Advances in Healing-on-Demand Polymers and Polymer Composites

Pengfei Zhang¹ and Guoqiang Li^{1,2,*}

¹Department of Mechanical & Industrial Engineering, Louisiana State University, Baton Rouge,
LA 70803, USA

²Department of Mechanical Engineering, Southern University, Baton Rouge, LA 70813, USA

Abstract

Healing-on-demand materials exhibit the capability to close cracks and heal the closed/narrowed cracks when needed and to recover functionality using intrinsic or extrinsic resources. In this review, advances in healing-on-demand polymers and polymer composites in the past decade are reviewed, covering different schemes and technologies used to trigger crack closure and to heal molecularly. A balanced review on non-load-bearing polymers and polymer composites as well as load-carrying polymers and polymer composites is presented. The progress in self-healing polymers and polymer composites has been well discussed recently in the literatures. In this review, therefore, less attention has been paid on what has been widely reported; we primarily focus on healing-on-demand materials concerned with large volume damage healing by a close-then-heal (CTH) strategy. The healing-on-demand material by the CTH approach undergoes a process of crack closure, followed by crack healing with healing agents. Healing theories, including those within the continuum damage mechanics framework, and healing efficiency evaluations are also reviewed. Perspectives on future development in this emerging research area are discussed.

Keywords: Healing-on-demand; Polymers; Polymer composites; Biomimetic; Close-then-heal; Shape memory.

***Corresponding author:** lguoqi1@lsu.edu; Tel.: 001-225-578-5302.

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Nomenclature

A6ACA	acryloyl-6-aminocaproic acid
β -CD	β -cyclodextrin
BDMA	benzyl dimethylamine
BIE	benzoin isobutyl ether
bPEI	branched poly(ethylenimine)
BPO	benzoyl peroxide
CDTE	cyanodithioester
CoPECs	compact polyelectrolyte complexes
Cp	cyclopentadiene
CuAAC	copper (I)-catalyzed alkyne-azide cycloaddition
DA	Diels-Alder reaction
DABBF	diarylbibenzofuranone
DB24C8	dibenzo[24]crown-8
DBTL	di- <i>n</i> -butyltin dilaurate
DCPD	dicyclopentadiene
DHEOMC	derivative 5,7-bis(2-hydroxyethoxy)-4-methylcoumarin
DNA	Deoxyribonucleic acid
DOPA	3,4-dihydroxyphenylalanine
DTHP	diglycidyl tetrahydro- <i>o</i> -phthalate
EMNa	sodium salt of poly(ethylene- <i>co</i> -methacrylic acid)
EMZn	zinc salt of poly(ethylene- <i>co</i> -methacrylic acid)
ENR	epoxidized natural rubber
GMA	glycidyl methacrylate
HGF	hollow glass fiber
HOPDMS	hydroxyl end-functionalized polydimethylsiloxane
HPA	2-hydroxypropyl acrylate
HPF	hollow polymer fiber
IPDI	isophorone diisocyanate
LMWOs	low-molecular-weight organogelators
M ₂	1,8-Bis(maleimido)-triethylene glycol
MAT	methacryloxypropyl-terminated
NHCs	N-heterocyclic carbens
PA	polyacrylate
PAA	poly(acrylic acid)
pAA-CDs	poly(acrylic acid) modified with cyclodextrins
pAA-Fc	poly(acrylic acid) modified with ferrocene
PAH	poly(allylamine hydrochloride)
PCL	poly(ϵ -caprolactone)
PDMAA	poly(N,N-dimethylacrylamide)
PDMS	poly(dimethylsiloxane)
PEG	poly(ethylene glycol)
PEI	poly(ethyleneimine)
PEMAA	poly(ethylene- <i>co</i> -methacrylic acid)

PFS	poly(2,5-furandimethylene succinate)
PIB	poly(isobutylene)
PIE	isonicotinate-functionalized polyesters
PK	polyketones
PLA	poly(lactic acid)
PMMA	poly(methyl methacrylate)
PNIPA	poly(N-isopropylacrylamide)
PISP	polyisoprene
POM	polyoxometalates
PVAc	poly(vinyl acetate)
PVA	poly(vinyl alcohol)
PS	polystyrene
PSS	poly(styrene sulfonate)
rDA	reversible Diels-Alder reaction
ROMP	ring-opening metathesis polymerization
SMA	shape memory alloy
SMP	shape memory polymer
TDCB	tapered double cantilever beam
TDI	2,4-toluene diisocyanate
TDS	thiuram disulfide
TfOH	Trifluoromethanesulfonic acid
TPU	thermoplastic polyurethane
TTC	trithiocarbonate
UPy	ureidopyrimidinone
VI	N-vinylimidazole

1 Introduction

With the popular use of polymer and polymer composites in industry, damage and fracture within these materials are inevitable [1-5]. Both expected loading such as fatigue load, and incidental loading such as foreign object impact, can lead to serious shortening of service life. Various efforts have been made over the past decades to improve the durability of polymer and polymer composites by designing new materials or developing crack-healing techniques. Bio-inspiration has played an important role in developing new crack-healing strategies [6].

The history and evolution of bio-inspired materials and damage-healing techniques have been examined in a number of published reviews, patents, and books [6-50]. Pioneer work mainly focused on the self-healing concept in thermoplastic and thermoset polymers and/or polymer composites through extrinsic or intrinsic resources, as well as the design and generic principles for self-healing systems. These systems include thermosetting polymers, thermoplastic polymers, composite materials, metallic systems, ceramics and ceramic coatings [51], and concrete [52-54]. Self-healing materials by nanotechnology was also developed [55-58]. There is no doubt that the previous endeavors have greatly advanced understanding of the self-healing abilities of polymers and polymer composites, or at least created a sense of what-to-do and what-not-to-do when designing a crack healing system. However, due to the fast development in this emerging field, there is a need to review these new developments within the framework of healing-on-demand polymers and polymer composites.

Here, we define a healing-on-demand material as one within which a crack, due to mechanical damage or degradation, may be closed and healed in time and in-situ, when the crack is detected or sensed by internal or external means. In other words, when needed, a healing-on-demand material exhibits the capability to permit crack closure and healing under in-service conditions, and to recover functionality using intrinsic or extrinsic resources. In this sense,

healing-on-demand does not necessarily mean completely autonomous healing or “self-healing”. It means that with some intervention such as bringing fracture surfaces in contact, heating, etc., healing can be triggered and proceed without additional intervention. For example, fractured polymer panels may not be able to heal themselves without external help to bring fracture surfaces into contact, regardless of intrinsic healing (without healing agent) or extrinsic healing (with healing agent). Within this definition, some healing schemes, usually not reviewed in-depth within the “self-healing” literature, belong to the broader framework of healing-on-demand. Actually, as indicated by Li [47], healing-on-demand may be more appropriate in describing in-service healable materials, because in real world structures, for example a panel under fixed boundary condition and/or under external loading, some help or intervention, although perhaps minimal, is almost always needed to heal wide-opened cracks or large damage volumes.

Fig. 1 shows a concept of healing-on-demand materials, through which inspection and maintenance techniques have been developed to prolong service life of engineering materials. We believe that there is a need for distinction between materials scientists and engineers with respect to self-healing. Five stages of crack healing have been proposed for healing through physical molecular entanglement by Wool and O’Connor [59]. They are (i) surface rearrangement, (ii) surface approach, (iii) wetting, (iv) diffusion, and (v) randomization. For healing through chemical bond interaction, there are four stages, which are (i) surface rearrangement, (ii) surface approach, (iii) chemical reaction, and (iv) dynamic equilibrium. In general, materials scientists are mainly concerned with surface rearrangement, wetting, diffusion or chemical reaction, and randomization or dynamic equilibrium, i.e., reestablishment of physical entanglements or chemical bonds. The stage of surface approach does not cause enough attention. In the lab, fractured specimens are usually brought into contact manually before healing starts. As indicated by Wool [7], and echoed by Binder [48] and Li [47], this manual operation

represents the largest challenge in the real world applications. From the point of view of engineers, one could not bring a fractured skin panel together by hand in a Boeing aircraft and may not bring a fractured specimen together manually if the boundary of the specimen is fixed [47]. However, crack healing cannot occur without external help to bring the fracture surfaces in contact. Therefore, engineering applications face additional challenge to self-healing materials. We believe that it is time to consider the practical constraint of how to bring the fracture surfaces in contact.

[Insert **Figure 1** here]

In this review, we discuss the potential challenges and opportunities from the point of view of engineering applications. We focus mainly on the crack closing and healing principles for polymers and polymer composites that have emerged over the past decade. Especially, healing-on-demand load-carrying polymer composites and shape memory polymer based crack healing structural composites, which have not been a focus in previous reviews, are discussed in more detail and depth in this review. The close-then-heal strategy, which has been demonstrated by shape memory polymer matrix, shape memory polymer fiber, and polymeric artificial muscle in healing large volume damage for functionality restorations, will be reviewed. The associated healing theories and healing efficiency evaluations will also be reviewed.

2 Healing of Polymers

Polymers used in industrial applications are designed with a specific service life. Loss of structural capacity or functionality can occur because of incidental damage or degradation over time. It will be a tragedy if polymers fail within their designed lifespan. In order to maintain their service life even after structural damage, polymeric materials have been designed to have the ability to heal themselves on-demand. The study of healing-on-demand polymers, in general, is

continuously progressing. More exciting discoveries in this area are expected as numerous studies are evolving.

According to the published literatures, the methods for triggering healing-on-demand in polymers include extrinsic stimuli such as pH [60-64], salt [65], thermal treatment [66-74], water [75, 76], light [77-83], sonication [84], and electrical treatment [85]. The intrinsic healing mechanisms include labile bonds [86-91], fusion [92], reversible dissociation-association [93, 94], host-guest interaction [95, 96], metallo/ligand complexation [97], and dynamic covalent bonds [98, 99]. In some cases [62, 66-70, 72, 73, 82, 89], both extrinsic and intrinsic stimuli are involved.

Crack healing polymers have been well reported and summarized by pioneer works; however, in this review, we will focus primarily on the crack approaching methods as well as the damage healing mechanisms. As given in Table 1, the healing-on-demand polymers published since 2007 are summarized based on damage type, crack approaching method, healing mechanism, healing measurement, efficiency, repeatability, healing condition, and healing time. Not all reported research works are included in the table. We only include those that have clear descriptions on crack approaching method and damage healing mechanism so that comparisons can be made. The crack modes, crack approaching methods, and healing mechanisms under on-demand conditions will be mainly discussed based on the summarization in Table 1.

