An Overview on Self-Healing Smart Composites

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Abstract　The crack healing by hollow fibre delivery of chemical adhesives, along with the recently formulated concept of self-healing smart composites, is reviewed in this paper. The latter, whereby the procedure of microcapsules induced crack self-healing, is thoroughly investigated. Discussion comprises a number of topics including the structures of healing agents and catalysts employed, microcapsule forming and exterior attachments with a catalyst, in-situ polymerisation kinetics, crack self-healing in neat epoxy and composites, healing efficiency and microscopes of healed composites. A typical dual phase self-healing system involves microencapsulated dicyclopentadiene (DCPD) performing ring-opening metathesis polymerization (ROMP) under an embedded Ru catalyst complex within an epoxy matrix. For neat epoxy resin the healing efficiency is as high as 90% at ambient temperature, while for carbon fabric reinforced composites it is approximately 45% at room temperature and up to 80% at 80℃. Norbornene (NB) and its derivates have a similar self-healing function. An un-catalysed thermal reversible reaction of a multi-furan and multi-maleimide can form endless re-mendable cross-linked polymerization to heal cracks automatically. A comparison of the characteristics of various self-healing agent systems and composites are proposed.

Key words　Smart materials, Healing, Repairing, Self-healing, Polymer matrix composites

自愈合机敏复合材料综述

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文　摘　综述了中空纤维释放黏结剂的裂纹愈合及近期开发的机敏裂纹自愈合复合材料的研究进展。对后者微胶囊促使的机敏裂纹自愈合进行了详尽的阐述,其中包括愈合剂和催化剂的结构、微胶囊的形成和外表连接催化剂、愈合剂系统原位聚合反应、纯环氧树脂基体和复合材料中的裂纹自愈合、愈合效率及愈合复合材料微观表征等方面。一个典型的双相自愈合系统是包含于微胶囊中的二聚环戊二烯(DCPD),通过埋于环氧基体中的钌络合物催化剂进行开环转位聚合反应(ROMP),形成新的聚合物来愈合裂纹。在纯环氧树脂基体中,上述自愈合系统在室温下的愈合效率可高达90%,而在碳纤维复合材料中室温下的愈合效率大致是45%,在80℃可提高到80%。降冰片烯(Norbornene)及其衍生物具有同以上系统相似的自愈合功能。三聚呋喃和四聚马来酰亚胺可在无催化剂作用下,进行热可逆的、无终止的交联聚合反应,自动愈合裂纹。同时,对以上三种自愈合剂系统及复合材料的特点进行了比较。

关键词　机敏材料,愈合,修补,自愈合,聚合物基复合材料

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1 Introduction

The emergence and development of materials has defined the progression of human civilisation. The evolution to modern society can be mapped through a number of material stages, primarily, the Stone Age, Bronze Age, and Iron Age. More recently the age of synthetic materials, marked through the invention of synthetic phenol-formaldehyde, commonly known as Bakelite, by Bakeland in 1907, and the composites age, marked by the occurrence of glass fibre reinforced polyester in 1942 in England. It is now seen that, in recent years, civilisation has stepped into a fifth age of smart materials [1~2]. Smart materials respond and adapt to environmental stimuli with changes in particular properties (mechanical, electrical, thermal), structures, compositions, or functions. These changes are often a means of structure sensing and can be used to provide information about damage, strain/stress, temperature, thermoelectricity, etc [3~5]. Smart materials are a progressive evolution of new materials and design concepts. This technology, originally developed and demonstrated for aerospace, has applications in all fields of engineering.

Optical fibres, shape memory alloys (SMA) and piezo-electric ceramics have all been applied in smart composite structures to detect impact damage, matrix cracks, delaminations, and interface degradation owing to fatigue and wet/thermal environments [1, 3, 6~7]. Besides the capability of self-sensing, the concept of self-healing has also been developed in composites. Self-healing was first developed in concrete, and then in a range of polymers and polymer matrix composites [8~15]. C. Dry developed a self-healing process for concrete in the early 1990s. Under this method the concrete was embedded with hollow glass microcapillary pipettes filled with a form of superglue. When the concrete was loaded and cracking occurred, the glass pipes broke and delivered the adhesive, and thereby healed the cracks [9~10]. D. Jung invented a new concept of micro-encapsulated self-healing in 1997 in polyester matrix composites [15]. More recently, the researchers have conducted intensive studies into microcapsule induced self-healing composites [13~14]. M. Kessler, S. White and co-workers, selected dicyclopentadiene (DCPD) as a healing chemical agent and bis (tricyclohexylphosphine)-benzylidene ruthenium (Ⅳ) dichloride (Grubb's catalyst) as a reaction catalyst in their investigations. A combination of the two agents induced ring-opening metathesis polymerization (ROMP) can form a polymer adhesive that would heal the cracks [16~18].

Additionally, two new healing agent systems are also investigated. N. Grove and A. Skipor proposed that Norbornene (NB) and its derivates may also perform ROMP healing cracks automatically with a transition metal complex as a catalyst [19~21]. X. Chen developed un-catalysed thermal reversible reactions, which form endless re-mendable cross-linked polymerization to heal cracks [22].

The studies of self-healing smart composites are a hot spot in the field of composites. Thermosetting polymer matrix composites are susceptible to damage in the form of cracking. In fibre reinforced plastic composites (FRP), cracks are in the forms of 1) fiber-matrix interfacial debonding, 2) ply delamination, and 3) matrix cracking [23~24]. Often these cracks form deep within the structure making repairing virtually impossible. The crack self-healing in composites by microencapsulated healing agents provides a better attempt to solve these questions.

This paper forms an overview of the literature so far composed in regards to smart self-healing composites. Remarks and proposal are made on self-healing smart composites in a hope to provide general information as well as beneficial assistance for further researches.

