to reconnect the cleavage groups by DA reaction, and then an endothermic peak appears again at 131 °C for DA1. It is evident that DA reaction between the disconnected furan and maleimide moieties has definitely taken place in the thermal treatment process. The recovery efficiency of the second DA reaction in comparison to the original cured DGFA polymer is about 77 % as given by the ratio of ΔH_1 (enthalpy of DA1) over ΔH_0 (enthalpy of DA0). It is noted that ΔH_0 is 122.9 J/g, corresponding to 80.2 kJ/mol (per DA bond), which is quite close to the exothermal enthalpy per mole DA bond formation [224]. This means that all of DA bonds can be cleaved during the first retro-DA reaction, and the crosslinked epoxy networks do not block the retro-DA reaction.

Thermally remendable processes of artificial damages (made by impact with a falling iron ball) on the cured DGFA are illustrated in Figure 15. Since the interfaces of cracks have a higher refractive index, they are easily visually monitored. All the samples were thermally treated at different temperatures (100–125 °C) for 20 min for dis-

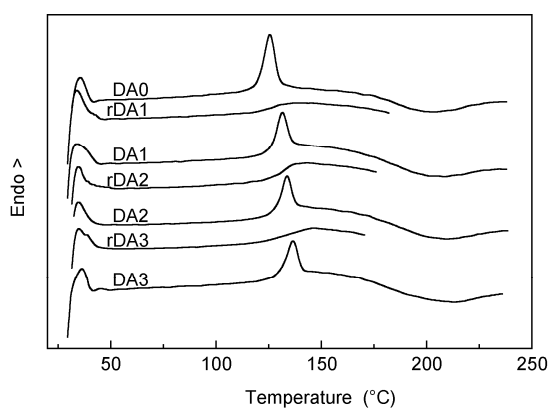


Figure 14 DSC heating traces of DGFA/MHHPA/DPMBMI crosslinked polymer (heating rate: 5 °C/min) [223]. DA0: as-manufactured sample. rDA1: DA0 treated at 140 °C for 20 min, and then quenched to room temperature. DA1: rDA1 treated at 80 °C for 72 h, and then cooled inside an oven by switching off electricity supply. rDA2: DA1 treated at 140 °C for 20 min, and then quenched to room temperature. DA2: rDA2 treated at 80 °C for 72 h, and then cooled inside the oven by switching off electricity supply. rDA3: DA2 treated at 140 °C for 20 min, and then quenched to room temperature. DA3: rDA3 treated at 80 °C for 72 h, and then cooled inside the oven by switching off electricity supply.

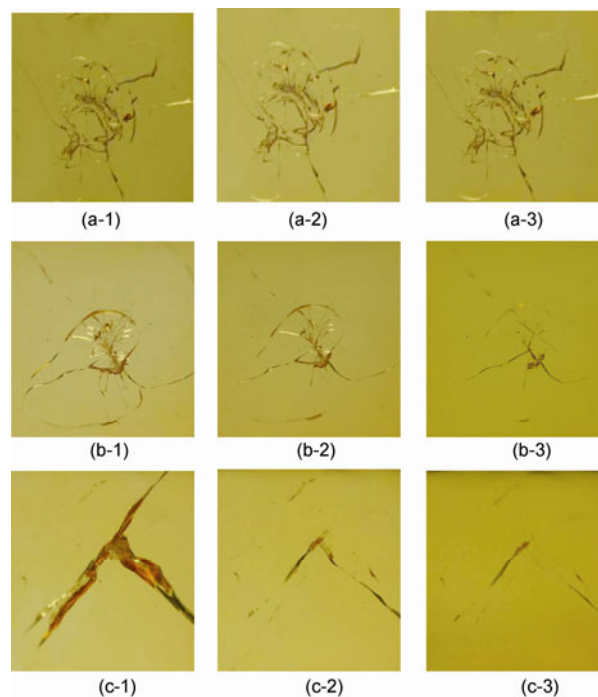


Figure 15 Visual inspection of thermal remendability of cured DGFA polymer [223]. The damaged samples were firstly treated at (a) 100 °C, (b) 119 °C and (c) 125 °C for 20 min, separately. Then, they were moved to an oven preset at 80 °C for (1) 0 h, (2) 12 h and (3) 72 h, respectively.

connecting DA covalent bonds via retro-DA reaction, and then annealed at 80 °C for a while to repair the cracks by DA reaction between the disconnected furan and maleimide moieties.