[Insert **Table 1** here]

2.1 Crack Initiation and Surface Approaching

As shown in Fig. 1, the need for healing is triggered by damage or cracking. Cracking in materials can be initiated by various internal and external means. Fig. 2 shows the types of crack initiation modes based on the summarization in Table 1. For example, ballistic impact could

create shear plug through the thickness if the impact energy is sufficient or random cracks on the back face if the energy is insufficient. The hole or cracks can be patched due to the elastic spring back such as ionomers [100-104]. Razor cut could initiate a deep cut or even cut materials into two halves. The crack is usually closed by bringing the two halves together manually [83, 107, 119]. Sawing is another type of cut similar to razor cut [100, 101]. An accidental damage might result in a random microcrack or structural-scale wide-opened crack depending on the impact energy or damage location [62]. There is no need to bring fractured surfaces together for the scratch damage since the name implies that only scratch marks are created on polymer material surfaces. These scratches may close due to swelling when being submersed into a solution, or close with the shape memory effect when exposed to triggering factors (e.g., UV light, thermal treatment) [81, 123-125]. The polymer materials under compression suffer from buckling and can ultimately fracture. A crack might propagate to a large size if a precrack is introduced to the body prior to buckling [71]. It can be closed through elastic recovery but if a fracture occurs, it is a challenge to heal it. Tensile stretch might result in different damage modes [126]. The mode investigated includes breaking the specimen into two halves [83, 99, 110]. The fracture surfaces were brought into contact to march towards each other manually prior to the healing process. The crack initiated by bending can be closed due to elastic recovery; for wider cracks, they can be closed with the help of compression to push the cracks into contact after the removal of external bending load [67, 68].

Although all the cracks in Table 1 are created by external means, they may not be predictable in real world structures such as those under impact load; on the other hand, the crack propagation is somewhat predictable. This gives us an opportunity to close or fill in the cracks by bringing fracture surfaces into contact. Because manually bringing fracture surfaces into contact is very difficult in real world load-bearing structures, the true challenge in self-healing of load

carrying structures is how to bring the fractured materials in contact, regardless of visible crack on the surface or nonvisible crack within the body of the material.

[Insert **Figure 2** here]

2.2 Crack Healing Mechanisms

For all polymers, crack healing follows a two-stage process. On-demand fracture surface approaching is the first stage. In the second stage, healing through physical or chemical means is performed on the surfaces in proximity or in-contact. The crack healing mechanisms have been well assessed by recent review papers and books on self-healing polymers [21, 47, 50, 127, 128]. To avoid overlaps, we will briefly review and summarize the healing mechanisms based on the categorization in Fig. 3. The mechanisms are categorized into two groups, physical molecular interdiffusion and chemical bond interaction, which is further subdivided into covalent and non-covalent bond interactions, and intermolecular force.

[Insert **Figure 3** here]

2.2.1 Molecular Interdiffusion

Polymers can regain their mechanical functionalities through physical interaction (e.g., molecular interdiffusion). Continued interdiffusion, randomization, and long-term relaxation of the polymer chains are required in order to achieve optimal healing performance. There are several factors that can affect the crack healing performance, such as molecular reptation time, healing temperature, co-surfactant effect, and concentration. For example, sodium-chloride (NaCl) has been used as an initiator for increasing the mobility of the chain segments with the aim at accelerating damage healing process. In order to make the healing faster and more complete, compact polyelectrolyte complexes (CoPECs) were prepared by mixing solutions of PAA and PAH, and compacting by ultracentrifugation in the presence of NaCl [65, 129]. It

showed that the CoPECs healed the fracture surfaces when they were brought into contact for 15 min in a salt concentration of 2.5 M NaCl, as presented in Fig. 4. The healing behaviors of the compounds indicate that the healed sample strength depends on the contact time and NaCl concentration. With increasing salt concentration, the mobility of the chain segments increases; and the more the mobile segments, the faster the chains diffuse and the faster the fracture surfaces heal.

[Insert **Figure 4** here]

2.2.2 Reversible Covalent Bond

Making covalent links reversible is one of the strategies to heal cracks and prolong service life of polymers. The reversible bonds allow dynamic bond reactions between covalent links by maintaining constant the total number of network links and average functionality of polymers. Some chemical covalent bond reactions for crack healing applications are presented in Table 2. The reversible covalent bonds have the potential to heal damage-induced cracks in thermoset by restoring mechanical functionalities under on-demand thermal or water stimuli [130-132]. For example, Montarnal et al. reported a concept for healing cross-linked polymer network by dynamic bond exchange reactions [133]. A cross-linked sample broken into pieces was reheated over 180°C and reprocessed in an injection molding machine. It was found that the initial geometry and properties have been recovered due to the healed polymer chains at a high temperature. Transesterification reaction occurs between two β -hydroxyl-esters, leading to rearrangement of network topology while preserving the total number of links and integrity of the network functionality.

[Insert **Table 2** here]

In contrast to the dynamic bond exchange, reversible Diels-Alder (rDA) and hetero Diels-Alder (HAD) reactions could make the cross-linked polymer network a temperature-sensitive polymerization-depolymerization equilibrium [136-138]. For example, Zhang et al. reported a thermally healing-on-demand thermoset polymer in order to resolve the issue on recycling of thermosetting materials at the end of life cycle [68]. The thermoset polymer was prepared by the Paal-Knorr reaction of the PK with furfurylamine, where the PK was used as precursor for DA reactions. When the fractured sample was heated over 110°C, which was above its glass-transition temperature, the thermoset polymer became soft because of the opening of the DA adduct, then reactions occurred between the PK-furan and bis-maleimide, leading to regeneration of the DA adduct. Upon cooling, the sample recovered its original shape, which was repeatable without any loss in mechanical properties. The uniqueness in this healing-on-demand behavior persists in its ultrafast healing response, such as 5 minutes upon heating (among 110–150°C) during the healing event.

Repeatable crack healing through photostimuli and simultaneously macroscopic fusion of separate pieces can be achieved by photo-reversible reshuffling reaction [79, 82, 83, 135]. For example, Ling et al. reported a monomer synthesized by cross-linked polyurethane containing dihydroxyl coumarin derivative 5,7-bis(2-hydroxyethoxy)-4-methylcoumarin (DHEOMC). Upon photo stimulation, the fracture surfaces were successfully healed within two hours. The dynamically reversible C-ON bond and S-S bond shows an interesting behavior of frequent cleaving but immediate rebonding when under certain hemolysis temperatures [71]. Upon the thermal treatment at 130°C, covalent C-ON bonds fission and radical recombination synchronously took place among alkoxyamine moieties. Eventually, the fracture surfaces could be completely healed after 2.5 hours. It was pointed out that the alkoxyamine could be used for

healing structural applications on-demand based on dynamically reversible C-ON bonds no matter they appear in linear or cross-linked polymers.

2.2.3 Noncovalent Bond Interaction

As classified in Fig. 3, the noncovalent bond interaction includes reversible non-covalent bonds (ionic bond [100, 101], and metallic bond [66, 74, 77]), and intermolecular force (e.g., hydrogen bond [139, 140], and Van der Waal's bond [141]). In terms of pure ionomer of EMAA or in the form of ionomer blends of EMAA and functionalized elastomers ENR and PISP, the healing of puncture-induced damage is due to the ionic bond interactions in their molecular structure. Below the order-disorder transition (T_i) temperature, ionomers are solid. While upon temperature change, the structure of ionomer rearranges itself over time due to the ionic interactions or aggregations. Metallic bond in polymer is designed for the crack healing applications in electric field, magnetic field, or optical field. One example is that, due to the endowed conductive properties, the structure status of the polymer can be monitored real-time through its electrical feedback. The structure status includes microcrack initiation, stress history, and so on. The unique features can be lost if used improperly, like internal damage. An organometallic polymer was developed by compounding between N-heterocyclic carbenes (NHCs) and transition metals at molecular level [66]. As shown in Fig. 5a, the chemical dynamic equilibrium between molecules, like a monomer species (1) and an organometallic polymer (2), is controlled by an external stimulus. The synthesis of such a polymer was a challenge as pointed out in their work because of the requirement for the synthesis of appropriately functionalized multitopic NHCs poised for polymerization. Owing to the transition metals and structurally dynamic equilibrium, the synthetic organometallic polymer was an electrical conductive and crack-healing material. The healing-on-demand mechanism is elucidated in Fig. 5b. The created microcrack results in inherent electrical resistance change (i.e., high-resistance/low-current). As

a result, the voltage bias generates localized heat at the microcrack site. In turn, local heat overcomes the fracture surface kinetic barriers, leading to reformation of the broken NHCs-metal bonds. Consequently, the system is electrically driven back to its original state (i.e., low-resistance/high-current) and the microcrack is healed.

[Insert **Figure 5** here]

A group of polymers perform their crack healing via intermolecular force, such as host-guest interaction [85, 142], dynamic polar group [70], weak hydrogen bond of π - π stacking [141], hydrogen bond through dynamic olefin metathesis [122], and hydrogen bond interaction between terminal-carboxyl groups [63], UPy groups [90, 139], PA-amide groups [109, 111], supramolecular clusters [112], and hydroxyl groups [140]. The on-demand conditions for driving crack healing can be pH aqueous solution, water, heat treatment, UV light, electrical field, and magnetic field. For example, the acryloyl-6-aminocaproic acid hydrogel exhibited repeatable damage healing ability at low pH, at which the terminal-carboxyl groups were protonated to generate hydrogen bonds with other terminal-carboxyl groups or amide groups across the interface [63]. Fig. 6 shows the performance of hydrogel healing via change in pH. The weld of the fracture surface took only two seconds, but it took 24 hours for complete crack healing. Another pH-responsive repeatable healing-on-demand hydrogel was investigated by Krogsgaard et al., by incorporating additional features of mussel adhesive proteins [64]. The 3,4-dihydroxyphenylalanine was attached to amine-functionalized polymeric hydrogel. The healing was a result of the formation of networks through the reaction with ion at pH of 8.0. The healing event was completed within 45 min.

[Insert **Figure 6** here]

3 Healing of Polymer Composites

The repair of damage-induced crack in polymer composites has been well discussed including both intrinsic and extrinsic strategies [6, 8, 12, 14, 15, 20, 47, 127, 128, 143, 144]. Like in Section 2, here we focus on several specificities such as composite type, damage type, crack approaching method, healing mechanism, healing measurement, healing efficiency, repeatability, healing condition and time, as summarized in Table 3. The healing-on-demand polymer composites can be categorized into five types, which will be discussed in the following subsections.

3.1 Capsulated Polymer Composites

These polymer composites incorporate capsules of various sizes uniformly distributed within the matrix materials. Based on the size, capsules can be categorized into micro size [145-150] and nano size [57, 151, 152]. They are filled with liquid healant or liquid crosslinking hardeners (e.g., catalyst). Healant can be a crack healing agent, which is used for mechanical property restoration; or can be a function restoration agent for conductivity restoration [153-155], anticorrosion [156], and water resistance [157]. Upon fatigue loading or incidental loading, the capsules are ruptured by propagating micro-cracks in the matrix. The loaded healant is released from the capsules, filling in the propagated micro-cracks via capillary action, and comes into contact with crosslinking hardeners; or released liquid crosslinking hardener comes into contact with embedded healant to initiate polymerization at the micro-crack site, leading to healing-on-demand healing, in autonomous manner. As shown in Fig. 7, crack healing by capsules includes both single capsulated polymer composites and dual-capsulated polymer composites. In Fig. 7(a), the “question mark” indicates that the capsule can be filled with either liquid healant [158-165] or crosslinking agent [166, 167], depending on the design of the material system. Fig. 7(b) indicates that two types of capsules are embedded in the polymer matrix, which are encapsulated

with healing agent and crosslinking hardener individually [168, 169], or healing agent and liquid initiator individually [170].

