SELF HEALING IN POLYMERS AND POLYMER COMPOSITES: A REVIEW

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ABSTRACT|

The development and characterization of self-healing synthetic polymeric materials have been inspired by biological systems in which damage triggers an autonomic healingresponse. This is an emerging and fascinating area of research that could significantly extend the working life and safety of the polymeric components for a broad range of applications. Formation of microcracks is a critical problem in polymers and polymer composites during their service in structuralapplications. Development and coalescence of microcracks would bring aboutcatastrophic failure of the materials andthen reduce their lifetimes. Therefore, early sensing, diagnosis and repair of microcracks become necessary for removingthe latent perils. In this context, the materials possessing self-healing function are ideal for long-term operation. Self-repairingpolymers and polymer composites have attracted increasing research interests.Attempts have been made to developsolutions in this field. The present article reviews state-of-art of the achievements on the topic.. It is a challengingjob to either invent new polymers with inherent crack repair capability or integrate existing materials with novel healingsystem.

Keywords: Smart Polymers, Polymer Composites, Self-Healing, Cracks

I. INTRODUCTION

Self-healing materials are polymers, metals, ceramics and theircomposites that when damagedthrough thermal, mechanical,ballistic or other means have the ability to heal and restore thematerial to its original set of properties. Few materials intrinsicallypossess this ability, and the main topic of this review isthe design for self-repair. This is a very valuable characteristicto design into a material since it effectively expands the lifetimeuse of the product and hasdesirable economic and human safetyattributes.

Polymers and polymer composites have been widely used in tremendous engineering fields because of their advantages including light weight, good processibility, chemical stability in any atmospheric conditions, etc. However, long-term durability and reliability of polymeric materials arestill problematic when they serve for structural application [1]. Exposure to harshenvironmentwould easily lead to degradations of polymeric components. Comparatively, microcracking is oneof the fatal deteriorations generated in service, which would bring about catastrophic failure of thematerials and hence significantly shorten lifetimes of the structures.

Since the damages deep inside materials are difficultto be perceived and to repair in particular, thematerials had better to have the ability of self-healing.In fact, many naturally occurring portions inanimals and plants are provided

with such function[2–6]. In the case of healing of a skin wound, forexample, the defect is temporarily plugged with afibrin clot, which is infiltrated by inflammatorycells, fibroblasts, and a dense capillary plexus ofnew granulation tissue. Subsequently, proliferationof fibroblasts with new collagen synthesis and tissueremodeling of the scar become the key steps.For healing of a broken bone, similar processes areconducted, including internal bleeding forming afibrin clot, development of unorganized fiber mesh,calcification of fibrous cartilage, conversion of calcification into fibrous bone and lamellar bone.

Clearly, the natural healing in living bodiesdepends on rapid transportation of repair substanceto the injured part and reconstruction of the tissues.Having been inspired by these findings, continuousefforts are now being made to mimic natural materialsand to integrate self-healing capability intopolymers and polymer composites. The progresshas opened an era of new intelligent materials.On the whole, researches in this field are still in theinfancy. More and more scientists and companiesare interested in different aspects of the topic. Innovativemeasures and new knowledge of the relatedmechanisms are constantly emerging. Therefore, itmight be the right time to review the attempts carriedout so far in different laboratories in the world.According to the ways of healing, self-healingpolymers and polymer composites can be classifiedinto two categories: (i) intrinsic ones that are able toheal cracks by the polymers themselves, and (ii)extrinsic in which healing agent has to be preembedded.

II. INTRINSIC SELF-HEALING

The so-called intrinsic self-healing polymers andpolymer composites are based on specificperformanceof the polymers and polymeric matrices thatenables crack healing under certain stimulation(mostly heating). Autonomic healing without externalintervention is not available in these materialsfor the time being. As viewed from the predominantmolecular mechanisms involved in the healingprocesses, the reported achievements consist of twomodes: (i) physical interactions, and (ii) chemicalinteractions.