2 Hollow fiber induced self-healing

Self-repairing smart materials are a range of materials possessing the inherent ability to heal cracks themselves in suitable circumstances without the requirement of manual intervention. In most cases full restoration or an improvement in mechanical properties

is expected. Self-healing through hollow fibre delivery of adhesives to repair cracks was first invented in concrete. C. Dry, in the early 1990s, proposed the concept of releasing chemicals into the cement matrix to alter the matrix permeability, repair cracks, prevent corrosion and to act as sensors for remedial action [9~10, 25~26]. Fig. 1 is the preliminary diagram of crack self-repairing in concrete, demonstrating cement matrix with self-repairing capability[9]. Two kinds of adhesives, a cyanoacrylate superglue, and a three-part methylmethacrylate (MMA) monomer and cobalt initiator, both stored in hollow glass pipettes, had been used to heal cracks in concrete. Results showed the adhesive systems worked very well. The two liquids leaked from the pipettes into the cracks and entirely filled them with a solid Plexiglas-like matrix within 24 h. The bending strength showed the adhesive repaired samples carried more load in the second bending test (+130%) [10, 26].

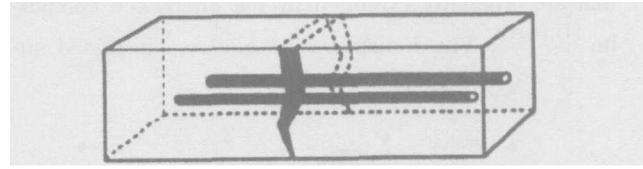


Fig. 1 Adhesive delivery to self-repair crack in cement matrix

More recent studies have focused on the processing of incorporating hollow fibres in addition to the normal set of solid reinforcing fibres in PMC [12, 25]. Fig. 2 shows a schematic design of the self-repair mechanism, showing the release of the repair solution into cracks, debonded interfaces, and damaged areas in a PMC [10, 12]. In plain-weave S-2 glass fabric reinforced vinyl ester matrix and epoxy matrix composites, borosilicate glass microcapillary pipettes were incorporated to store the damage-repairing solution [12]. The results showed the presence of glass tubing did not affect the impact failure behaviour of the composite in the energy regime considered, thereby qualifying the self-healing process.

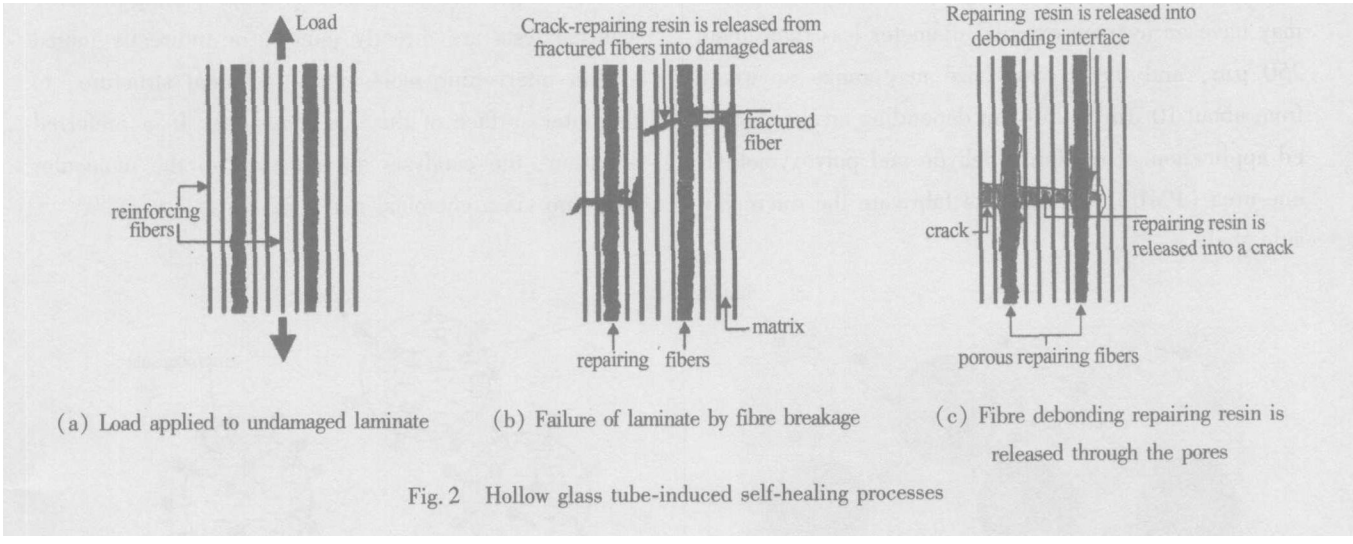


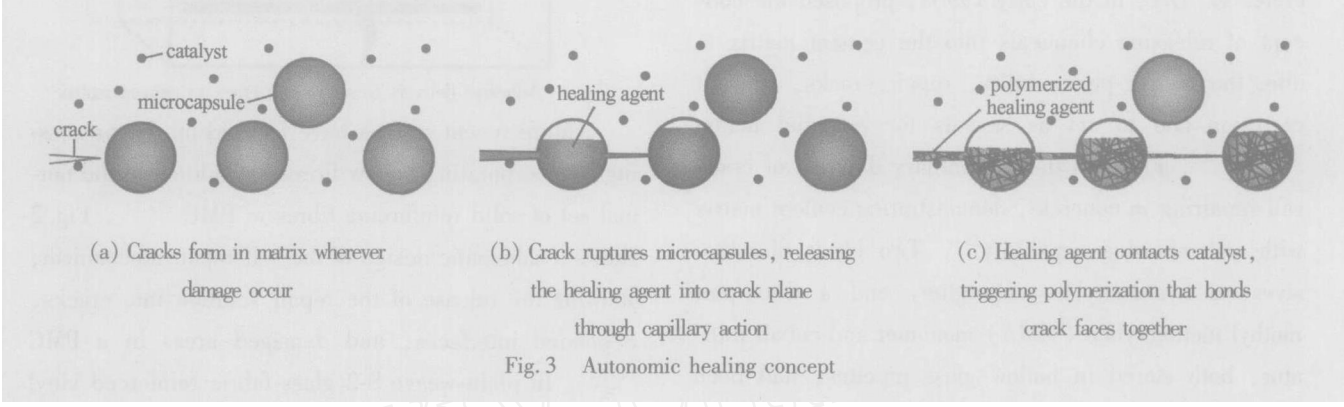
Fig. 2 Hollow glass tube-induced self-healing processes

A big problem arising from the translation of the healing process from concrete to PMC lies in the insertion of the glass tubes, which either is a contaminant, or arises the complicated and changeable composite processing and deteriorates the performances of composite structures. The effect of these drawbacks is reasonably limited the hollow glass fibre-induced self-healing processes in real life application.