[Insert **Table 3** here]

[Insert **Figure 7** here]

Since a microcapsule crack healing system with the ability to heal cracks for mechanical property restoration was reported on structural polymer composites [171], microencapsulation has motivated studies from multiple academic disciplines to a wide variety of industrial applications. Healant was encapsulated in a microcapsule and the catalyst was well dispersed within the composite matrix in the first reported single-microcapsule polymer composite. The catalyst deactivation, as well as the potential side reactions between catalyst and polymer matrix after embedding the catalysts in the matrix, was a major challenge facing this type of healing-on-demand composites. Faced with these challenges, two solutions have been proposed: (1) no catalyst and (2) catalyst protection.

Yang et al. reported a catalyst-free crack healing polymer composites by incorporating IPDI-loaded microcapsules [159]. The crack healing behavior was triggered by humid or wet environment, in which the ruptured healant IPDI was polymerized. Photo-induced healing through the use of ruptured healant methacryloxypropyl-terminated PDMS was reported by Song's group, who prepared a polymer composite with crack healing ability within 4 hours upon exposure to sunlight [190]. The advantage of this system persists in its repeatability in damage healing due to the reversible polymerization between the healant and host matrix.

The agent for catalyst protection could be wax if solid catalyst is used [176-178, 183, 245], and polyester shell or glass shell if liquid catalyst is used [191, 192, 195]. Since both healant and catalyst are capsulized, it is called dual-microcapsule polymer composite. Obvious

advantages of this system are: (1) better thermal tolerance; (2) better corrosion resistance if shelled by glass; (3) fast polymerization speed (i.e., fast crack healing rate) due to two liquid phases.

3.2 Hollow-fiber Reinforced Polymer Composites

Crack healing in hollow-fiber reinforced polymer composites was investigated through (1) one-part liquid healing agent, (2) two-part liquid healing agent and liquid hardener, and (3) two-part liquid healing agent and encapsulated catalyst [208].

The hollow glass fiber (HGF) used in this system is an ideal medium for storing healing agents due to its good mechanical properties as structural reinforcement, which provides impact protection to some extent. Microcrack damage within structural polymer composites leads to fracture of the hollow glass fiber, which releases liquid agents to fill in the microcracks by capillary action and heal them through healing agent polymerization. Compared to the HGF preparation technique, the preparation of hollow polymer fiber (HPF) is much more effective. The healing agents or catalyst-solvent were filled into polymer fibers during the processing of hollow polymer fiber, forming a core-shell bead-on-string morphology. The advantage of this technique is the capability in controlling the diameter of HPF from micro- to nanometer scales [246]. In contrast to the functionalized capsule-based coatings, the HPF-based healing-on-demand coatings could solve a number of issues with chemical incompatibilities between various matrices and healing agents associated with the dispersing capsules in the matrix precursors.

3.3 Vascular Networks based Healing-on-Demand Polymer Composites

The microcapsule and hollow fiber serve the function of liquid storage and delivery. By implementing vascular networks, the healant from a reservoir is delivered to a damage site via a network of vessels. The advantage of vascular based healing-on-demand polymer composites is

that it provides the healing ability for large damage volume and multiple healing events as well as the replenishment of the healant. The branching macrovascular network was inspired by human circulatory system [226] and plant vasculature system [247, 248], as shown in Fig. 8. This branching network is to avoid the loss of healing repeatability due to bleeding clots. Additionally, 3D vascular system gives higher potential for fast healing response [230].

[Insert **Figure 8** here]

The healant or crosslinking hardener was protected by a shell from directly contacting the host matrix in the microcapsule system as well as the hollow fiber system. However, in the vascular network system, the healant or crosslinking hardener was in direct contact with the matrix while in delivery. This is one of the concerns when implementing vascular network for crack healing purposes. In the case of large volume damage, it requires overcoming the interplay between mass transport, environmental factors, intrinsic forces (such as surface tension), and extrinsic forces (such as gravity) that act on the liquid reagents [222, 223]. How to heal large-scale or wide-opened crack without mass loss is a challenge. To date, there are two approaches to deal with the challenge. One is the close-then-heal (CTH) method proposed by Li's group (to be discussed in the next section), and the other is the method proposed by White's group [222]. By using a vascular system of microchannels, White et al. proposed two stages: (1) gel-stage (liquid to gel) to plug the hole quickly and prevent bleed-out of the healing agent; (2) polymerization-stage (gel to polymer) to undergo polymerization of the healing agent and heal the large volume crack. By evaluating the impact damage on the healed sample, about 62% of the impact energy (on a time scale of 3 h room temperature curing) was recovered. The challenge is that the surface tension would become insufficient to retain the unreacted fluid when the damage size exceeds a certain threshold, leading to bleeding-out of healant.

3.4 Healing in Layer-by-Layer Coating/Film

A skin material with flexibility, healing-on-demand and damage sensing was studied and fabricated by using a layer-by-layer technique with copperclad imidized polyimide sheets and Loctite Impruv 365 UV-curable epoxy, which was used as structural adhesive as well as crack-healing fill material [232]. After an intentional puncture, the damaged skin can heal itself through the flow of UV-curable epoxy under UV exposure in a matter of minutes. This fast healing behavior is one of the advantages exhibited by healing-on-demand skin.

Andreeva et al. designed a healing-on-demand anticorrosion coating system on aluminum alloy based on pH-sensitive polyelectrolyte/inhibitor sandwich-like nanostructures [249]. The PEI, PSS and 8-hydroxyquinoline nanolayers were deposited on the pretreated aluminum alloy under the layer-by-layer deposition procedures. The nanometer-thick novel coating protected the aluminum alloy effectively from corrosion. The healing behavior of the coating prevented the propagation of corrosion on metal surfaces based on the suppression of accompanying physicochemical reactions. The mechanisms for healing-on-demand of the corrosion damaged areas included pH neutralization, passivation by inhibitor, and healing by mobile polymer layers. Once the corrosion occurred, the inhibitor was released to the damage site on the substrate surface to prevent adsorption of chloride ions. Due to the changes of local pH, the polyelectrolyte complex was swollen and polymer chains diffused through the rupture surfaces. The gradual evolution of ionic bonds results in damage healing from the healing-on-demand coating system.

Water-induced healing synthetic materials are used for applications from food packaging to sub-water coating [250, 251]. A healing-on-demand polyvinyl based coating blend was reported by Ensslin et al., who used the blends of PVAc and PVA-PEG in the field of pellet coating [252]. The PVAc/PVA-PEG coating in the damage site started to swell under the exposure to water, leading to the closing of holes, craters, and clefts, which prevent a burst release. However, the crack-healing efficiency needs further investigation.

3.5 Solid-state Healant Embedded in Polymer Composites

The intrinsic self-healing polymers described in Section 2 could be fabricated into small pellets and dispersed into a polymer composite matrix as a healant. In this system the crack is healed once the embedded healable particles are in contact, through molecular interdiffusion [253], dynamic covalent bonding [254-256], non-covalent bonding [239], intermolecular force [257, 258], and so on. However, crack approaching is a prerequisite and is a challenge when the crack opening is wide.

4 Close-Then-Heal Strategy for Polymer Composites

From the above reviews, it is seen that some healing schemes need external help, i.e., bringing fracture surfaces into contact manually before healing occurs. While this is legitimate in lab scale specimens, it represents one of the greatest challenges in real world structures. This is because in large scale structures, fractured structural elements cannot be brought in contact manually. If they are forced together, new damages may form [47].

It is a straightforward idea to utilize the shape memory effect for crack closure because cracks can be treated as a type of pseudo plastic deformation, and the shape memory effect can restore the original shape upon external stimuli. However, the ability to close cracks depends on (1) the level of programming and (2) the constraint during shape recovery [47]. For some shape memory effect based applications such as coatings, the system uses scratching, indentation, or cracking itself as programming. Clearly, if there is no significant barrier to resist the shape recovery, such as a free-standing specimen or panel, the crack can be closed if the shape recovery ratio is close to 100%. However, if there is a significant barrier to resist free shape recovery, such as a specimen or panel with fixed boundary or under external tensile load, the crack cannot be closed. Therefore, energy storage by programming is usually required and is a

better way for crack closure as it can be designed to consider the level of barrier to resist shape recovery and the shape recovery ratio [47].

In their review paper, Hu et al. clearly defined two types of crack healing schemes based on shape memory effect [259]. One is free shape recovery and the other is constrained shape recovery. Most recently, Yougoubare and Pang compared the two popular shape memory effect based crack closure schemes [260]. One is shape memory assisted self-healing (SMASH) proposed by Rodriguez et al. [261] and Luo and Mather [262], and the other is close-then-heal (CTH, firstly close the crack through confined expansion of the SMP matrix, and then heal it by embedded thermoplastic particles), which was proposed by Li et al. [242, 244] based on their previous test results of healable SMP syntactic foam [263]. According to Yougoubare and Pang, the fundamental difference between SMASH and CTH is that SMASH targets non-load carrying materials, uses no constraint during shape recovery, does not conduct programming, and is usually suitable for microcracks and small indentations; on the other hand, CTH focuses on load carrying material, considers constrained shape recovery, needs programming depending on the width of crack to be closed, and is suitable for wide-opened crack and large indentation. It must be emphasized that shape memory effect does not necessarily heal the material. It only narrows or closes the crack. In order to heal the crack, it must be combined with other physical or chemical healing schemes such as shape memory polymer with self-healing capability or a combination of shape memory polymer with external healing agent [47]. In the following, we will review the shape memory effect based self-healing schemes, particularly SMASH and CTH. After the discussion on the topics of SMASH and CTH, the crack healing mechanisms, within the healing-on-demand polymer materials framework, will be covered via healing theories.

4.1 Shape Memory Assisted Crack Healing

Over the past decade, shape memory materials have been used to improve the healing-on-demand process by providing functionality to partially or fully close cracks. A poly(ϵ -caprolactone) (PCL) based composite system is one of the examples used to explain this approach [261]. The advantages of shape memory polymer materials are the ability to sustain high strain (up to 500-800%), low response temperature, tunable elastic modulus, and low density [264]. Rodriguez et al. reported SMASH of polyurethane blends with varying compositions. The blends were synthesized via the incorporation of a covalently cross-linked network by end-linking end-functionalized n-PCL as a thermoset for shape-memory and a linear l-PCL thermoplastic for healing. Upon the on-demand thermal treatment at 80°C, the fractured surfaces were driven back for contact by the n-PCL shape-memory ability; and then, surface wetting and chain diffusion by l-PCL occurred at the crack surface. The equilibrium and randomization of PCL networks were achieved over time and thus the fracture surface was healed, as shown in Fig. 9. This damage-healing application overcomes the above mentioned limitation, i.e., crack closure without manually pushing the fractured parts together.