As shown in Figure 15(a), no crack repair is observed when the heat treatment temperature (100 °C) is lower than the starting temperature of retro-DA reaction (110 °C). When heat treatment is carried out at a temperature (119 °C) higher than the onset temperature of retro-DA reaction, most of cracks can be healed after DA reaction treatment at 80 °C (Figure 15(b)). Some larger cracks finally remain unhealed probably due to the relatively low retro-DA treatment temperature, and/or material loss during damaging, and/or misalignment of the cracked portions. In the case of higher retro-DA reaction temperature (125 °C), which is close to the glass transition temperature of cured DGFA polymer (128 °C), larger cracks can also be repaired owing to the enhanced segment mobility (Figure 15(c)). These results clearly demonstrate that the synthesized epoxy has been provided with thermal remendability as expected.

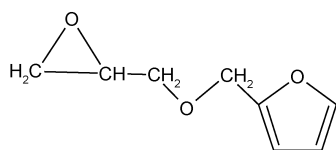
To quantify thermal remendability of the cured polymer in terms of healing efficiency that has been applied for assessment of mechanical property recovery in self-healing materials, the method suggested by Nemat-Nasser *et al.* [225], i.e., double cleavage drilled compression (DCDC) test, was used. The design allows for controlled incremental crack growth so that the cracked specimen remains in one piece after the test, ensuring realignment of the fracture

surfaces prior to healing. During the measurement, cracked virgin specimen was treated at 110 °C for 20 min (for disconnecting DA bonds), and then at 80 °C for 72 h (for reconnecting the disconnected furan and maleimide moieties). The healing efficiency was estimated to be 66%.

Scheme 2 shows that each DGFA molecule contains two epoxide groups and one furan, so that the fraction of DA bonds in the ultimate material must be lower than that of crosslinked bonds of epoxy. Under the circumstances, the healing efficiency of cured DGFA has to be not satisfactory enough. Therefore, another epoxy monomer, furfuryl glycidyl ether (FGE, Scheme 4), was synthesized [226]. It has a similar structure like DGFA, while the fraction of furan is higher. Having been cured by anhydride and maleimide, the FGE based polymer also acquires thermal reversibility. Almost complete rehabilitation is observed, as characterized by the average healing efficiency of 96%.

In fact, synthesis of FGE does not represent the optimal solution. Although the concentration of furan is increased (as compared with DGFA), which helps to improve the healability, the cured version of FGE might have lower glass transition temperature and poorer mechanical properties as each FGE molecule carries only one epoxide group. Again, it is put in a dilemma by the requirements of thermal remendability and mechanical performance like DGFA.

In consideration of complementarity of the structure and properties between DGFA and FGE, blends of DGFA and FGE might be able to offer balanced performance. Blending of polymers is a popular approach used in plastics industry [227, 228]. Two or more polymers are blended together to create a new material with different properties. It is more cost-effective and time-saving than design and synthesis of completely new polymers. Polymer blends can be broadly divided into three categories: miscible, partially miscible, and immiscible blends. Due to the inherent structural



Scheme 4 Molecular structure of FGE.

similarity between DGFA and FGE (refer to Scheme 2 and Scheme 3), it is known that the blends of DGFA and FGE should be completely miscible, and would fulfill the envisaged task [229].

As shown in Table 2, although tensile and flexural properties of the blends decrease with increasing the concentration of FGE due to its lower crosslinking density, most blends have comparable load bearing capability like the cured commercial bisphenol-A epoxy. The moduli of DF91–DF73 are slightly higher than that of bisphenol-A epoxy, while their strengths are moderately lower. On the whole, the data of properties are satisfactory.