3 Microencapsulated smart self-healing

The microencapsulated crack healing system consists of a catalytic network formation of an encapsulated add-monomer, which is held within a capsule embedded in the epoxy matrix, when a crack occurs and breaks the microcapsules, the encapsulated monomer polymerises under the catalyst and heals the crack, leading to reattainment of the mechanical properties

that are originally exhibited by the uncracked composite [13, 18, 27]. Fig 3 displays the microencapsulated autonomic healing concept [13].



(a) Cracks form in matrix wherever damage occur

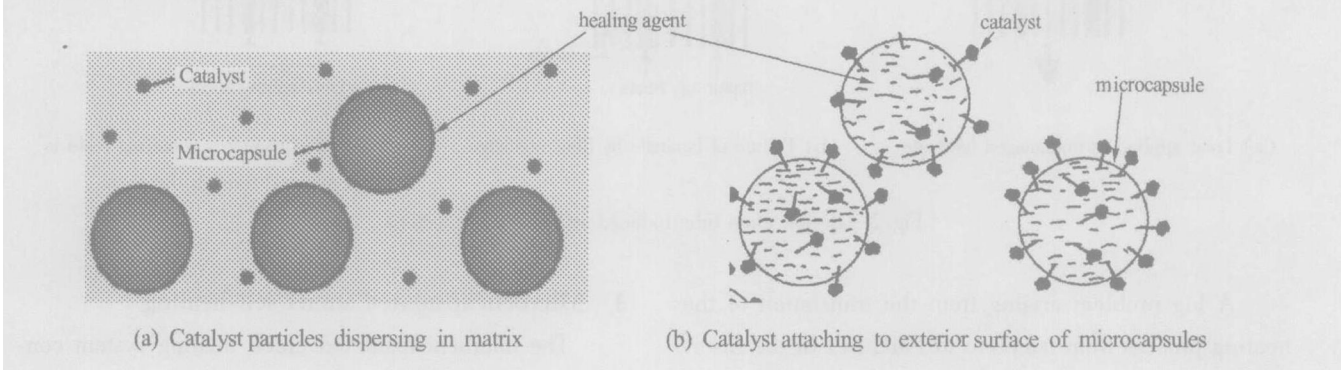
(b) Crack ruptures microcapsules, releasing the healing agent into crack plane through capillary action

(c) Healing agent contacts catalyst, triggering polymerization that bonds crack faces together

Fig. 3 Autonomic healing concept

The introduction of the microcapsules is considered to be superior to the former stated hollow fiber delivery healing process. The microcapsules, also referred to as hollow microspheres, microbubbles or microballoons, are small spherical bodies fabricated with solid walls to enclose the material that is polymerizable in the presence of the catalysts. The microcapsules may have an average external diameter less than about 250 μm, and the average size may range anywhere from about 10 μm to 250 μm depending on the intended application. Urea-formaldehyde and polyoxymethylene-urea (PMU) were used to fabricate the microcapsule shells [13, 15].

The catalysts can either be dispersed within the matrix, or directly attached to the exterior surface of the microcapsules, as shown in Fig 4 [13, 20]. The exterior attachment of catalysts is of great importance for self-healing composites as it implies a degree of shared surface area between the healing agent and catalyst thereby improving the efficiency of the healing process. The catalysts are directly joined, or indirectly joined via an intervening molecular attachment structure, to the outer surface of the microcapsules. In a preferred situation, the catalysts are attached to the molecular structure via a chemical reaction.



(a) Catalyst particles dispersing in matrix

(b) Catalyst attaching to exterior surface of microcapsules

Fig 4 Schematics of catalyst conditions

The surface treatment of microcapsules, such as by silane coupling agents, can improve the wettability to the matrix and fibres [14, 20]. The adhesion between the capsules and the matrix of the composite influences whether the capsule will rupture or debond in the presence of an approaching crack.

4 Typical self-healing systems and composites

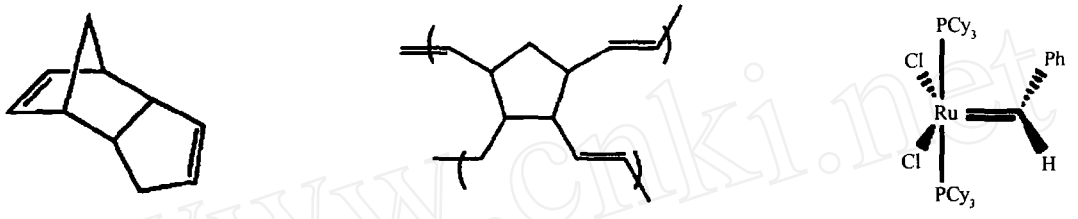
4.1 DCPD and Ru based Grubbs' catalyst

4.1.1 Healing agent chemistry

S. White and co-workers have conducted comprehensive research into the DCPD and Ru based Grubbs' catalyst. The results are presented in detail below.

(1) Structures of DCPD

Dicyclopentadiene (DCPD) is a by-product of the ethelene production process conducted in the petrochemical industry. Generally, this ethelene is found to contain fairly large amounts of DCPD (ca. 15% ~ 17%). The DCPD monomer, stable with 0.01% ~ 0.02% p-tert-butylcatechol, possesses low viscosity and excellent shelf life. The standard structure of the monomer, the monomer in its cross-linked (ring-opened) condition are shown in Fig.5 (a) and (b) [13~14] respectively.