[Insert **Figure 9** here]

Luo and Mather proposed a new SMASH strategy tailored for coating/corrosion-inhibition applications [262]. Nonwoven nano- and micro-PCL fibers were distributed in a shape memory thermoset matrix by an electrospinning process. Both fibers and matrix served as coating agents on a steel substrate. The randomly oriented and evenly distributed PCL fibers can heal larger cracks and defects due to the more significant flow of the liquefied PCL fibers compared to the previous SMASH example. The working principals during the healing-on-demand process include two steps, which take place simultaneously: (1) crack closure due to the shape memory behavior of the SMP matrix, which releases stored strain energy in the plastic

zone after thermal treatment, and (2) crack rebinding (i.e., healing) due to the melting and flow of the PCL fibers. It was reported that the crack-healing performance could be conducted by heating at 80°C for 10 min, leading to almost completely restored corrosion resistance.

4.2 Close-then-Heal

It is emphasized here that, the CTH strategy is different from SMASH. The healing-on-demand composite by CTH approach, as proposed, undergoes a process of crack closure by constrained shape recovery, followed by crack healing through healing agents. As compared to SMASH, the boundary condition of the specimens or structural components per the CTH scheme does not need to be free, and the shape recovery ratio does not need to be 100%. Therefore, the CTH scheme is appropriate for real world load-bearing structures because these structures are generally constrained at the boundary and/or under external loading during the healing process, and the shape memory capacity of SMPs degrades with time.

It is worth mentioning that CTH is in line with the widely accepted five-step healing theory proposed by Wool and O'Connor [59]. The first two-steps, (i) surface rearrangement, (ii) surface approach, correspond to “Close” in CTH, and the last three steps, (iii) wetting, (iv) diffusion, and (v) randomization, correspond to “heal” in CTH.

A concern with CTH may be that one needs to design or manually provide the external confinement. Actually, the external confinement or constraint needed in CTH is provided naturally by the materials and structures. According to CTH, only local or *in-situ* heating surrounding the crack in a specimen or panel is needed to close the crack and heal it. The rest of the specimen or panel is still “cold”, which provides the external constraint. Furthermore, constraint can be provided by the architectural configuration of composite structures, such as sandwich face sheets [263], 3-D woven fabric [265], grid skeleton [266], etc.

Another concern with crack closure by shape recovery is that the SMP could be very soft at high temperatures. In several experimental studies, the healing temperature is always slightly above the glass transition temperature, but sometimes even within the glass transition temperature zone [263, 265, 266], as long as one can find a healing agent which melts and bonds at that healing temperature. When the healing temperature is slightly higher than the glass transition temperature but still within the glass transition zone or slightly above the zone, the SMP is still stiff enough. Also, as indicated in several of previous studies, one only needs to heat up locally surrounding the crack according to CTH. The rest of the structure is still “cold”. Therefore, the overall structure is still very stiff [47, 267]. Furthermore, research has proved that time-temperature equivalent principle holds for shape recovery, which suggests that, as long as the healing temperature is within the glass transition zone, the shape recovery can occur even at a temperature slightly below the glass transition temperature [268]. What needed is a longer healing time. Again, as long as one can find a suitable healing agent, CTH can proceed when the SMP is still considerably stiff.

Currently, the CTH scheme has evolved into three sub-systems, i.e., SMP as a matrix, SMP as a dispersed reinforcing phase, and polymer artificial muscle as an inherent actuator. In other words, the crack closing can be driven either by a compression programmed shape memory polymer matrix or tension programmed shape memory fibers or artificial muscles. The following three subsections will discuss in detail how the CTH scheme works in these three sub-systems.

4.2.1 Shape Memory Polymer as Matrix

Shape memory polymers are trained by a programming process, which is necessary to create a nonequilibrium configuration and enables them to have shape recovery capability [268-276]. The driving force for shape recovery is the conformational entropy of the molecular segments in terms of micro-Brownian thermal motion. Upon heating to the polymer glass

transition temperature (T_g) for cross-linked polymer network or melting temperature (T_m) for semi-crystalline polymer, the molecular mobility increases and the orientation of molecular chains tend to be random, accompanied by an increase in the conformational entropy. The increase in entropy creates the driving force for shape recovery. It is an autonomous process for molecules to recover from nonequilibrium to equilibrium states.

Li and John developed a new shape memory polymer based syntactic foam and foam cored sandwich composite for the purpose of repeatedly healing impact damage [263]. The syntactic foam was prepared by dispersing 40% by volume of glass microballoons into a shape memory polystyrene matrix. The foam cored composite sandwich plates were fabricated by vacuum assisted resin infusion molding (VARIM) technology. In order to have shape memory effect, the composite was programmed by a typical three-step programming process. In step 1, pre-deformation was initiated in a rubbery state at a temperature above the glass transition temperature of the shape memory polymer. In step 2, strain storage process was conducted by maintaining the pre-deformation constant while cooling down to below T_g . In step 3, the load was removed at the temperature lower than T_g . This completes the typical “hot” programming process (at a temperature above the glass transition temperature). It is noted that programming does not necessarily need a temperature event. Cold programming at a temperature below the glass transition zone also works as long as the prestrain level is beyond the yielding point of the shape memory polymer [268, 270]. It is noted that, the compression programming process was integrated with the fabrication process of the sandwich panel per the VARIM technology in Li and John’s study. After impact damage, the damage-healing of the shape memory polymer based composite was due to constrained shape recovery of the compression programmed foam core. The partial confinement to the damaged foam core was provided by materials surrounding the crack in the in-plane direction and by the skin in the transverse direction during the shape

recovery process. In this study, because the composite was programmed by transverse compression, it tended to have a volume growth during shape recovery. Because of the constraint, such a tendency was not allowed. As a result, the foam was pushed into any internal open space, leading to crack narrowing or closing. This fast response healing-on-demand shape memory polymer based composite could take up to seven damage and healing cycles. In order to provide better constraints during shape recovery process, a new architectural design was proposed, which led to inherent constraint to resist volume growth in the shape memory polymer matrix. The developed new composite architecture design included 3D woven fabric reinforced shape memory polymer composite [265] and grid stiffened composite sandwich structure [266]. The 3D woven fabric or the fiber reinforced grid skeleton provides strong constraint to the SMP foam core, in addition to its reinforcement effect.

While the previous studies by Li et al. have utilized constrained shape recovery for closing impact induced cracks, the molecular length scale healing was not conducted. Li and Nettles firstly proposed a two-step healing scheme of close-then-heal (CTH), similar to the biological healing of wounds in the human skin, for molecularly and repeatedly healing structural length scale cracks [242]. This scheme was further elaborated by Li and Uppu [244]. Fig. 10 shows the schematic of the CTH scheme of the proposed syntactic foam. The SMP based structure obtains its permanent shape first. Afterwards, the structure is programmed at a temperature above T_{gs} but below T_{gp} by compression to reduce structure volume. A temporary shape of the structure is achieved for working after cooling down below T_{gs} . If some internal damage such as matrix cracking is formed by service loading during lifetime, the material can be heated above T_{gs} and the material tends to expand in volume (shape memory effect). Due to the external confinement, however, the expansion of the structure is resisted; as a result, the SMP matrix is pushed towards any internal open space, leading to narrowing or closure of the cracks.

The incorporated thermoplastic particles are then heated to melt and the molten thermoplastic flows into the narrowed crack space by capillary force. The thermoplastic molecules then diffuse into the fractured SMP matrix and establish physical entanglement with the SMP molecules, which are driven by concentration gradient and shape recovery pressure at a temperature above T_{gp} . After cooling below T_{gs} , a solid thermoplastic wedge is formed, which glues the fracture surfaces together and prolongs service lifetime. Li and Uppu indicated that each constrained shape recovery (crack closing) represents a new round of compression programming. Also, the thermoplastic healing agent can be melted and solidified quite a few times. Therefore, the healing is repeatable and only one time programming is needed before service. Another feature of this system is that it depends on physical change only. No chemical reaction is involved in the system, which ensures repeatability. It is noted that, while CTH is conceptually divided into two steps, it is actually one step in practice, i.e., heating up all the way to the bonding temperature of the thermoplastic healing agent.

[Insert **Figure 10** here]

In order to validate the CTH scheme, a particulate composite with shape memory polystyrene matrix dispersed by copolyester healing agent was prepared and tested. By studying the copolyester-polystyrene shape memory polymer composite and the SMP based syntactic foam, it is shown that the close-then-heal scheme works, which leads to healing of structural-length scale damage repeatedly, efficiently, molecularly, and timely [243, 244, 265]. As pointed out by Li et al., the combination of thermoplastic particles and close-then-healing healing process was able to heal wide-opened cracks with a small amount of healing agent (as low as 3% by volume) [244]. The “do-it-yourself” manner [277] in crack closing and healing in polymer matrix has been applied to various applications including syntactic foam [278-281], sealant [282-284], fiber reinforced polymer composites [285], and healable composite joint [286].

4.2.2 Shape Memory Fibers as Dispersed “Suture”

While healing of cracks in SMP matrix has been successful, the challenge is how to heal cracks in conventional thermosetting polymers which do not have shape memory capability. One way to do this is to add shape memory fibers to the matrix, similar to embedded sutures when doctors stitch wounds in human skin. For shape memory fibers based polymer composites, the self-healing mechanism is similar to the two-step close-then-heal (CTH) scheme. The created matrix crack is narrowed or closed by embedded pre-tension programmed shape memory fibers first through constrained shrinkage, followed by crack healing by healing agents, like liquid healing agent/hardener or molten thermoplastic [47]. From recent publications, the shape memory fibers embedded in polymer composites include shape memory alloy (SMA) wires and shape memory polymer (SMP) fibers. This approach, utilizing shape memory alloy wires or shape memory polymer fibers to pull cracked surfaces closer by thermal-activated shape recovery forces, was mainly studied by White’s group, Huang’s group, and Li’s group.

The difference between shape memory polymer material based and shape memory alloy material based polymer composites is the level of cracks that can be closed. SMA wires are featured as having large recovery force but small recovery strain, which is opposite to SMP fibers.