5 Self-healing based on photoreversible reaction

Self-healing based on photoreversible reactions is quite attractive because the use of light is clean, cheap and readily available [19]. It would be advantageous to have polymers that unconsciously mend when exposed to environmental conditions like sunlight. Nevertheless, research in this aspect has only just begun. Although exterior paint that obscures scratches on car surfaces was developed by automotive industry, for example, it works due to heating of the sun rather than photochemistry, which induces viscoelastic recovery of the polymer. Only fine scratches appearing in the form of plastic deformation that have not yet led to chain scission can be recovered.

We demonstrated that reversible photochemical reaction can effectively occur in conventional solid polyurethane by introducing hanged coumarin groups into the main chains [231]. Owing to the photosensitive nature and improved mobility of coumarin that serves as a reversible crosslinker in the polyurethane network, not only cracks in the polymer but also mechanical strength of ruptured parts can be recovered for multiple times under ultraviolet irradiation or even direct sunlight.

Coumarin, a traditional perfume substance from plants, possesses attractive photo-responsiveness, which was firstly discovered in solutions or crystals of coumarin derivatives. Since the 1990s, reversible photochemical reaction between coumarin moieties, which were incorporated into polymeric chains, has been investigated in liquid phase. It was found that they are capable of photodimerization via [2+2]

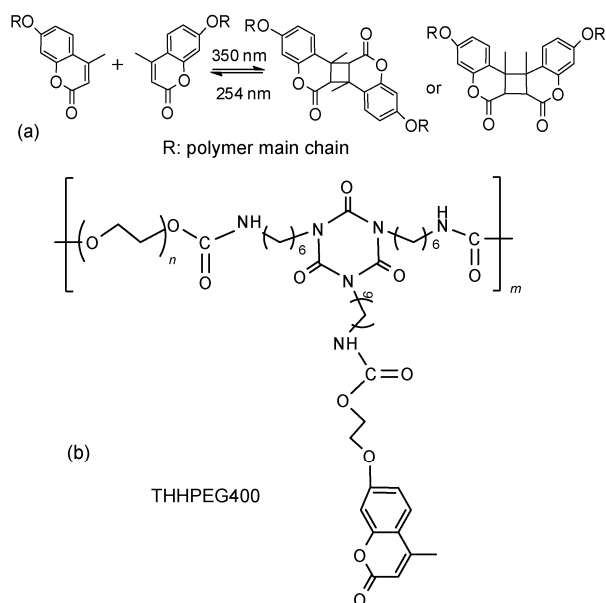
Table 2 Mechanical properties of the cured blends of DGFA and FGE [229]^{a)}

Properties	Bisphenol-A epoxy cured by MHPA [230]	DF10	DF01	DF91	DF82	DF73	DF64
Young's modulus (GPa)	1.8	2.5	0.9	2.3	2.1	1.77	1.35
Tensile strength (MPa)	65	53	19	48.2	44.5	37.6	28.6
Elongation at break (%)	–	1.5	0.5	1.4	1.5	1.6	1.4
Flexural modulus (GPa)	2.6	4.6	1.6	4.2	3.8	3.3	2.4
Flexural strength (MPa)	128	110	32	100	92.4	78	58
Healing efficiency (%)	–	65.9	96.0	68.2	74.0	76.9	81.1

a) DF_{ij} represents DGFA/FGE blend at molar composition of *ij*. DF91, for example, it stands for the DGFA (0.9)/FGE(0.1) blend. Additionally, the molar ratio of epoxide and anhydride groups in all the cured blends is fixed at 1:0.8 and that of furan and maleimide groups is 1:1.

photocycloaddition with $\lambda > 300$ nm UV irradiation and photocleavage upon irradiation at 254 nm (Scheme 5(a)) [232, 233]. These photoreactions are fully reversible, and can thus be used to repair damaged polymers. In this context, biomimetic self-healing might be available based on the photo-responsive behavior in nature. So far, however, most of the previous studies in this aspect have been concerned with the reaction mechanism, and only a few have dealt with applied studies including photo-controlled drug release within solvents [234, 235] and photo-alignment of liquid crystalline polymers [236, 237].