2.1. Self-Healing Based on Physicalinteractions

Compared to the case of thermosetting polymers,crack healing in thermoplastic polymersreceivedmore attention at an earlier time. Wool and coworkerssystematically studied the theory involved[7, 8]. They pointed out that the healing processgoes through five phases: (i) surface rearrangement,which affects initial diffusion function andtopological feature; (ii) surface approach, related tohealing patterns; (iii) wetting, (iv) diffusion, themain factor that controls recovery of mechanical properties, and (v) randomization, ensuring disappearanceof cracking interface. In addition, Kimand Wool [9] proposed a microscopic model for thelast two phases on basis of reputation model thatdescribes longitudinal chain diffusion responsiblefor crack healing.

Unlike thermoplastics, heating induced healing ofthermosetting polymers depends on crosslinking ofunreacted groups. Healing of epoxy, for instance,has to proceed above the glass transition temperature[19]. Then, the molecules at the cracking surfaceswould interdiffuse and the residual functionalgroups react with each other. A 50% recovery ofimpact strength can thus be obtained [20]. Duringthe repair study of vinyl ester resin, Raghavan andWool reported critical strain energy release rate,*GIC*, for the interfaces after crack healing (i.e.annealing above the glass transition temperature) is1.7% of the virgin value. Lower crosslink densityfavors the repair effect [21].

Thermoplastic/thermosetting semi-interpenetratingnetwork is factually amaterial associated withrepeatable self-healing ability. The group of Jonesintroduced a soluble linear polymer to a thermosettingepoxy resin [22–24]. The selected thermoplasticispoly(bisphenol-A-co-epichlorohydrin), whichis highly compatible with the matrix diglycidylether of bisphenol-A based resin. Upon heating afractured resin system, the thermoplasticmaterialwould mobilize and diffuse through the thermosettingmatrix, with some chains bridging closedcracks and thereby facilitating healing. When thishealable resin was compounded with cross ply glassfiber, effective healing of composites transversecracks and delamination has been demonstrated.

The requirements for such thermal diffusion of ahealing agent were summarized as follows [23]. (i)The healing agent should be reversibly bonded (e.g.through hydrogen bonding) to the cross linked networkof the cured resin below the minimum healingtemperature to limit its effect on thermo mechanicalproperties. (ii) The healing agent should becomemobile above this minimum healing temperature sothat it can diffuse across a hairline crack, such as atransverse crack, to provide a recovery in strength.(iii) The addition of the linear chain moleculeshould not significantly reduce the thermo mechanicalproperties of the resin matrix.

III. EXTRINSIC SELF-HEALING

In the case of extrinsic self-healing, the matrix resinitself is not a healable one. Healing agent has to beencapsulated and embedded into the materials inadvance. As soon as the cracks destroy the fragilecapsules, the healing agent would be released intothe crack planes due to capillary effect and healsthe cracks. In accordance with types of the containers,there are two modes of the repair activity: (i)self-healing in terms of healant loaded pipelines,and (ii) self-healing in terms of healant loadedmicrocapsules. Taking the advantages of crack triggered delivery of healing agent, manual intervention(e.g. heating that used to be applied for intrinsicself-healing) might be no longer necessary.

3.1. Self-Healing In Terms of Heal Ant Loaded Microcapsules

The principle of this approach resembles the aforesaidpipelines but the containers for storing healingagent are replaced by fragile microcapsules.Because the technique of microencapsulation hasbeen rapidly developed since its emergency in1950s and mass production of microcapsulescan be easily industrialized, self-healing compositesmight be thus used in practice accordingly.Jung *et al.* prepared self-healing polyester compositewith pre-embeddedpolyoxymethylene urea(PMU) microspheres The crack repair agent ismostly composed of styrene monomers and highmolecular weight polystyrene. The latter helps tolower the rate of diffusion of styrene or diethenylbenzene into polyester matrix. The system of 23%polystyrene (Mn= 2.5·105), 76.99% styrene and atrace amount of inhibitor proved to offer the optimumhealing efficiency. Jung *et al.* also tried to utilizeepoxide monomer loaded PMU microcapsulesfor rebinding the cracked faces in polyester matrix.Solidification of the epoxy resin (i.e. the repairaction) was triggered by the naturally occurringfunctional sites or embedded amine in the composites.In a latter work by White *et al.*, it was consideredthat the method was not easible as theamine groups did not retain sufficient activity. Zako*et al.* proposed an intelligent material system using40% volume fraction unmodified epoxy particles torepair microcracks and delamination damage in aglass/epoxy composite laminate. By heating to120°C, the embedded epoxy particles (~50 μm)would melt, flow to the crack faces and repair thedamage with the help of

the excessive amine in thecomposite. In addition to the poor activity of theamine as mentioned above, manual intervention(i.e. heating) was necessary in this case.