SMA has the capability to memorize its original shape after a large pseudoplastic deformation when subjected to external force [287-291]. It tends to contract if it is heated above the austenite transformation temperature. Such shape recovery behavior of SMA has been applied to intrigue crack narrowing in the self-healing applications [292-297]. Kirkby et al. investigated the influence of SMA wires on the self-healing properties by combining SMA wires with a self-healing polymer [292, 293]. In their study, the microcapsulated liquid healing agent and wax-protected Grubb’s catalyst microspheres were mixed and embedded in the polymer

matrix. The SMA wires were embedded in the polymer composite as well. After a crack was opened in a tapered double cantilever beam specimen, the SMA wires exhibited shape memory functionality, leading to the crack closure by passing a current through the wire. The 0.5 A current provided to each SMA wire generated heat and increased the temperature to above 80°C, which in turn improved the degree of polymerization of the healing agent during the healing process. The healing-on-demand composite showed that significant improvements have been achieved in the polymer composite by incorporating SMA wires that bridge over the opened cracks. Furthermore, SMA spring was embedded in a cylindrical silicone melting glue (SMG) sample to pull fracture surfaces into contact [275]. As compared with SMA wires, the advantage of SMA spring is the efficient stress transfer from shape recovery and larger recovery strain, under thermal stimulus. Hence, it generates high compressive force during the crack closing process, leading to fast and efficient crack healing, which is about 5 min to heal a cylindrical sample with a diameter of 7.56 mm. Li indicated that the efficiency for a shape memory fiber to narrow or close cracks depends not only on recovery force, but also on recovery strain, or on recovery energy density [47]. He further indicated that, due to the very limited recovery strain of SMA wires, SMP fibers may be more appropriate for closing cracks with wider opening. He also indicated that, in order to overcome the constraint during crack narrowing process, increasing the recovery stress of SMP fibers is needed to further enhance the crack closing efficiency of SMP fibers because SMP fibers have already had considerable recovery strain.

The healing-on-demand polymer composite by SMP fibers was firstly reported by Li and Shojaei [298], who incorporated pre-stretched shape memory polyurethane (SMPU) fibers in polymer composite as a grid skeleton (ribs and z-pins). Macroscopic crack was introduced in a local site on the composite. When local heating was applied, the crack was closed or narrowed as a result of the constrained recovery of the SMPU fiber ribs and z-pins (constrained shrinkage).

Following closure of the crack, the dispersed thermoplastic particles were melted and flowed into the narrowed or closed crack by capillary force, and diffused into the fractured surface by concentration gradient and shape recover pressure. By cooling down to below the glass transition temperature of the SMP fibers, the solid wedge was formed, leading to crack healing. Fig. 11 shows the two-step self-healing behavior by continuous SMPU fibers, i.e., close-then-heal mechanism. Li et al. investigated the healing-on-demand application further in polymer composite by pre-tensioned continuous SMPU fibers [267, 299]. It was shown that the cold-drawing programming process was necessary for healing efficiency enhancement. It is noted that they used fixed boundary condition in the on-demand healing test, i.e., free shape recovery of the beam specimens was not allowed. This suggests that the SMP fiber based CTH scheme can be used in real world structures or structure components, which are usually constrained at the boundary.

[Insert **Figure 11** here]

Unlike SMA wires, SMP fibers have low recovery force. In order to increase its recovery force, SMP fibers need to be heavily programmed. The reported technique for SMP fiber programming is the cold-drawing programming, i.e., pre-tensioning at a temperature below the glass transition zone. The programmed SMP fibers exhibit higher stress recovery than the non-programmed ones [300]. The stress recovery is necessary for crack closure; otherwise the shape recovery would not be able to overcome the barriers and to bring the fracture surfaces together into contact. The greatest challenge in the use of SMP fibers is its structural relaxation after cold-drawing programming, which potentially hinders the utilization of shape memory polyurethane fibers for healing-on-demand applications. Zhang and Li studied the structural relaxation behavior of tension programmed SMPU fibers based on molecular-level force model, reptation model, and thermodynamics theory [301]. They pointed out that the programmed SMPU fibers

can recover enough force for crack closing even after a time scale of 13 years of structure relaxation, which provides a theoretical background that the programmed SMPU fibers, after years of hibernation, still possesses the crack closing ability when triggered by thermal stimulus.

Li and Zhang extended the investigation on the healing-on-demand polymer composite from the programmed continuous SMPU fiber to programmed short SMPU fiber [302]. Continuous SMPU fibers were programmed firstly and then cut into short fibers. Short SMPU fibers and thermoplastic particles were embedded into a conventional thermoset polymer matrix. After three-point bending damage of notched beam specimens, the specimens were heated to 80°C, following the CTH scheme, and resulting in crack healing. It again proved that this subsystem can heal millimeter-wide cracks repeatedly, efficiently, and timely.

4.2.3 Polymer Artificial Muscle as Inherent Actuator

In all animals and humans, muscle is a soft tissue that constitutes of a part of the musculoskeletal system. It is the only component of the system that enables our body to move through contracting and even fast contracting at higher speed upon stimuli. Analogous to natural muscle, polymer artificial muscle from fishing line could contract fast and deliver large strokes from inexpensive high strength polymer fibers, such as commercial fishing lines [303, 304, 305]. Since repeatable contraction is based on anisotropic thermal expansion in fishing line axial and radial direction, it contracts even after many actuation events without considering its structural relaxation and chemical stability [306]. Structure relaxation has been a challenge topic for shape memory materials when used for crack healing applications at a long-term time scale. Therefore, it is worth studying polymeric artificial muscles when using the CTH scheme in healing damage induced cracks. Zhang and Li have reported embedding a uniaxial polymer artificial muscle into a thermoset polymer composite beam to close wide-opened cracks [307]. Three-point bending damage to the notched beam specimens can be healed even at a constrained boundary condition

upon local heating, undergoing the close-then-heal procedure. The fractured beams were heated locally for 10 min. The healing efficiency was investigated at both free boundary condition and fixed boundary condition, by measuring fracture peak load. The fast contraction of artificial muscle brings the fractured surfaces in spatial proximity; following crack closure, the molten healing agent fills in the crack via capillary action and bonds the two fracture surfaces by diffusion and randomization. Fig. 12(a) shows an illustration of natural muscle contraction. Physically, the contraction of muscle generates tension on both connections. Fig. 12(b) schematically presents the crack closing or narrowing due to on-demand artificial muscle contraction and healing of the healing-on-demand polymer composite. With 60% prestrain of the reinforcing polymer artificial muscle, over 60% of healing efficiency was achieved at free boundary condition and 54% at fixed boundary condition after repeated damage-healing cycles. Fig. 12(c) shows the crack closing and healing performance.

[Insert **Figure 12** here]

4.3 Healing Theories and Healing Efficiency Evaluation

4.3.1 Healing Theory within the Continuum Damage Mechanics Framework

In the continuum damage mechanics framework, damage is represented by a damage variable. Healing can be treated as the opposite process of damage. Therefore, healing variables can be defined the same way as damage variables. Polymer damage usually involves finite deformation and thus it is highly nonlinear, and both viscoelasticity and viscoplasticity need to be considered. In damage-healing studies, damage inside the material at the micro-scale level could be represented by measuring changes in elastic modulus via damage variables [308-310]. Voyiadjis et al. [311-313], Shojaei and Li [314], and Shojaei et al. [315] used this idea to model the viscoplastic-viscodamage-viscohealing behavior of shape memory polymer matrix during damage and healing.

By introducing internal variables, the Helmholtz free energy (HFE) function is obtained and decomposed as follows [311]:

$$\begin{aligned} \psi & \left(\varepsilon_{ij}, \varepsilon_{ij}^p, \alpha_{ij}, p, d_{ij}, d_{ij}^K, d^I, h_{ij}, h_{ij}^K, h^I \right) \\ & = W\left(\varepsilon_{ij}, \varepsilon_{ij}^p, d_{ij}, h_{ij}\right) + H\left(\alpha_{ij}, p, d_{ij}^K, d^I, h_{ij}^K, h^I\right) + G_{dh}\left(d_{ij}, h_{ij}\right) \end{aligned} \quad (1)$$

where HFE is a function of thermodynamic fluxes and is decomposed into elastic part

$W\left(\varepsilon_{ij}, \varepsilon_{ij}^p, d_{ij}, h_{ij}\right)$, hardening function $H\left(\alpha_{ij}, p, d_{ij}^K, d^I, h_{ij}^K, h^I\right)$, and damage-healing function $G_{dh}\left(d_{ij}, h_{ij}\right)$. The damage-healing function took into account the microcrack as well as

microsurface propagation and recovery. The idea is that part of the energy in a damaged material is converted to surface energy and the remaining energy is converted to heat. When a healing event occurs, the surface energy reduces due to the polymer chain diffusion process of the healing agent.

By conjugating thermodynamic forces for each flux, the healing criterion for the generalized healing surface is defined as [312]:

$$\begin{aligned} & f^h\left(y^h, y^{hK}, y^{hl}, \sigma, y^{pK}, y^{pl}, y^d, y^{dK}, y^{dl}\right) \\ & = f^{h1}\left(y^h - y^{hK}\right) - f^{h2}\left(y^{hl}\right) - f^{h3}\left(\sigma, y^{pK}, y^{pl}\right) - f^{h4}\left(y^d, y^{dK}, y^{dl}\right) - w_0^h \leq 0 \end{aligned} \quad (2)$$

where w_0^h is the initial size of the healing surfaces. The first two terms f^{h1} and f^{h2} show the respective kinematic and isotropic hardening/softening because of the healing process and f^{h3} and f^{h4} represent the effect of the plastic deformation. The derived healing criterion is a function of the relevant healing mechanism. It is argued that the healing of damage is activated when $f^h = 0$ and $\dot{f}^h = 0$.

The overall mapping procedure between the real damaged and fictitious healed effective configurations is shown in Fig. 13. Within the continuum damage mechanics (CDM) framework, the Cauchy stress tensor σ_{ij} shows the stress condition in the real damaged configuration, while the effective stress tensor $\bar{\sigma}_{ij}$ represents the stress condition in the effective healed configuration. The vector of dAn_i represents the real damaged area, and the vector of $d\bar{A}n_i$ serves as the effective fictitious area. The effective area, where the loads are carried, increases during the healing process due to healed microscale damages. Hence, it indicates that the effective area grows as the damage heals.

It has been argued to use an indirect measurement method to calibrate damage and healing based on elastic modulus changes during the damage and healing process [308]. The fourth-order anisotropic healed elastic modulus E_{ijkl}^h after accomplishing the damage healing process was expressed in term of a new fourth rank healing variable tensor h'_{ijkl} [311]:

$$E_{ijmn}^h = \bar{E}_{ijmn} + \bar{E}_{klmn} \left(h_{ijkl}^{(1)} - k_{ijkl}^{(1)} - k_{pqkl}^{(1)} h_{ijpq}^{(1)} \right) \quad (3)$$

$$E_{ijmn}^h = \bar{E}_{ijmn} + \bar{E}_{ijpq} \left(h_{pqmn}^{(2)} - k_{pqmn}^{(2)} - k_{pqkl}^{(2)} h_{klmn}^{(2)} \right) \quad (4)$$

where k_{ijkl} is a fourth-order anisotropic damage variable tensor. If $h'_{ijkl} = 0_{ijkl}$, it indicates that no healing at all. In the case that the effective area after healing is equal to the original area, a full recovery event is obtained, and the elastic modulus $h_{ijkl}^{\max} = k_{ijkl}^{\max}$.