Scheme 5(b) shows the structure of the photoresponsive polyurethane (THHPEG400) proposed by our group, which is the polymeric product of tri-functional homopolymer of hexamethylene diisocyanate (tri-HDI) with polyethylene glycol (PEG400, $M_w = 400$) as the skeleton and 7-(hydroxyethoxy)-4-methylcoumarin (HEOMC) as the pendant group. Unlike most coumarin derivatives, HEOMC can carry out photodimerization even in the solid state. The coumarin moieties in HEOMC help to establish photoreversible crosslinks among linear THHPEG400 by forming cyclobutane rings via photodimerization under UV light at $\lambda = 350$ nm. As the bond strength of cyclobutane rings is lower than other covalent bonds, scission of cyclobutane rings would preferentially occur in the case of crack propagation, reproducing coumarin moieties. By re-applying UV light at $\lambda = 350$ nm, the above photodimerization proceeds again and heals damages. In case the mechanically induced cleavage of cyclobutane rings is not efficient enough, UV irradiation at $\lambda = 254$ nm can be introduced to initiate photocleavage of the rest of cyclobutane rings on the damaged surface, which further



Scheme 5 (a) Photodimerization and photocleavage of coumarin derivatives in polymer. (b) Chemical structure of THHPEG400 [231].

increases the amount of coumarin moieties and healing efficiency.

The monomer HEOMC is obtained by modifying 7-hydroxyl-4-methylcoumarin (HMC) with 2-bromoethanol to convert the aromatic hydroxyl into aliphatic one, which is easier to react with isocyanate. The resultant ether linkage on the side chain is believed to increase mobility of coumarin moieties, facilitating photodimerization (i.e., healing reaction) of cleft coumarin dimers in bulk polyurethane. Prior to the assessment of photochemical self-healing capability, the amount of coumarin moieties and photoreversibility of fractured surface of crosslinked THHPEG-400 film was studied by reflectance infrared spectroscopy (Figure 16). For this purpose, THHPEG400 film (200 μm thick) was firstly crosslinked via photodimerization induced by 350 nm UV irradiation for 90 min. Then, the film was broken apart by cutting and stretching. Compared with the spectrum of the surface of virgin film (refer to spectrum a in Figure 16), the absorptions at 1617 and 1718 cm^{-1} on the spectra of fractured surface of the film are apparently higher (refer to spectra (b) and (c) in Figure 16). Because the peak at 1617 cm^{-1} represents lactone C=C absorption (including

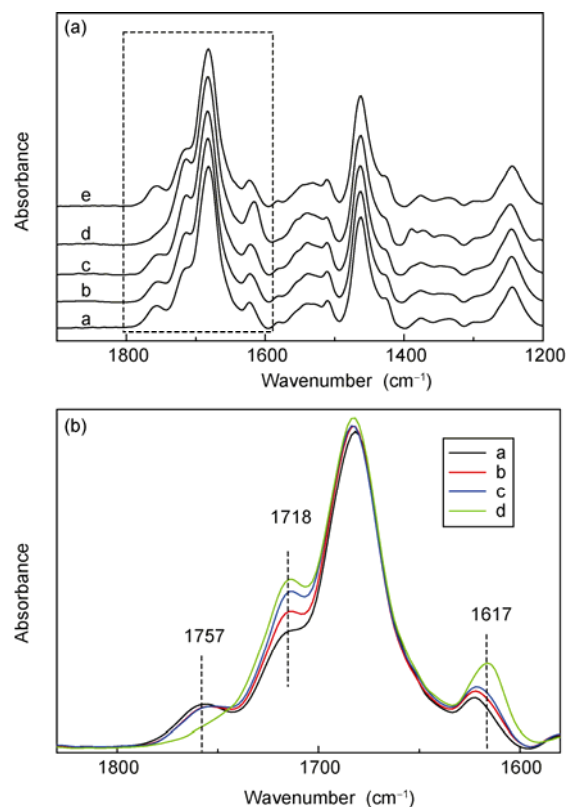


Figure 16 FTIR spectra of original and fractured surfaces of crosslinked THHPEG400 film [231]. (a) Spectrum taken from the surface of virgin film that had been irradiated with 350 nm UV light for 90 min. (b) Spectrum of cut surface. (c) Spectrum of tensile fractured surface. (d) Spectrum of tensile fractured surface exposed to 254 nm UV illumination for 1 min. (e) Spectrum of tensile fractured surface successively exposed to 254 nm UV illumination for 1 min and 350 nm for 90 min.