(a) DCPD monomer (b) Ring-opened DCPD (c) Grubbs' catalyst

Fig. 5 *Structures of healing agent system*

(2) Grubbs' catalyst

Bis(tricyclohexylphosphine) benzylidene ruthenium(Ⅳ) dichloride, also referred to as Grubbs' catalyst, has a structure as illustrated in Fig.5(c) — a ruthenium carbine complex structure [13~14]. Grubbs' catalyst is highly reactive for the purposes of double-bond metathesis while exhibiting exceptional tolerance to other functional groups, as well as oxygen and water. It has been shown that exposure of Grubbs' catalyst to a primary amine curing agent leads to some degradation of chemical activity of the catalyst. Tertiary amine systems show little chemical interaction with Grubbs' catalyst.

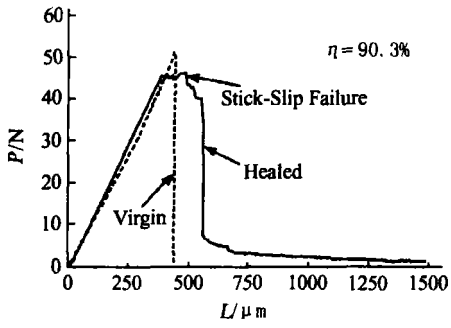
(3) ROMP

Grubbs' catalyst interacts with DCPD monomers to initiate a living ring opening metathesis polymerisation (ROMP) reaction at room temperature. If additional monomer is supplied at any time to the end of the forming chain, further ROMP may occur and the chain may extend [13,16]. The living polymerisation guarantees the multi and repeated healing processes as meeting the diverse set of requirement.

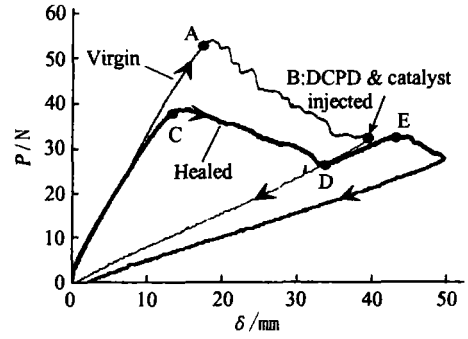
(4) DCPD monomer and catalyst in-situ polymerisation

Epon 828 epoxy resin and diethylenetriamine (DETA) were used as the matrix resin system. A tapered double-cantilever beam (TDCB) test has been used to investigate the crack healing behaviour by providing a crack-length-independent measure of mode I interlaminar fracture toughness [18,24]. TDCB fracture specimens were tested to failure. The mixtures of catalyst and DCPD monomers were injected into the fracture planes, and the samples were fastened tightly with C-clamps. After 24 h to 48 h, samples were retested to determine the healed fracture toughness. A typical TDCB load-displacement curve is shown in Fig.6 (a) [18]. Crack healing efficiency is calculated simply as the ratio of interlaminar fracture toughness between the healed and virgin samples.

The effect of the ratio of Grubbs' catalyst to DCPD monomer was investigated in four sets of samples with ratios of 2, 4.4, 10 and 40 g/L. The results are depicted in Tab.1. It can be seen that the level of healing efficiency increases with the concentration of catalyst, but decreases exponentially with gel time, taking approximately 600, 235, 90 and 25 s, respectively [18,24]. It has been shown that with a ratio of 4.4 g/L for catalyst to monomer, nearly 100% healing efficiency may be achieved.



(a) Neat epoxy resin



(b) 8H satin weave E-glass/epoxy

Fig 6 Representative load-displacement curves for crack healing (manual injection)

Tab. 1 Influence of catalyst concentration on healing efficiency in neat epoxy (manual injection)

concentration Grubbs(g) DCPD(l)	Fracture Toughness/MPa·m$^{1/2}$ Virgin	Healed	Healing Efficiency
40 :1	0.55 ±0.05	0.71 ±0.08	Full heal
10 :1	0.56 ±0.04	0.61 ±0.09	Full heal
4.4 :1	0.55 ±0.05	0.53 ±0.10	(97 ±15)%
2 :1	0.54 ±0.04	0.45 ±0.08	(84 ±8)%

The experiments were also conducted for E-glass fabric reinforced epoxy (Epon 828/DETA) composites. Fig 6(b) shows load-displacement curves for crack healing by direct injection of the catalyst and DCPD monomer. The results in tab. 2 show that the maximum healing efficiency is 80% for satin fabric/epoxy composites with the fabric structure shown to have a large affect on the healing behaviour [16].

Tab. 2 Crack healing efficiency in E-glass/epoxy composites (manual injection)

Weave	No. of Specimens	G_{IC} Virgin, avg (±1SD) /J·m^{-2} Initiation	Plateau	G_{IC} Healed, avg (±1SD) /J·m^{-2} Initiation	Plateau	η/% Initiation	Plateau
Plain	9	726(±40)	1 283(±141)	335(±111)	655(±223)	46	51
8H Satin	6	528(±100)	842(±171)	420(±147)	564(±58)	80	67

(5) Self-activated healing

The self-activated samples, consisting of epoxy and an embedded catalyst but no microcapsules, were tested to failure and subsequently healed by manual injection of DCPD monomer into the crack plane. Virgin and healed values of fracture toughness were measured and are plotted in Fig 7 with their corresponding values of healing efficiency [18]. The fracture toughness of the healed samples was found to increase with the level of catalyst

The results for self-activated E-glass reinforced epoxy composites with an embedded catalyst are shown in tab. 3 [16]. It is evident that the healing efficiency is much lower than that of manual injection of mixtures, and also lower than that of self-activated healing in neat epoxy (Fig 7).