[Insert **Figure 13** here]

4.3.2 Chain Diffusion Theory

As discussed above, solid healing agent such as thermoplastic has been used in healing cracks in polymer composites, including the CTH strategy. During the healing process, physical molecular interdiffusion has been involved. The healing theory is discussed as follows.

Crack healing in polymeric materials follows a five-stage healing theory [59, 315-317], which includes (i) surface rearrangement, (ii) surface approach, (iii) wetting, (iv) diffusion, and (v) randomization. Surface rearrangement and surface approach experience a process by bringing two similar polymeric surfaces into good contact at a temperature above the glass transition. Brownian motion is highly active above this temperature on the interfaces; healing is achieved by the high mobility molecules when a mass of polymer chains move across the interface due to the reduction in thermodynamic barriers (diffusion), and entanglement of molecules (randomization).

The wetting phenomenon in crack healing process was discussed by Wool and O'Connor, concerning the line mode healing for cracks, crazes, and voids [59]. The wetted pools in a domain propagated over the entire domain and interface until they reached an impingement and coalescence of wetted areas. The wetting rate depends on different stages of wetting, which are instant wetting, constant rate wetting, and Gaussian wetting. Among these five stages of healing, the stages of wetting, diffusion and randomization are very important because the healed polymer material mechanical property is determined in these stages by the intrinsic healing function. However, the first two stages, especially stage 2 (surface approach), is also the same important. As indicated by Wool [7], and echoed by Li [47] and Binder [48], bringing the fractured parts in contact represents one of the grand challenges in real world structures. This is also why closing the crack by shape memory effect is necessary, as discussed above.

The behavior of polymer chain diffusion and randomization has been widely studied over the past decades. De Gennes [318] has discussed the molecular chain diffusion and

randomization by a tube model [319, 320], through which the molecular chain was allowed to reptate randomly through one-dimensional back-and-forth Brownian motion, along the randomly coiled conformational tube during a certain time. The diffusion mechanism was discussed by Bousmina et al., who described the diffusion process by Fick's law [321]. Fig. 14 shows the diffusion and randomization behavior in the polymer/polymer interface based on the reptation theory. At $t = 0$, two pieces of polymeric surfaces are brought into contact at a temperature above the glass transition temperature. At the moment $t_1 > 0$, the molecular chain starts to slip out the initial tube and into a new random-shape conformational tube (i.e., α, β, γ). At $t_2 > t_1$, the chain reptates completely into the new tube. Due to step reptational relaxations, the tube renewal process will continue until reaching a dynamic equilibrium conformation. In Fig. 14c, the reptation time for chains A and B, located on both sides of the interface with completely reptational diffusion to an equilibrium state, is obtained as follows:

$$\tau_{rep} = \frac{\xi N^3 b^4}{\pi^2 e^2 k_B T} \quad (5)$$

where ξ is the friction coefficient, N is the number of monomers, b is the effective bond length, e is the segmental chain length, k_B is Boltzmann's constant, and T is the absolute temperature. Obviously, the diffusion time before reaching the equilibrium state depends on the polymeric material properties and temperature.

[Insert **Figure 14** here]

As discussed above, the interpenetration distance χ is the average distance of the segments from the interface between A and B, which is given by [316]:

$$\chi \propto \langle l \rangle^{1/2} \quad (6)$$

where $\langle l \rangle$ is the average of chain motion $l(t)$.

Because the wetting and diffusion stages as well as randomization stage determine the mechanical property development, the healed fracture stress is as follows:

$$\sigma = \sigma_0 + \sigma_d \quad (7)$$

where σ_0 is the stress due to wetting, and σ_d is the stress due to the reptation of randomly coiled chains at a distance χ normal to the interface. Assuming that the randomly coiled tubes have Gaussian conformations, the stress σ is postulated as:

$$\sigma \propto (t/M)^{1/4} \quad (8)$$

where M is the molecular weight of the polymeric material. It indicates that for a certain polymeric material, the healed fracture stress depends on the diffusion and randomization process.

Shojaei et al. [313] further considered the contribution of shape recovery pressure applied on the narrowed fracture interface to the healing efficiency. They found that the diffusion depth or the healing efficiency increases asymptotically as the healing temperature or shape recovery pressure increases.

4.3.3 Healing Efficiency Evaluation

The performance of healing is determined based on a certain criteria. Wool and O'Connor studied the recovery ratio of stress $R(\sigma, t)$ and energy $R(E, t)$ in the case of line mode healing. The general expressions are:

$$R(\sigma, t) = \left[R_0 + \left(\frac{K}{\sigma_\infty} t^{1/4} * \dot{\psi}(t) \right) \right] * \dot{\phi}(t) \quad (9)$$

$$R(E, t) = \left[R_0 + \left(K' t^{1/4} + G t^{1/2} \right) * \dot{\psi}(t) \right] * \dot{\phi}(t) \quad (10)$$

where R_0 is the wetting parameter, σ_∞ is the fracture strength of the virgin polymeric material, K and G are material parameters, $\dot{\psi}(t)$ is the diffusion rate according to the diffusion initial function $\psi(t)$, and $\dot{\phi}(t)$ is the wetting rate according to the wetting distribution function $\phi(t)$. The theoretical healing efficiency in strength and energy are calculated via Eqs. (9) and (10), which can be compared to experimental data.

The dimensionless recovery ratios R additionally can be examined and compared based on elongation strain ε , tensile modulus Y , fatigue life N , and general spectroscopy of molecular microstructural parameters via infrared before being healed (i.e., in the virgin state) and after being healed:

$$R(\varepsilon) = \varepsilon / \varepsilon_\infty \quad (11a)$$

$$R(Y) = Y / Y_\infty \quad (11b)$$

$$R(N) = N / N_\infty \quad (11c)$$

$$R(I) = I / I_\infty \quad (11d)$$

where the subscribe ∞ denotes the original material property before damage.

Actually, healing efficiency can be determined by many parameters, depending on the property that is to be recovered. These properties, and thus the healing efficiency measurements, can be physical, mechanical, or other functional properties. So far, the majority of healing-on-

demand studies are focused on recovery of mechanical properties. Therefore, mechanical measurements such as strength, stiffness, ductility, toughness, etc. have been dominating. As discussed by Li [47], even for fracture toughness measurement, the fracture modes need to be clearly defined, such as Mode I, Mode II, and Mixed Mode I & II, because different fracture modes will yield different healing efficiencies. The dependence of the strength and toughness on the thickness of the healing agent layer has been studied experimentally [126, 322-326].

5 Conclusions and Future Perspectives

In the past several decades, the desire for lighter, tougher, stronger, and smarter materials in transportation vehicles, energy production, storage, and transport, military equipment and vehicles, infrastructure, chemical processing equipment, offshore oil and gas equipment, and consumer goods, has driven the use of polymers and polymer composite materials. Polymers or polymer composite materials, while have high specific strength, stiffness, corrosion resistance, and design tailorability, are prone to damage due to the various weak interfaces and other inherent properties such as brittleness of thermoset polymers. Therefore, healing-on-demand polymers and polymer composites have been growing at an unprecedented speed, which have emerged as an interdisciplinary class of materials that need collaboration from various science and engineering fields such as mechanical, chemical, biological, electrical, and civil engineering, as well as mechanics, mathematics, physics, and chemistry. Many polymers can heal themselves as long as they are manually brought into contact, which may be the biggest obstacle for real world applications, particularly in load bearing engineering structures, where manually bringing fractured structural components in contact is prohibited.

As observed from Table 1 and Table 3, the development of crack healing in materials undergoes two stages. In the first development stage, almost all attention was paid to how to heal damage on bulk material, film, or coating for solo functionality restoration. Repeatability in

healing was not concerned. In the second development stage, repeatability as well as multiple functionalities restoration has become a main topic when conducting crack healing. Physical or chemical healing mechanism between fracture surfaces has been well explored by previous researchers. However, fracture surface approaching is always intentionally or unintentionally neglected.

All the healing mechanisms used in healing-on-demand polymers and polymer composites share an essential concept: close-then-heal (CTH). For healing-on-demand polymers the cracks are closed either by their elastic behaviors (such as ionomer) or by manual relocation (most intrinsic healing polymers), followed by crack-healing process through chemical and/or physical interactions across the fracture surfaces under thermal treatment, or chemical treatment, or photo treatment, or electrical treatment, or none treatments under ambient condition. When the CTH scheme is integrated with shape memory polymers, the crack closing step is achieved by constrained shape recovery, which is triggered by heating or by other means depending on the functional groups in the SMP. Such an approach is more realistic for real world structures because a crack in a large engineering structure cannot be closed manually.

SMP matrix based or SMP fiber based or polymeric artificial muscle based system can close and heal wide-opened cracks (up to millimeter scale) per the CTH scheme repeatedly, efficiently, molecularly, and timely. However, minimal human intervention is required to trigger the healing mechanism, such as providing local heating. One of the major advantages of the SMP fiber is that it has good interfacial bonding between the functional fibers and the host matrix. If the fiber is given multi-functionality, like electrical conductivity, it can generate local heat by electricity and thus may lead to fast, repeatable, and more autonomous healing-on-demand effect because the electrical conductivity can be used as a damage sensing device, making the healing more towards an autonomous fashion [47]. Adding damage sensing capability to the CTH system

opens up new opportunities to make autonomous healing. In addition, the crack closure in CTH depends on both recovery stress and recovery strain [47]. While SMPs have considerable recovery strain, their recovery stress is comparatively low. Further endeavors should be towards increasing the recovery stress of SMPs and artificial muscles. Both physical means (e.g., cyclic programming) and chemical means (e.g., changing the composition or controlling the sequence of polymerization by mimicking biopolymers, for example, proteins and DNAs) deserve investigation.

Further development in the CTH scheme may also include a combination of shape memory and other intrinsic healing schemes such as shape memory ionomer, shape memory supramolecular, etc. [47], or use intrinsic healable polymers as healing agents. For example, ionomer particles, which have weak shape memory capability, may be compression programmed before embedding into conventional polymer matrix. When triggered by heating, the embedded ionomer particles will expand, which will push the fracture surfaces marching towards each other, and the molten ionomer particles can heal the crack. In other words, ionomer can serve as both a crackling closing device and a healing agent. Still another alternative may be the two-way SMP. This type of SMP expands when cooling down and shrinks when heating up. This unique behavior, which is opposite to the common physical behavior of materials, can be very useful in healing-on-demand applications.