We reported a two-component healant consisting ofepoxy-loaded microcapsules as the polymerizablepart and 2-methylimidazole/CuBr2 complex(CuBr2(2-MeIm)4) as the latent hardener, whichwas pre-dispersed in composites' matrix to fabricateself-healing composites . As soon as cracksdestroyed the capsules, the epoxy oligomer wouldbe released into the crack planes due to capillaryeffect and cured under initiation of the latent hardenerat a temperature ranging from 130 to 180°C.

The features of this healing system lie in the following.(i) When the healing agent is applied toepoxy based composites, the miscibility betweenthe crack adhesive and matrix is guaranteedbecause of identity of their species. (ii) The latenthardener possesses long-term stability and is hardlyaffected by the surrounding environment.Moreover, it can be well pre-dissolved in uncuredcomposites' matrix, leading to homogenous distributionof the reagent on the molecular scale. Thusthe epoxy released from the ruptured microcapsulesmight meet the latent hardener everywhere (Figure1). The two-component healant is able to takeeffect in the woven glass fabric/epoxy compositelaminates.

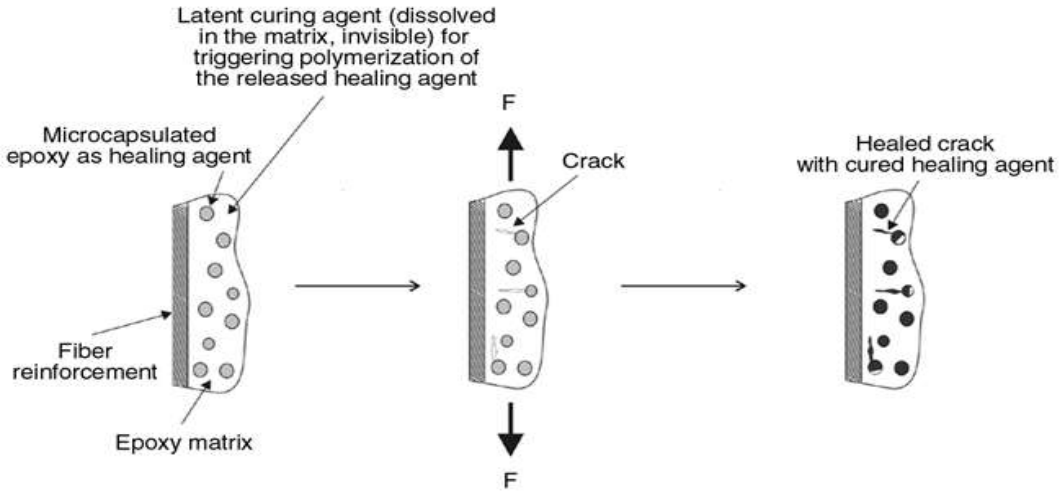

Figure 1. Schematic Drawing of The Principle of Self-Healing Epoxy Based Laminates with Epoxy Loaded Microcapsules and Latent Hardener (Reprinted from Composites Science & Technology, Vol 67, Yin T., Rong M. Z., ZhangM. Q., Yang G. C.: Self-healing epoxy composites – Preparation and effect of the healant consisting ofmicroencapsulated epoxy and latent curing agent, 201–212, Copyright (2007)

The group of White *et al*., the pioneer in develop in gself-healing polymeric materials, systematically investigated self-healing strategy based on ring opening metathesis polymerization (ROMP) of micro encapsulated dicyclo pentadiene (DCPD) and reported a series of important findings. Healing is triggered when damage in the form of acrack ruptures the microcapsules, causing DCPD to be released into the crack plane where it comes in contact and mixes with the pre-embedded Grubbs' catalyst (Figure 1). For increasing catalysis efficiency, the catalyst was capsulated by wax and recrystallized, respectively. Delamination damage in woven glass/epoxy composites was found to be repaired by the healing agent. In addition, fatigue crack growth in epoxy can also be retarded by the

released fluid. Effect of DCPD loaded microcapsule size on the performance of self-healing polymers was studied. Rule *et al*. indicated that the amount of liquid that microcapsules deliver to a crack face changed linearly with microcapsule diameter for a given weight fraction of capsules.