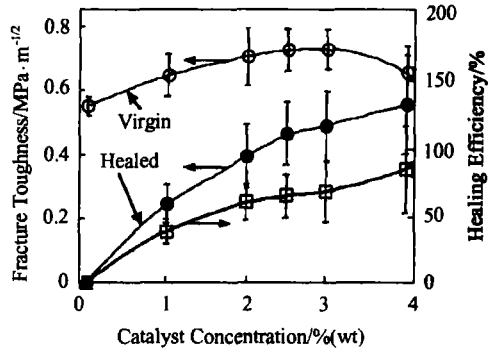


Fig 7 Fracture toughness and healing efficiency as a function of catalyst concentration in neat epoxy (self-activated healing)

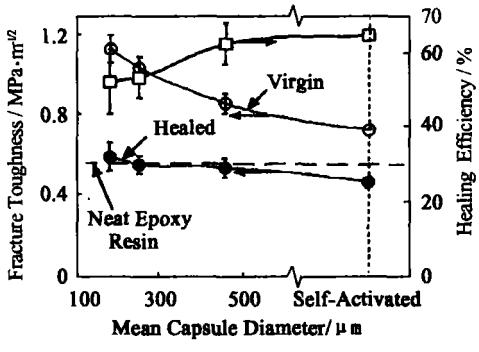
The drop in both toughness and healing efficiency may be associated with the clumping or non-uniform dispersion of the catalyst particles. In addition, the low polymerisation rate has a significant effect on the amount of the monomer that diffuses into the matrix thereby leaving the crack plane dry [16].

Tab. 3 Self-activated crack healing efficiency in E-glass/epoxy composites

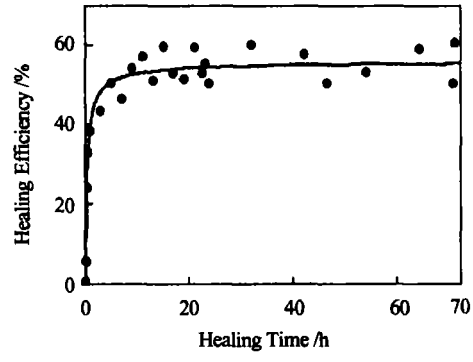
Weave	No. of Specimens	G_{IC} Virgin, avg. (±1SD) /J·m^{-2}		G_{IC} Healed, avg. (±1SD) /J·m^{-2}		η/%	
		Initiation	Plateau	Initiation	Plateau	Initiation	Plateau
Plain	10	644 (±280)	1 052 (±222)	111 (±47)	198 (±57)	17	19
8H Satin	8	585 (±199)	1 040 (±138)	38 (±56)	87 (±117)	6.5	8.4

4.1.2 Microencapsulated healing in neat epoxy

Urea-formaldehyde microcapsules, containing DCPD monomer, were manufactured with average diameters of (180 ±40) μm, (250 ±80) μm and (460 ± 80) μm by using the emulsion in situ polymerisation micro-encapsulation method. Shell wall thickness was (190 ±30) nm for all batches [27]. A self-healing polymer composite composed of microencapsulated DCPD monomer and Grubbs' catalyst was incorporated into an epoxy resin sample. The effects of microcapsule size on the healed fracture toughness and healing efficiency was investigated with 2.5 wt% Grubbs' catalyst and 10 wt% DCPD monomer encapsulated microcapsules, as shown in Fig 8 (a) [18]. The divergence of healing efficiency increased significantly with increased capsule diameter. The self-healed specimens with 460 μm diameter capsules exhibited the greatest healing efficiency, recovering, on average, 63% of the virgin load.



(a) Influence of microcapsule size on fracture toughness and healing efficiency



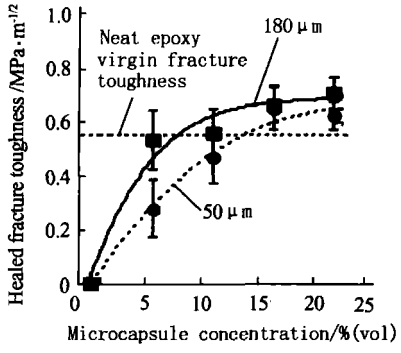
(b) Development of healing efficiency

Fig 8 Fracture toughness and healing efficiency in neat epoxy

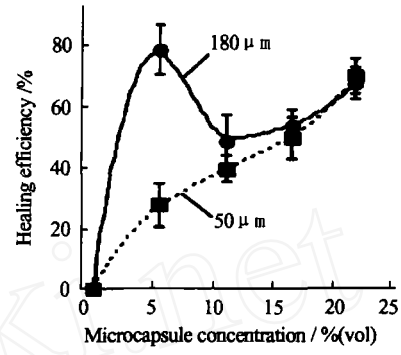
Samples with 10 wt% of 180 μm diameter capsules and 2.5 wt% of catalyst were manufactured to investigate the development of healing efficiency. Healed fracture tests were performed at time intervals ranging from 10 min to 72 h after the virgin sample tests. The resulting healing efficiencies versus time are plotted in Fig 8 (b) [18]. It can be seen that a significant healing efficiency developed within 25 min, which closely corresponds to the gelation time of the poly-DCPD. Steady-state values of healing efficiency were reached within 10 h.

Microcapsule concentration has been shown to have a significant influence on the fracture toughness and healing efficiency. To investigate this effect for the self-healing case, samples were manufactured with 0 to 20 wt% of 50 μm and 180 μm diameter capsules sepa-

rately with 2.5 wt% of catalyst, measured 24 h after virgin fracture. The results are shown in Fig 9 [24]. For the 180 μm diameter and with 5.0 wt% capsule concentration fraction, an average healing efficiency of (80 ±5) % was measured.



(a) healed fracture toughness



(b) healing efficiency

Fig 9 Influence of microcapsule concentration on self-healing behaviour

4.1.3 Self-healing composites

Carbon fibre-reinforcement with 3K tow plain weave architecture was used to fabricate a structural composite material. The microcapsules of the DCPD monomer used had a mean diameter of 166 μm. The central layers where the delamination was introduced were filled with 20 wt% microcapsules of the DCPD monomer and 5 wt% of a ROMP catalyst (Grubbs' catalyst). Freshly fractured specimens were clamped shut with modest pressure and allowed to heal at room temperature for 48 h. Upon retesting, the healing efficiency was measured by the recovery of the level of interlaminar fracture toughness.

Fig 10 shows the typical loading-displacement curves for virgin and healed self-healing carbon fibre structural composites[29].