In real world structures, on-demand healing includes structures that are under in-service conditions. Several preliminary explorations have been conducted, such as healing of continuous SMP fiber reinforced polymer beam specimens under fixed boundary conditions [267], polymeric artificial muscle reinforced polymer beam specimens under clamped boundary conditions [307], and short SMP fiber reinforced syntactic foam beam specimens under constant tensile loading [328]. It has been clearly demonstrated that with these in-service conditions

(fixed boundary conditions, tensile load, etc.), the healing efficiency is reduced. Therefore, in order to validate the performance of real world healing-on-demand structures, it is highly desired that the lab scale specimens be subjected to in-service conditions when conducting healing-on-demand studies.

Healing with external healing agent usually accompanies phase changes. For example, thermoplastic healing agent experiences solid to liquid and liquid to solid phase change, including diffusion and randomization, during the healing process. Currently, continuum damage mechanics (CDM) is used to provide the theoretical healing framework, i.e., healing is treated as a reverse process of damage. However, CDM cannot directly consider the process of the phase change. Also, the current CDM based healing theory is mathematically complex and involves a large number of curve fitting parameters. Therefore, more physics based models are needed. Other theoretical frameworks other than CDM may also deserve investigation. Phase field model, which describes the phase evolution in a physical or chemical process is evolving rapidly in materials science research, and may provide a viable alternative [327].

Healing efficiency is currently evaluated primarily by Mode I fracture test (crack opening). In real world load-bearing structures, various stress conditions exist, which may lead to Mode II (in-plane shear), Mode III (out-of-plane shear or tear), and mixed mode fracture. Therefore, evaluations of healing efficiency in terms of Mode II, Mode III, or mixed fracture modes are also needed.

In summary, although considerable progress has been made in healing-on-demand studies, this area is still in its early stage. Many more issues need to be overcome before they can be used in engineering structures. We believe that this is the time to consider the practical challenges facing self-healing applications, in addition to the fundamental science. The purpose of this review is to throw out a minnow to catch a whale. We believe that with the collaboration

between materials scientists and engineers, healing-on-demand engineering structures will become a reality in the foreseeable future.

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Fig 1. Conceptual healing-on-demand in prolonging material service life. As damage occurs, engineering polymers/polymer composites suffer from functional and structural degradation over service life. Crack closing and healing are triggered by the response to the lower bound (function limit) of the function, i.e., on-demand, and thus recovers its functionality to initial status repeatedly for prolonging service life.

Fig 2. Types of crack modes initiated by various loadings.

Fig 3. Types of crack healing mechanisms of smart polymers including physical interaction and chemical bond interactions.

Fig 4. Procedures of preparing, cutting, healing, and stretching of the compact polyelectrolyte (all at room temperature). [65], Copyright 2014. Reproduced with permission from John Wiley & Sons Inc.

Fig 5. (a) Compounds formed between NHCs and transition metals in polymeric materials. The structurally dynamic equilibrium between a monomer species (left) and an organometallic polymer (right) is controlled via a thermal treatment. M = Ni, Pd and Pt; R = alkyl, benzyl and aryl. (b) Self-healing scheme of an electrically conductive, self-healing organometallic polymer. When used as an electrical wire or incorporated into a device, upon the formation of a microcrack, the total number of electron percolation pathways within the material should decrease, resulting in increase in inherent electrical resistance, which leads to the generation of heat localized at the microcrack due to the voltage bias. The generated thermal energy thus hurdles the kinetic energy barriers, driving the system back to its original state. A: amperes; V: volts. [66], Copyright 2007. Reproduced with permission from the Royal Society of Chemistry.

Fig 6. “Wound” healing behavior of polymeric hydrogel. At low pH (i.e., less than 3.0), molecular network was regenerated at the fracture surface due to the protonation of terminal-carboxyl groups, leading to the recovery of fracture surface. However, in the case of high pH (i.e., larger than 9.0), the two healed hydrogels separated due to the deprotonation of hydrogel carboxyl groups. And it rehealed again when exposed to low pH. [64], Copyright 2013. Reproduced with permission from the American Chemical Society.

(a)

(b)

Fig 7. Microcapsulated polymer composites: (a) single-microcapsule; (b) dual microcapsule.

Fig 8. Branching vasculature networks in animal (e.g., human) body and plant.

Fig 9. Crack closure due to the n-PCL shape-memory ability along with temperature and spontaneously crack rebonding due to the melt and molecular diffusion of linear l-PCL at the crack site (stereo micrographs scale bar: 500 μ m). [261], Copyright 2011. Reproduced with permission from the American Chemical Society.

T_{gs} : Glass transition temperature of the SMP based foam;
 T_{gp} : Glass transition temperature for amorphous thermoplastic particle or melting temperature for semi-crystalline thermoplastic particle.

Fig 10. Schematic of the close then heal (CTH) scheme of the proposed smart foam. Compression programming process is required and necessary to enable the smart foam to have shape memory ability. Crack is narrowed or closed at a temperature above the T_{gs} of the SMP based foam by the shape recovery of the foam, which is confined by surrounding materials. Narrowed crack is filled in by molten thermoplastic at a temperature above the T_{gp} of the thermoplastic particle. Fracture surface would be bonded together after cooling down. Programming process: from (a) to (c); damage and crack narrowing process: (d) and (e); crack healing process: from (f) to (h). Here the T_{gp} of thermoplastic particle must be higher than the T_{gs} of SMP based foam. [244], Copyright 2010. Reproduced with permission from Elsevier.

Fig 11. Two-step healing-on-demand composite by continuous shape memory polyurethane fibers. After the macroscopic crack was created in the composite, the macrocrack was closed firstly by the stimuli-responsive contraction of SMPU fibers, followed by the second step when the thermoplastic particles melt and flow into the narrowed crack to bond the crack. When the composite specimen was cooled down to room temperature (below T_g), its service strength was recovered. [299], Copyright 2012. Reproduced with permission from the Royal Society of Chemistry.

Fig 12. (a) Structure of nature muscle. (b) Schematic of on-demand healing process: (i) a polymer composite sample reinforced by polymer artificial muscle (light golden coiled fiber) and thermoplastic particle (light golden spheres) in a matrix (blue); (ii) crack initiated by external load during service life; (iii) crack closed by thermally activated artificial muscle and healed by the healing agent; (iv) solid wedge formed after cooled down, establishing continuity between the healing agent and the matrix. (c) Crack before closing and after healed. [307], Copyright 2015. Reproduced with permission from Elsevier.

Fig 13. The overall mapping procedure between the real damaged and fictitious healed effective configurations: (a) damaged configuration, (b) fictitious effective configuration after the healing process. [311], Copyright 2012. Reproduced with permission from the Royal Society of Chemistry.

Fig 14. Reptation model for molecular diffusion and randomization behavior across the interface during healing. [321], Copyright 1998. Reproduced with permission from the American Chemical Society.

TABLES

Table 1 Healing-on-demand polymers investigated during 2007-2015

(NM: not mentioned)

Polymer Entry	Damage Type	Crack Approaching Method	Healing Mechanism	Healing Measurement	Efficiency	Repeatable (Y/N)	Healing Condition	Time	Ref.
PEMAA Copolymers	a) sawing or cutting; b) puncture	a) put together manually; b) elastic recovery	interdiffusion due to friction induced heat	pressurized burst test	NM	Y	at -30 to 25°C	NM	[100, 101]
Ionomers Surllyn 8940®	ballistic impact	“shape memory” effect	interdiffusion	fractional elastic healing ratio	over 90%	Y	above 105°C	500s	[102-104]
ENR	ballistic impact	elastic recovery	interdiffusion due to friction induced heat	pressurized air flow	NM	NM	at RT	NM	[105]
Ionomer blends of EMNa and EMZn+ENR	ballistic impact	elastic recovery	interdiffusion due to friction induced heat	pressurized air flow	NM	NM	at RT	NM	[106]
PDMAA and PNIPA hydrogel	cut	put together manually	interdiffusion and hydrogen bonding	tensile peak load	100%	NM	25-80°C	0.3 to 100h	[73]
bPEI/PAA polymer	cut	flow to contact in water	polyelectrolyte diffusion	cyclic voltammetry	NM	NM	in water at RT	5 min to 24h	[76]
PAA/PAH CoPECs	cut into pieces	put together manually	interdiffusion	tensile peak stress	100%	NM	in NaCl solution	over 3h	[65]
LMWOs based supramolecular gel	cut into pieces	put together manually	interdiffusion	visual observation	NM	NM	at RT	over two days	[92]
n-butyl acrylate based zinc ionomer with magnetic nanoparticles	cut into pieces	put together manually	interdiffusion	tensile strength or tensile strain	90%	NM	70°C or in magnetic field	30m or 15m	[107]
A6ACA hydrogels	cut	put together manually	reversible hydrogen bond of terminal-carboxyl groups	fracture stress	66±7%	Y	in pH solution (pH<3)	24h	[63]

Fatty acids and urea based rubbers	cut	put together manually	hydrogen bond re-association	tensile strength	NM	Y	at RT	3h	[87]
UPy-unit based supramolecular polymers	cut into pieces	put together under pressure	reversible UPy hydrogen bonds	visual observation	NM	Y	at RT	10s	[90]
PDMSs based supramolecular elastomers	cut into pieces	put together under pressure	hydrogen bond re-association	tensile strength	86%	NM	at RT	24h	[91]
Amino acid based metallohydrogels	cut into pieces	put together manually	multiple hydrogen bonding interaction	visual observation	NM	Y	at RT	3h	[108]
PMMA based copolymer	cut into pieces	put together manually	hydrogen bonding between PA-amide groups	tensile strength	70-90%	Y	60°C	24h	[109]
TDI based polyurethane	tensile fracture	put together manually	hydrogen bonding and chain segment movement	tensile strength	82%	Y	at RT	1 week	[110]
PMMA-PA-amide copolymer	cut into pieces	put together manually	multivalent hydrogen bonds between soft PA-amide brushes	tensile strain	80%	NM	at RT	24h	[111]
Four-arm star bromide-telechelic polymers	cut into pieces	put together manually	hydrogen bonding interaction between supramolecular clusters and covalent crosslinking via CuAAC	visual observation	NM	Y	40°C	24h	[112]
Copper-coordination polymer network PIE	cut into pieces	put together manually	restructuring of copper-coordination bonds and rearrangement of molecular chains	tensile strength	92%	Y	with 5% water at 45°C	1h	[113]
Mendomer 401	bending	put back into contact	reversible Diels-Alder reaction	microscopes	NM	NM	110°C	10 min	[67]
Thermosetting PK-	bending	compress into	DA and Retro-DA	three-point	72.3%	NM	120°C	20	[68]