the contribution of phenyl backbone absorption) and that at 1718 cm^{-1} is related to C=O of coumarin lactone before dimerization, the increase in intensity of the two peaks suggests that cyclobutane rings in the crosslinked film must have been partly cleft and recovered to coumarin moieties due to mechanical damage. A careful inspection of spectra (b) and (c) indicates that the degree of cleavage of cyclobutane rings on the tensile fractured surface is higher than that on the cut surface. This might be the result of different molecular mechanisms involved in material breakage. In the case of cutting, the damage is obligatorily produced along the predetermined cut direction regardless of bond strengths, so that the amount of cleft coumarin moieties is limited, proportional to the concentration of coumarin moieties homogeneously dispersed in the material. When tensile stress is applied, the unstable cyclobutane rings favor crack initiation and propagation, and more coumarin moieties are preferentially cleft.

Considering that high efficiency of crack healing needs more cleft coumarin moieties to be involved in re-dimerization, tensile fractured surface of THHPEG400 film was exposed to UV illumination at $\lambda = 254\text{ nm}$ for 1 min. According to the results of the previous UV-vis, infrared and Raman spectroscopy studies, the treatment should further increase the amount of coumarin moieties. The remarkable intensification of the absorptions at 1617 and 1718 cm^{-1} proves this is the case (refer to spectrum (d) in Figure 16). Moreover, the absorption at 1757 cm^{-1} , which is attributed to C=O of coumarin lactone after dimerization, is no longer observed in spectrum (d). It means that all the cyclobutane rings on the fractured surface have been cleft owing to the 254 nm UV irradiation. When the fractured surface was re-irradiated by 350 nm UV light for 90 min, the resultant coumarin moieties can take part in dimerization to reform crosslinked structures once more. As a result, spectrum e looks nearly the same as spectrum (a).

On the basis of the above structural study, crack re-mendability of the crosslinked polyurethane was qualitatively checked as follows. A $\sim 200\text{ }\mu\text{m}$ thick THHPEG400 film was firstly irradiated with 350 nm UV light for 90 min, and then cut by a razor. Afterwards, the damaged film was successively exposed to 254 nm UV light for 1 min and 350 nm for 90 min to heal the crack (Figure 17(a, b)). The second cut was made across the first one (that has been healed) at an angle of $\sim 60^\circ$, and repaired following the same UV exposure conditions (Figure 17(c, d)). The third cut was made from opposite direction across the intersection of the former two cuts, and repaired again with UV light (Figure 17(e, f)). Disappearance of the intersection, which had been subjected to three cut-repair cycles, reveals the multiple healing ability of the material.

Tensile tests were conducted to quantify the ability of damaged THHPEG400 to restore strength. After testing, the fractured surfaces of specimens were firstly irradiated with

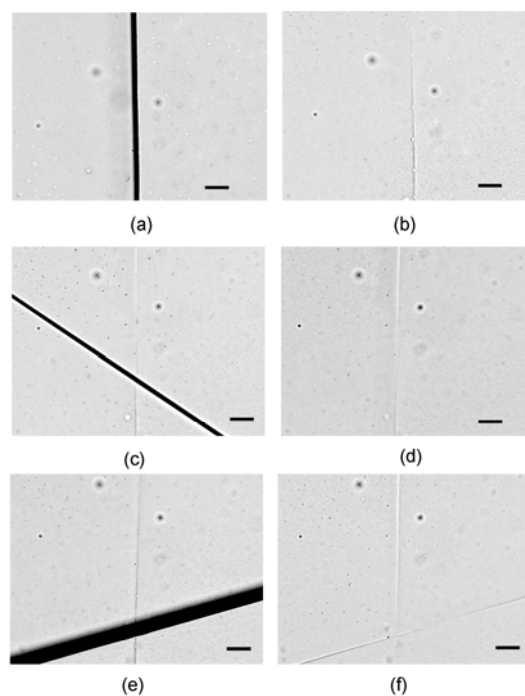


Figure 17 Optical images showing repeated healing of razor wounds on crosslinked THHPEG400 film [231]. (a) The first cut; (b) effect of the first repair; (c) the second cut; (d) effect of the second repair; (e) the third cut; (f) effect of the third repair. Healing conditions: irradiation with 254 nm UV light for 1 min followed by irradiation with 350 nm for 90 min. The scale bars represent $20\text{ }\mu\text{m}$ in length.