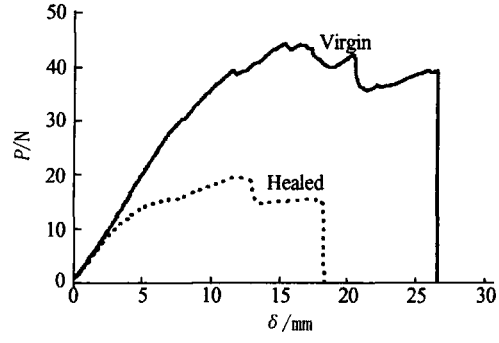


Fig 10 Typical loading-displacement curves for self-healing samples (48 h at room temperature)

Tab. 4 shows the values of fracture toughness and healing efficiency. It can be seen that the healing efficiency is about 38% on average with a maximum of nearly 45%. By elevating the healing temperature to 80℃, the healing efficiency increased to 66% on average with a maximum of over 80% [29].

Tab. 4 Fracture toughness and healing efficiency for self-healing structural composites

Specimen type	No. of samples	K_{IC} Virgin avg /MPa·m$^{1/2}$	K_{IC} Healed avg /MPa·m$^{1/2}$	K_{IC} Healed peak /MPa·m$^{1/2}$	η_{avg} /%	η_{max} /%
Self-healing (at room temp.)	8	2.085 (0.22)	1.08 (0.20)	1.29 (0.25)	38	45
Self-healing (at 80℃)	4	2.79 (0.30)	1.83 (0.20)	2.23 (0.18)	66	80

4.1.4 Microimages of self-healing composites

Evidence of polymerisation of a healing agent following crack damage is shown by environmental scanning electron microscopy (ESEM) and infrared spectroscopy [13]. ESEM micrographs reveal the presence of a thin polymer film on the fracture surface. Infrared

spectroscopy of this film reveals an absorption at a value 965 cm^{-1}, characteristic of ring-opened poly-(DCPD). The ESEM image in Fig 11 shows one area of the fracture plane of a healed specimen in which the poly-(DCPD) film is still attached to the interface, visible on the right side of the image [13].

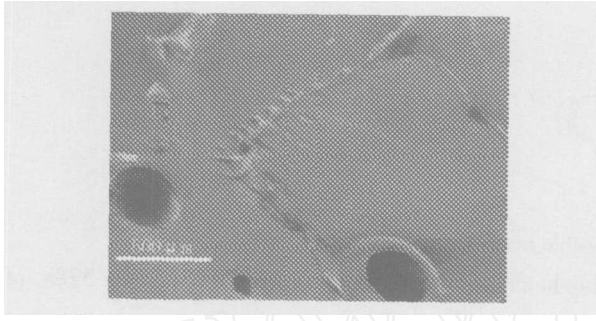


Fig 11 ESEM image in self-healing epoxy polymer

A typical virgin fracture surface for a self-healing structural composite specimen is shown in Fig 12.

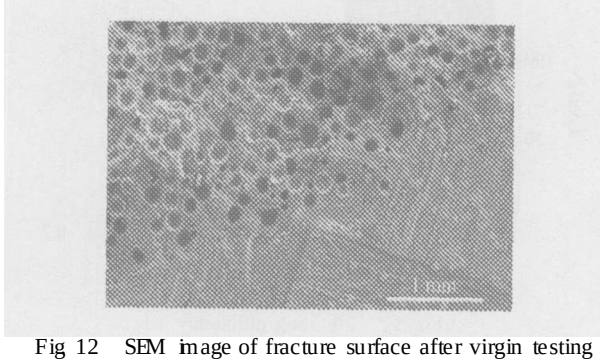


Fig 12 SEM image of fracture surface after virgin testing

It can be seen that the fracture is primarily interfacial between the fibre and matrix (bottom right of the image); very few of the microcapsules can be seen to have broken[23]. In regions where crack propagation was confined to the matrix (top left of the image) the level of broken microcapsules present increases. It can be seen in Fig 13 that there are several strands of poly-(DCPD) on the surface that have bridged the delamination before ultimately rupturing and collapsing in a folded film on the fracture surface[23]. The numerous bands and finger-like projections of the film is evidence that a significant amount of plastic flow of the healing agent has occurred.

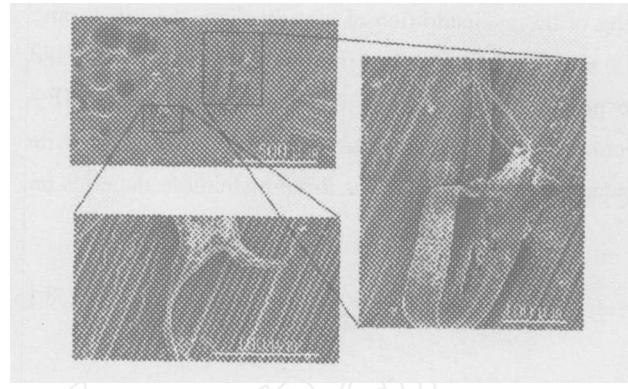


Fig 13 SEM image of healed fracture surface tested after 30 min healing time

4.2 Norbornene, its derivates and catalysts

Norbornene ring-opening metathesis polymerisation (ROMP) represents the current production processes employed for cyclo-olefin polymers[28]. Based on DCPD as the main monomer, saturating the double bond in norbornene ROMP with different combinations of a substituent (R) can produce polymers with varying structures and properties. Fig 14 shows the forming of NB serial monomers[28].

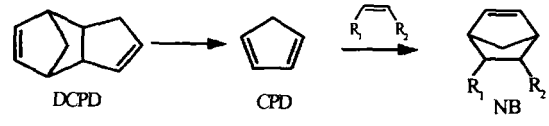


Fig 14 Forming of NB monomer

A norbornene monomer and a derivative thereof may each perform ROMP and may both therefore be used as the healing agent[20]. The catalysts used may be RuCl, $Ru(H_2O)_6$-(toluene sulfonate)$_2$, K_2RuCl_5, and the like.