Self-healing performance eached maximum levels only when sufficient healing agent was available to entirely fill the crack. Based on these relationships, the size and weight fraction of microcapsules can be rationally chosen to give optimal healing of a predetermined crack size. By using this strategy, self-healing was demonstrated with smaller microcapsules and with lower weight fractions of microcapsules. Blaiszik*et al*. further produced smaller capsules (down to220 nm) using so nication techniques and an ultra hydrophobeto stabilize the DCPD droplets. It is believed that the Nano capsules will make self-heal in gmaterials responsive to damage initiated at a scale that is not currently possible and compatible with composites where the reinforcement spacing requires smaller capsules for applications such as self-healing thin films, coatings, and adhesives.

3.2. Self-Healing in Terms of Healant Loaded Pipelines Hollow glass Tubes and Glass Fibers

The core issue of this technique lies in filling thebrittle-walled vessels with polymerizablemedium,which should be fluid at least at the healing temperature.Subsequent polymerization of the chemicalsflowing to the damage area plays the role of crackelimination. Dry first identified the potential applicabilityof hollow glass tubes [32–35]. Similarapproach was adopted by Motuku*et al*. [36] andZhao *et al*. [37]. Because the hollow glass capillarieshave diameters (on millimeter scale) muchlarger than those of the reinforcing fibers in composites,they have to act as initiation for compositesfailure [38]. Instead, Bleay*et al*. employed hollowglass fiber (with an external diameter of 15 μm andan internal diameter of 5 μm) to minimize the detrimentaleffect associated with large diameter fibers[38]. Complete filling of healing agent into the tinytubes was achieved by vacuum assisted capillaryaction filling technique.

Accordingly, three types of healing system weredeveloped (Figure 2) [32]. (i) Single-part adhesiveall hollow pipettes contained only one kind ofresin like epoxy particles (that can be flowableupon heating and then cured by the residual hardener)or cyanoacrylate (that can be consolidatedunder the induction of air). (ii) Two-part adhesive.In general, epoxy and its curing agent were used inthis case. They were filled into neighboring hollowtubes, respectively. (iii) Two-part adhesive. Onecomponent was incorporated into hollow tubes andthe other in microcapsules.With the aid of the pre-embedded healing system inhollow pipettes, Motuku and co-workers studiedthe healing ability of glass fiber/unsaturated polyestercomposites subjected to low velocity impact[36]. The species of healing agent, characteristicparameters of the hollow pipes (amount, type oftubing materials and spatial distribution), compositespanel thickness, and impact energy level werefound to be critical to the healing efficiency. Meanwhile,Bleay*et al*. proved that the epoxy basedcomposites reinforced by hollow glass fibers containingsolvent diluted two-part epoxy becamerepairable as assessed by compression after impact test [38].

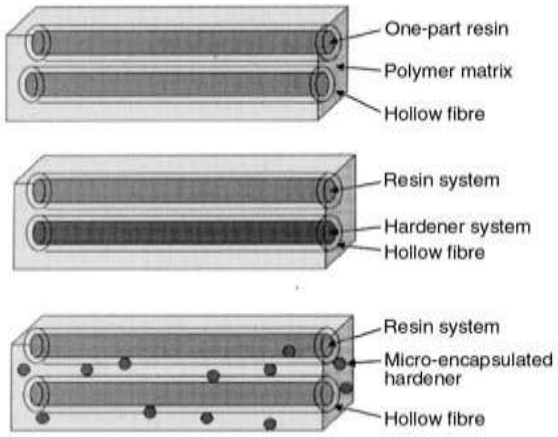

Figure 2. Schematic Diagram Of Repair Concept For Polymermatrix Composites Using Pre-Embedded Hollow Tubes [38] (Reprinted from Composites PartA: Applied Science and Manufacturing, Vol 32,Bleay S. M., Loader C. B., Hawyes V. J., Humber stoneL., Curtis P. T.: A Smart Repair Systemfor Polymer Matrix Composites, 1767–1776.