furan	contract			bending load				min	
Bis(hydroxymethyl) furan based polymer: poly(2,5-furandimethylene succinate) with Bismaleimide	tensile fracture	put together under pressure	reversible DA reaction between PFS and M ₂	tensile toughness	72.3%	NM	at RT	1-10 days	[99]
Spherosilicate based polymer	cut into pieces	put together manually	reversible DA reactions	transmission light microscopy	NM	NM	135°C	10 min	[114]
Thiourethane based crosslinked polycaprolactone polymer	cut	bring together due to shape memory effect	reversible DA reaction between trisfuranic thiourethane and trimaleimidic urethane	tensile strength	90%	Y	60°C	24h	[115]
CDTE/Cp based polymer	cut into pieces	press into together	Hetero DA reactions between CDTE and Cp	tensile strength	98%	Y	120°C	10 min	[116]
Polyurethane elastomer	cut into pieces	put together manually	reversible fission / recombination of C-ON bonds in alkoxyamine	tensile strength	70%	Y	80°C in argon	2.5h	[117]
Supramolecular DB24C8 gels	accidental damage	put together manually	crown ether based host-guest interaction	rheological measurement on modulus	above 95%	NM	at RT	10 to 30s	[62]
pAA based supramolecular hydrogels	cut into pieces	put together manually	host-guest interaction between pAA-CDs and pAA-Fc	wedge-shape strain compression test on adhesion strength	84%	NM	at RT	24h	[95, 96]
CD/VI based supramolecular	cut into pieces	put together manually	host-guest between CD and p(VA-co-	tensile modulus	92%	Y	under magnetic	3 h	[118]

gels			HPA)	field at RT					
β -CD-Ad hydrogel	cut into pieces	put together manually	host-guest interactions between CD exogel and Ad exogel	tensile stress	88%	Y	with water at RT	48 h	[119]
covalently crosslinked rubber	cut	put together manually	disulfide interchange reaction	tensile peak load	100%	NM	80°C	2h	[72]
TTC based crosslinked polymer	cut into pieces	put together under pressure	reshuffling reactions of trithiocarbonate units	tensile modulus	94±18%	Y	in nitrogen under UV	4h	[79]
TDS based crosslinked polymer	cut into pieces	put together under pressure	reshuffling Thiuram Disulfide moieties	peak tensile stress	97%	NM	in air under visible light	24h	[82]
Crosslinked cPEG hydrogel	cut	put together manually	reversible boronic-catechol complexation	visual observation	NM	NM	at RT		[61]
covalent crosslinked polymer gels	cut	put together manually	reversible covalent acylhydrazone bonds	visual observation	NM	NM	at RT	7h	[60]
DOPA-Fe ^{III} crosslinked hydrogel	cut	put together manually	redox covalent crosslinking	dynamic oscillatory rheology on storage modulus	124%	Y	in pH>8	45 min	[64]
Boronic esters based crosslinked polymer	cut into pieces	put together manually	reversible and exchangeable covalent bonds in boronic esters	tensile strength	89%	Y	with water at RT	3 days	[120]
Stearyl methacrylate (C18) based hydrogel	cut into pieces	put together manually	reversible dissociation-association of C18 network	uniaxial elongation measurement	100%	NM	at RT	10s	[93, 94]
DABBF based gel	cut into	put together	dynamic radical	tensile	98%	NM	under air	24h	[98]

	pieces	manually	exchange reaction of DABBF units	strength			at RT		
Dihydroxyl coumarin based polyurethane	tensile fracture	put together manually	reversible photoreactivity coumarin	tensile strength	64.4%	NM	254 nm UV first then 350 nm UV	>2h	[83]
POM based hybrid hydrogels	cut into pieces	put together under pressure	electrostatic interaction between the cationic PG and the anionic EuW10	visual observation	NM	Y	with water at RT	3 min	[121]
Amide-containing cyclooctene network based polymer	cut	put together under pressure	dynamic olefin metathesis reaction	tensile toughness	90%	NM	50°C	3h	[122]

Table 2 Chemical covalent bond reactions for crack healing application.

Entry	Covalent Bond	Molecular Chain Reactions	Ref.
1	dynamic bond exchange		[133]
2	reversible Diels-Alder reaction		[134]
3	hetero Diels-Alder reaction		[116]
4	reversible C-ON bonds		[71]

5 photo-reversible
reshuffling
reaction

6 disulfide
interchange
reaction

Table 3 Healing-on-demand polymer composites investigated during 2001-2015

(NM: not mentioned)

Composite Type	Damage Type	Crack Approaching Method	Healing Mechanism	Healing Measurement	Efficiency	Repeatable (Y/N)	Healing Condition	Time	Ref
micro-capsulated polymer composite	TDCB fracture test	release of healing agent DCPD from microcapsule	ROMP polymerization of DCPD with solid Grubbs' catalyst (I)	mode-I fracture toughness	>75%	N	RT	>24h	[171-180]
micro-capsulated polymer composite	TDCB fracture test	release of healing agent DCPD from microcapsule	ROMP polymerization of DCPD with solid Grubbs' catalyst (I)	fatigue life	213%	N	RT	>10h	[181-183]
micro-capsulated polymer composite	TDCB fracture test	release of healing agent DCPD from microcapsule	ROMP polymerization of DCPD with solid Grubbs' catalyst (II)	fracture load	84%	N	125°C	24h	[184]
micro-capsulated polymer composite	TDCB fracture test	release of healing agent DCPD from microcapsule	ROMP interaction of exo-DCPD with waxed WCl_6	peak load	80%	N	RT	48h	[185]
micro-capsulated polymer composite	SENB fracture test	release of healing agent bisphenol-A epoxy from microcapsule and with help of paper clamps	polymerization of bisphenol-A epoxy initiated by $CuBr_2(2-MeIm)_4$	mode-I fracture toughness	>40%	N	130°C	>0.5h	[186-189]
micro-capsulated polymer composite	micro-cracks by pressing	release of healing agent MAT-PDMS from microcapsule	photopolymerization of MAT-PDMS initiated by BIE photoinitiator	water permeability test and chloride ion penetration test	NM	Y	under sunlight	4h	[190]

micro-capsulated polymer composite	impact test	release of EPON epoxy from microcapsule	cationic chain polymerization EPON epoxy by fiber protected $(C_2H_5)_2O \cdot BF_3$	impact strength	>76%	N	20°C	30 min	[191, 192]
micro-capsulated polymer composite	Izod impact test	release of GMA from microcapsule	polymerization of GMA with living PMMA	Izod impact strength	100%	Y	RT	24h	[166, 167]
dual micro-capsulated polymer composite	impact test	release of healing agent EPON 828 and TfOH from microcapsules	cationic chain polymerization of EPON 828 by TfOH	impact strength	79%	N	RT	100s	[193]
dual micro-capsulated polymer composite	torsion fatigue test	release of healing agent PDMS and liquid initiator from microcapsules	polymerization of PDMS initiated by platinum catalyst with initiator	fatigue crack growth	24% reduction	NM	RT	5h	[170, 194-197]
dual micro-capsulated polymer composite	TDCB fracture test	release of healing agent epoxy and curing hardener from microcapsules	curing hardening of epoxy resin by corresponding hardener	mode-I fracture toughness	>62%	N	RT	48h	[198-201]
dual micro-capsulated polymer composite	TDCB fracture test	release of catalyst DBTL and healing agent from microcapsules	polycondensation of HOPDMS with PDES initiated by DBTL	fracture load	46%	NM	50°C	24h	[202]
dual micro-capsulated polymer composite	3-point bending test	release of DTHP and BDMA from microcapsules	polymerization of DTHP by BDMA	fracture load	93-117%	NM	18-11°C	17h	[203]
dual micro-capsulated polymer	Tensile fracture test	release of azido-telechelic three-arm star PIB and trivalent alkynes from microcapsules	azide/alkyne-“click” reaction initiated by $Cu^I Br(PPh_3)_3$	tensile storage modulus	about 70%	NM	40-80°C	380s-10 min	[204, 205]

dual micro-capsulated polymer composite	impact test	release of healing agent PS and BPO from microcapsules	free radical polymerization of PS initiated by BPO	impact energy	65%	N	RT	24h	[206]
dual micro-capsulated polymer composite	TDCB fracture test	release of tetrathiol reagent and isocyanate reagent from microcapsules	covalent reaction of Thiol-isocyanate	fracture peak load	89-133%	NM	RT	24-120h	[207]
hollow glass-fiber reinforced polymer composite	4-point bending test	release of epoxy resin and hardener from hollow fiber plies	curing of epoxy resin by corresponding hardener	bending strength	>87%	N	RT-100°C	2-24h	[208-212]
hollow glass-fiber reinforced polymer composite	impact test	release of epoxy resin and hardener from hollow fiber plies	curing of epoxy resin by corresponding hardener	impact strength	>50%	N	RT-125°C	75 min – 96h	[213-216]
micro-vascular network in polymer composite	4-point bending test	delivery of epoxy resin and hardener from liquid reservoir through 3D vascular networks	curing of epoxy by corresponding hardener	fracture load	>42%	Y	RT	12-48h	[217-221]
vascular network in polymer composite	impact test	delivery of reactive liquid from liquid reservoir through vascular networks	forming dynamic acylhydrazone bonds through acidcatalyzed condensation between PEG and B3	impact energy	62%	Y	RT	24h	[222, 223]

vascular network in polymer composite	compression	delivery of EPON epoxy and aliphatic amidoamine hardener through vascular network	curing of EPON epoxy by the amine hardener	mode-I fracture toughness	86%	Y	RT	>24h	[224-231]
layer-by-layer in smart coating	puncture damage	release of UV-curable epoxy	curing of Loctite Impruv 365 UV-curable epoxy under UV light	microscope	NM	NM	365 nm UV light	60s	[232]
multilayer barrier film		release of metal oxide precursor TiCl ₄ from PLA fiber	forming solid titanium oxides due to TiCl ₄	water vapor permeability	64.5%	NM	NM	20 days	[233]
polymer composite embedded with solid-state healing agent	Charpy impact test	alignment by a liner and put together under pressure	reversible hydrogen bonding between solid-state healing agent polybisphenol-A-co-epichlorohydrin	mode-I fracture toughness	>65%	Y	140°C	2h	[234-237]
FG-TPU composite	razor cut	put together manually	interdiffusion of TPU chain in the response to input energy	tensile strength	>98%	Y	a) IR; b) electricity; c) electromagnetic waves	a) 3-5 min; b) 3 min; c) 0.7-3 min	[238]
polymer composite embedded with solid-state healing agent	SENB fracture test	NM	formation of large-scale EMAA-bridging ligaments along the delamination	peak load	85%	Y	150°C	30 min	[239]

polyurethane composite	tensile fracture test	shape memory effect	DA/rDA reaction between furan and maleimide moieties in the response to thermal treatment	failure load	60-85%	Y	140°C first then 80°C	0.5h first then 2h	[240, 241]
shape memory based composite	cut by sharp blade	shape memory effect	interdiffusion of healant polymer chain	peak load	>60%	Y	>80oC	0.5-1.5h	[242-244]