4.3 Un-catalysed thermally reversible re-mending reaction[22]

A truly "re-mending" material has been developed that is able to form covalent bonds at the interface of mended parts. The material consists of a highly cross-linked transparent polymer that exhibits multiple cycles of autonomic crack mending under a simple thermal treatment without the presence of a catalyst. A

thermally reversible Diels-Alder (DA) reaction consisting of the cycloaddition of a multi-diene (multi-furan, F) and multidienophile (multi-maleimide, M) is used to prepare the polymeric material. Monomer 1 (4F) contains four furan moieties on each molecule, while monomer 2 (3M) contains three maleimide moieties on each molecule. A highly cross-linked network (polymer 3, 3M4F) may be formed via the DA reaction of furan and maleimide moieties, while thermal reversibility may be accomplished by the retro-DA reaction, as shown in Fig 15.

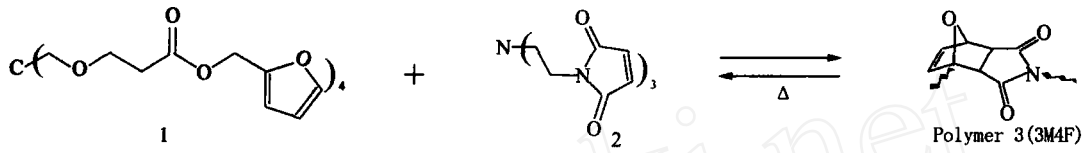


Fig 15 Thermally reversible reaction

The degree of cross-linking of 3M4F as a function of the reaction temperature is shown in Fig 16. At 24℃, polymerisation of up to 60% to 70% required 5 days. The process of polymerisation and cross-linking was found to be much faster at higher temperatures, reaching "completion" (95 ±5)% in just 3 h at 75℃.

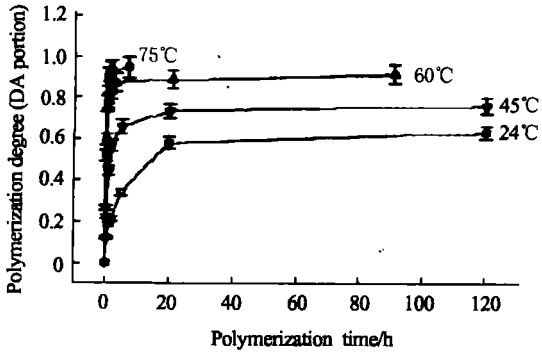


Fig 16 Degree of polymerisation versus time

Compact tension test specimens were used to determine the fracture-mending efficiency of the polymer. Application of a load, in the direction perpendicular to the pre-crack, resulted in fracture of the specimen. After structural failure, the two pieces were matched as closely as possible and were held together with a clamp. They were subsequently treated at 120 to 150℃ under nitrogen for approximately 2 h, and then cooled to room temperature. Representative load-displacement curves for a polymer specimen are plotted in Fig 17. The healed specimen exhibits approximately 57% of the original fracture load. At 150℃, an average mending efficiency of about 50% was achieved, whereas at 120℃ the average value was 41%.

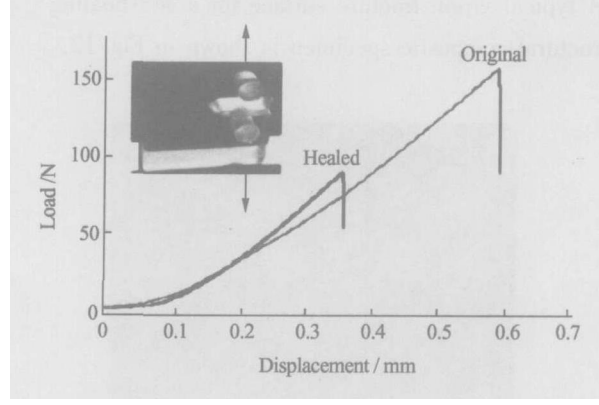


Fig 17 Mending efficiency

5 Remarks and Proposal

Microencapsulated self-healing composites have been extensively studied. The healing efficiency has been found to be as high as 90% in epoxy at room temperature, while near 40% at ambient temperature and 66% at 80℃ in carbon fibre composites. The healing efficiency as well as the compatibility with both the epoxy and fibre reinforcements should be of concern when considering NB, which is therefore only proposed as a possible healing agent. Crack healing for the thermal reversible reaction without a catalyst was only conducted in the 3M4F parent material. The processing and compatibility of the material with the epoxy matrix and fibre reinforcement also requires consideration.

The following lists compare the advantages and disadvantages of the above self-healing processes and materials in assistance of further research and improvements.

(1) Grubbs' catalyst will decompose at above 120℃. Therefore, this healing agent system may only be used for middle temperature cured epoxy composites. The more stable healing agent system over 180℃ should be studied.

(2) The long-term stability of the catalyst, and the ability of the material to self-heal multiple times remains a concern for DCPD and Grubbs' catalytic healing system.

(3) In comparison to the catalyst attachment to the microcapsules, the catalyst dispersion in the matrix has the following disadvantages: (a) the catalyst clumps together; (b) the catalyst does not finely disperse into the matrix material resulting in waste; (c) moreover, the homogenous catalyst approach results in dispersion of the polymerisation agent into areas (volumes) of the polymeric matrix where there is no available healing microcapsules; (d) the initiation and subsequent rate of the healing process may be too slow.

(4) For the polymeric material 3M4F, the maleimide monomer melts at too high a temperature (113℃), is coloured (yellow), and is insoluble in monomer 4F.

(5) Though polymer 3F4M can be cured in less than an hour at 130℃, a full curing may take many hours to complete.

(6) The service temperature of polymer 3M4F ranges from 80℃ to 120 ℃, which may be too low for many applications but close to ideal for others, such as self-mending electronic packaging, where cracking occurs due to differences in thermal expansion properties.

Self-healing smart composites are a leading edge field in material science & engineering. The basic principles and processes have been demonstrated by several pioneering researchers, however, there is still much to be investigated with regards to real life applications. Essentially, a great deal of opportunities and challenges exist for future material researchers.