Recently, Trask *et al*. considered the placementof self-healing hollow glass fibers layerswithin both glass fibre/epoxy and carbon fibre/epoxy composite laminates to mitigate damage andrestore mechanical strength. The hollow fiberswere bespoken withdiameters between 30 and100 μm and a hollowness of approximately 50%.The study revealed that after the laminates weresubjected to quasi-static impact damage, a significantfraction of flexural strength can be restored bythe self repairing effect of a healing resin storedwithin hollow fibers. For example,Pang *et al*. added UV fluorescent dye to thehealing resin within the hollow fibers so that bleedingof the repair substance in the composites can bevisualized.

IV. CONCLUSIONS

Achievements in the field of self-healing polymersand polymer composites are far fromsatisfactory,but the new opportunities that were found duringresearch and development have demonstrated it is achallenging job to either invent new polymers withinherent crack repair capability or integrate existingmaterials with novel healing system. Interdisciplinarystudies based on tight collaboration amongscientists are prerequisites for overcoming the difficulties.

Comparatively, extrinsic self-healing techniquesmight be easier for large-scale usage for themoment. The works and outcomes in this aspecthave broadened the application possibility of polymericmaterials. Also, the extended service life ofcomponents made from these intelligent materialswould contribute to reduce waste disposal. It isundoubtedly important for building up a sustainablesociety.Besides the approaches described in the above text(Table 1), ongoing attempts are continuously presentingnew concepts.

For example, Lee *et al*. consideredsolid-state devices that integrate ductilepolymeric layers and brittle semiconductor or metalfilms. Using computer simulations, theyshowed that adding nanoparticles to the polymersyielded materials in which the particles becamelocalized at nanoscale cracks and effectively form‘patches’ to repair the damaged regions. Trau*et al*. proposed healing under electric field in terms ofelectrohydrodynamic

aggregation of colloidaldielectric particles. By creating a semi-interpenetratingnetwork composed of a crosslinkedthermoset and a thermoplastic, Karger-Kocsis consideredthat both shape memory and self healingfunctions can be combined. In such a intelligentmaterial, the thermoplastic polymer (amorphousor semicrystalline) offers 'switching' and'healing' effects, whereas the crosslinked thermosetacts as the fixing phase.

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

Table 1. Self-healing in Polymers and Polymer Composites

Category of materials to be repaired	**Materials to be repaired**	**Healing system**	**Trigger mechanism**	**Healing mechanism**	**Assessment of healing effect**
Thermoplastic	Poly(methyl methacrylate), etc.	Bulk	Heating or solvent induced	Chain interdiffusion and entanglements	Compact tension (CT) test or photography
Thermoplastic	Poly(ethylene-comethacrylic acid)	Bulk	Thermo mechanically induced melting	Chain interdiffusion and entanglements	Visual inspection after sawing, cutting and puncture
Thermoplastic	Polycarbonate	Bulk (weak alkali/hydrolyzed chains)	Steam	Weak alkali catalyzed polymerization	Molecular weight and mechanical strength
Thermoplastic	Poly(phenylene ether)	Bulk (copper ion/oxygen/scission chains)	Heating	Copper ion catalyzed polymerization	Molecular weight
Thermoset	Epoxy	Bulk	Heating	Post-curing of residual functional groups	Impact strength
Thermoset	Epoxy, fiber/unsaturated polyester, and fiber/epoxy	Cyanoacrylate, epoxy, unsaturated polyester, etc.	Crack induced breakage of hollow tubes containing	Curing of healant	Tensile, flexural and impact tests; photography;

			healant		ultrasonic C-scan
Thermoset	Glass fiber/epoxy	Epoxy granules	Heating	Curing of healant	Three-point bending and tensile fatigue

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