254 nm UV light, kept in alignment and intimate contact without pressure, and illuminated by 350 nm UV light. Then, the healed specimens were tested again and healing efficiency was estimated by the ratio of tensile strengths of healed and virgin specimens. Figure 18 shows that tensile strength of crosslinked THHPEG400 can be repeatedly restored, and the efficiency of the first healing event is 70.2%. The decline of efficiency of the second and third remending might originate from reduction in photoreversibility and misalignment of fractured surfaces.

In fact, photocleavage of coumarin dimers (i.e., de-crosslinking of the polyurethane network) led by the irradiation at 254 nm only occurs at the fractured surface layer of the specimen used for the tensile tests due to the limited penetration depth of short wave UV light in the material. The dangling chains carrying cleft coumarin moieties on the fracture surface are highly mobile, which favors wetting and diffusion of molecules at the solid-solid contact of the damaged specimen, and helps to meet the molecular level movement requirement of crack healing [93]. Meanwhile, they are still bound to the inner crosslinked structure that is not influenced by photo-treatment and retains the original network of the film specimen, so that macroscopic flow of the material is prohibited. The above feature of the crosslinked THHPEG400 ensures its dimensional stability during repeated crack healing.

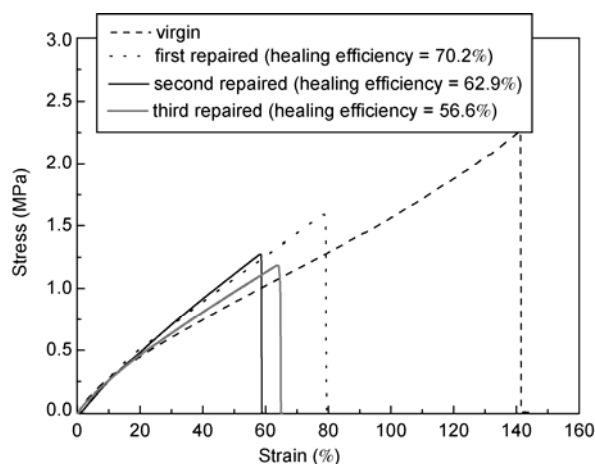


Figure 18 Typical tensile stress-strain curves of virgin and repaired THHPEG400 [231]. Healing conditions: irradiation with 254 nm UV light for 1 min followed by irradiation with 350 nm for 90 min. Because tensile strength of the virgin specimen cannot be fully restored, the reconnected interface became the weakest part, and had to break again during the subsequent tensile tests. This ensured that the second and third tensile failures happened to the same healed portion.

6 Conclusions

Owing to their smart nature, self-healing polymeric materials might solve technical problems that are hard to be solved or simply cannot be solved by conventional approaches. They have opened up broad prospects for key engineering communities and cutting-edge technologies. 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 light degradation, as well as unexpected impacts. There is still a long way to go 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.* [24], most of the self-healing studies to date have 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 polymeric materials are far from satisfactory, the new opportunities found during research 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 [238, 239]. Interdisciplinary studies based on tight collaboration among scientists and engineers are prerequisites for overcoming the difficulties. The related work and outcomes have broadened the application possibility of polymeric materials. Also, the extended service life of components made from these intel-

ligent materials would contribute to reduce waste disposal.

Comparatively, extrinsic self-healing techniques might be easier to be commercialized for large-scale usage within a relatively short period of time. This is because incorporation of healing agents into a target material approaches to conventional compounding techniques used in polymer engineering. From a long-term point of view, synthesis of brand-new polymers accompanied by intrinsic self-healing function through molecular design would be a reasonable way out. 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.

This work was financially supported by the National Natural Science Foundation of China (20874117, 50903095, 51073176 and U0634001), Doctoral Fund of Ministry of Education of China (20090171110026), and the Science and Technology Program of Guangdong Province (2010B010800021)

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