References

1 Khan Z M. Design and development of optic fiber smart structures in aerospace vehicles. ICAS Congress, 2002: 493

2 Rogers C A, Liang C, Fuller C R. Active damage control of hybrid material systems using induced strain Actuators. In: Proceeding of AIAA 32nd structure, structural dynamics, and materials conference, Paper No. AIAA 91-1145

3 Chung D D L. Composites get smart. Materials Today, 2002; (2): 30

4 Ogasa T, Kemmochi K. Research and development for environmentally conscious smart composites. Advanced Composite Materials, 1998; 7(4): 299

5 Michael Hill-King. Smart structures through embedding optical fibre strain sensing. Smart Materials Bulletin, 2001; (5): 7

6 Park G, Inman D J. Smart bolts: an example of self-healing structures. Smart Materials Bulletin, 2001; (6): 5

7 Rogers C A. Intelligent materials. Scientific American, 1995; 273 (3): 154

8 Avramova N. Study of the healing process of polymers with different chemical structure and chain mobility. Polymer, 1993; 34(9): 1 904

9 Dry C. Matrix cracking repair and filling using active and passive modes for smart timed release of chemicals from fibers into cement matrices. Smart Materials & Structure, 1994; (3): 118

10 Dry C, McMillan W. Three-part methylmethacrylate adhesive system as an internal delivery system for smart responsive concrete. Smart Materials & Structure, 1996; (5): 297

11 Jacobsen S, Sellevold E J. Self repair of high strength concrete after deterioration by freeze/thaw. Cement and Concrete Research, 1996; 26(1): 55

12 Motuku M, Vaidya U K, Janowski G M. Parameteric studies on self-repair approaches for resin infused composites subjected to low viscosity impact. Smart Materials & Structure, 1998; (8): 623

13 White S R, Sottos N R et al. Autonomic healing of polymer composites. Nature, 2001; 409: 794

14 White S R, Sottos N R et al. Multifunctional automatically healing composite materials. USP 6518330, 2003

15 Jung D, Hegeman A et al. Self-healing composites using embedded microspheres. Composites and Functionally Graded Materials in American Society of Mechanical Engineers, 1997: 265

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单纯固体传导隔热具有明显的优越性。

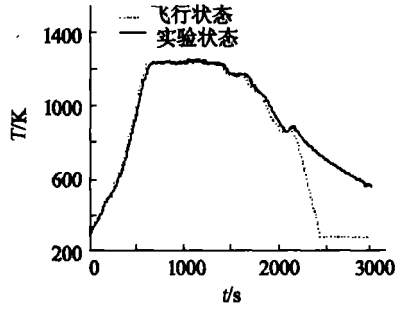

图 1 表面辐射平衡温度

Fig 1 Surface radiant equilibrium temperature

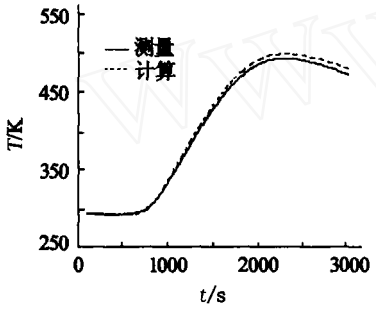

图 2 内部温度随时间的变化历程

Fig 2 Interior temperature variations with time

4 结论

本文的研究表明:传统的固体热传导难以解决长时间气动加热的隔热问题,利用多相(气-固)与复合传递机制(辐射、传导及对流)可以有效解决长时间气动加热的隔热问题。本文的算例表明多相的复合传递机制具有极大的隔热潜力。

参考文献

1 Kamran Dergabeigs Thermal analysis and design of multi-layer insulation for re-entry aerodynamic heating AIAA 2001: 2 834

2 Kamvan Darjabcig Heat transfer in high temperature fibrous insulation AIAA 2002: 3 332

3 Marschall J et al Internal radiation transport and effective thermal consluctivily of fibrous ceramic insulation AIAA 2001: 2 822

4 Petrov V A. Combined radiation and conduction heat transfer in high temperature fiber thermal insulation International Journal of Heat and Mass Transfer, 1997; 40(9): 2 241～2 247

5 Imakoma H, Sang K, Okazard U. The effective thermal conductivity of fibrous insulation International Chemical Engineering 1990; 36: 738～746

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(上接第 15页)

16 Kessler M R, White S R. Self-activated healing of delamination in woven composites Composites A, 2001; 32: 683

17 Kessler M R, White S R. Cure kinetics of the ring-opening metathesis polymerization of dicyclopentadiene Journal of Polymer Science A: Polymer Chemistry, 2002; 40: 2 373

18 Brown E N, Sottos N R, White S R. Fracture testing of a self-healing polymer composite Experimental Mechanics, 2002; 42: 372

19 Grove N R, Kohl P A et al Functionalized polynorbornene dielectric polymers: adhesion and mechanical properties Journal of Polymer Science B, 1999: 37: 3 003

20 Skipor A, Scheifer S, Olson B. Self-healing polymer compositions USP application number: 20040007784, 2004

21 Bielawski CW, Benitez D, Grubbs R H. An "endless" route to cyclic polymers Science, 2002; 297: 2 041

22 Chen X, Dam M A et al A Thermally re-mendable cross-linked polymeric material Science, 2002; 295: 1 698

23 Kessler M R, Sottos N R, White S R. Self-healing structural composite materials Composites A, 2003; 34: 743

24 Brown E N, White S R, Sottos N R. Microcapsule induced toughening in a self-healing polymer composite J. of Materials Science, 2004; 39: 1 703

25 Dry C. Procedures developed for self-repair of polymer matrix composite materials Composite Structures 1996; 35: 263

26 Dry C, Corsaw M, Bayer E. A comparison of internal self-repair with resin injection in repair of concrete Journal of Adhesion Science and Technology, 2003; 17: 79

27 Brown E N, Kessler M R et al In situ poly(urea-formaldehyde) microencapsulation of dicyclopentadiene Journal of Micro-encapsulation, 2003; 20: 719

28 Yamazaki M. Industrialization and application development of cyclo-olefin polymer Journal of Molecular Catalysis A: Chemical, 2004; 213: 81

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