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# Self-healing polymeric materials: A review of recent developments

Dong Yang Wu*, Sam Meure, David Solomon

*CSIRO Manufacturing and Materials Technology, Gate 5, Normanby Road, Clayton South, Victoria 3168, Melbourne, Australia*

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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 healing response. 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. An overview of various self-healing concepts for polymeric materials published over the last 15 years is presented in this paper. Fracture mechanics of polymeric materials and traditional methods of repairing damages in these materials are described to provide context for the topic. This paper also examines the different approaches proposed to prepare and characterize the self-healing systems, the different methods for evaluating self-healing efficiencies, and the applicability of these concepts to composites and structural components. Finally, the challenges and future research opportunities are highlighted.


*Keywords:* Polymeric materials; Self-healing; Composite repair; Biomimetic repair

**Contents**



*Corresponding author. Tel.: +61 3 9545 2893; fax: +61 3 9545 2829.
*E-mail address:* Dong.Yang.Wu@csiro.au (D.Y. Wu).

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## 1. Introduction

Polymers and structural composites are used in a variety of applications, which include transport vehicles (cars, aircrafts, ships, and spacecrafts), sporting goods, civil engineering, and electronics. However, these materials are susceptible to damage induced by mechanical, chemical, thermal, UV radiation, or a combination of these factors [1]. This could lead to the formation of microcracks deep within the structure where detection and external intervention are difficult or impossible. The presence of the microcracks in the polymer matrix can affect both the fiber- and matrix-dominated properties of a composite. Riefsnider et al. [2] have predicted reductions in fiber-dominated properties such as tensile strength and fatigue life due to the redistribution of loads caused by matrix damage. Chamis and Sullivan [3] and more recently, Wilson et al. [4] have shown that matrix-dominated properties such as compressive strength are also influenced by the amount of matrix damage. Jang et al. [5] and Morton and Godwin [6] extensively studied impact response in toughened polymer composites and found that matrix cracking causes delamination and subsequent fiber fracture. In the case of a transport vehicle, the propagation of microcracks may affect the structural integrity of the polymeric components, shorten the life of the vehicle, and potentially compromise passenger safety.

With polymers and composites being increasingly used in structural applications in aircraft, cars, ships, defence and construction industries, several techniques have been developed and adopted by industries for repairing visible or detectable damages on the polymeric structures. However, these conventional repair methods are not effective for healing invisible microcracks within the structure during its service life. In response, the concept of self-healing polymeric materials was proposed in the 1980s [7] as a means of healing invisible microcracks for extending the working life and safety of the polymeric components. The more recent publications in the topic by Dry and Sottos [8] in 1993 and then White et al. [9] in 2001 further inspired world wide interests in these materials [10]. Examples of such interests were demonstrated through US Air force [11] and European Space Agency [12] investments in self-healing polymers, and the strong presence of polymers at the First International Conference on Self-healing Materials organized by the Delft University of Technology of the Netherlands in February 2007.

**Nomenclature**

| | |
|---|---|
| $\varepsilon$ | elongation to break |
| $\eta$ | fatigue-healing efficiency |
| $\sigma$ | fracture stress |
| $\Delta K$ | change in $K_I$ during fatigue cycling |
| $\lambda$ | wavelength |
| A6ACA | acryloyl-6-amino caproic acid |
| BDMA | benzyl dimethylamine |
| CQ | camphorquinone |
| DA | Diels–Alder |
| DBTL | di-*n*-butyltin dilaurate |
| DCB | double-cantilever beam |
| DCPD | dicyclopentadiene |
| DETA | diethylenetriamine |
| DGEBA | diglycidyl ether of bisphenol-A |
| DMA | dimethylaniline |
| DSC | differential scanning calorimetry |
| $E$ | fracture energy |
| EMAA | poly(ethylene-*co*-methacrylic acid) |
| ENB | 5-ethylidene-2-norbornene |
| ESR | electron spin resonance |
| $G_Q$ | strain energy-release factor |
| HOPMDS | hydroxyl end-functionalized polydimethyl-siloxane |
| $I$ | molecular parameters |
| $K_I$ | stress intensity factor |
| $K_{IMax}$ | maximum stress intensity factor |
| $K_{IQ}$ | critical stress intensity factor |
| LDPE | low-density polyethylene |
| MA | methacrylic acid |
| $M_w$ | molecular weight |
| $N$ | number of cycles in a fatigue test |
| NBE | norbornene |
| NMA | nadic methyl anhydride |
| NMR | nuclear magnetic resonance |
| OH | hydroxyl group |
| PBE | polybisphenol-A-*co*-epichlorohydrin |
| PC | polycarbonate |
| PDES | polydiethoxysiloxane |
| PEEK | polyether–ether–ketone |
| PET | poly(ethylene terephthalate) |
| PMMA | poly(methyl methacrylate) |
| PMEA | poly(methoxy ethylacrylate) |
| PROMP | photo-induced ring-opening metathesis polymerization |
| PS | polystyrene |
| ROMP | ring-opening metathesis polymerization |
| SEM | scanning electron microscopy |
| TBC | *paratert*butylcatechol |
| TCE | 1,1,1-tris-(cinnamoyloxymethyl) ethane |
| TDCB | tapered double-cantilever beam |
| TEGDMA | triethyleneglycol dimethylacrylate |
| TEM | transmission electron microscopy |
| TEMPO | 2,2,6,6-tetramethyl-piperidine-1-oxy |
| $T_g$ | glass transition temperature |
| TGA | thermo-gravimetric analysis |
| UDME | urethane dimethacrylate |
| UF | urea-formaldehyde |
| UV | ultraviolet light |

Conceptually, self-healing polymeric materials have the built-in capability to substantially recover their load transferring ability after damage. Such recovery can occur autonomously or be activated after an application of a specific stimulus (e.g. heat, radiation). As such, these materials are expected to contribute greatly to the safety and durability of polymeric components without the high costs of active monitoring or external repair. Throughout the development of this new range of smart materials, the mimicking of biological systems has been used as a source of inspiration [13]. One example of biomimetic healing is seen in the vascular-style bleeding of healing agents following the original self-healing composites proposed by Dry and Sottos [8]. These materials may also be able to heal damage caused by insertion of other sensors/actuators, cracking due to manufacturing-induced residual stresses, and fiber de-bonding.

An ideal self-healing material is capable of continuously sensing and responding to damage over the lifetime of the polymeric components, and restoring the material's performance without negatively affecting the initial materials properties. This is expected to make the materials safer, more reliable and durable while reducing costs and maintenance. Successful development of self-healing polymeric materials offers great opportunities for broadening the applications of these lightweight materials into the manufacture of structural and critical components.

Healing of a polymeric material can refer to the recovery of properties such as fracture toughness, tensile strength, surface smoothness, barrier properties

and even molecular weight. Due to the range of properties that are healed in these materials, it can be difficult to compare the extent of healing. Wool and O'Connor [14] proposed a basic method for describing the extent of healing in polymeric systems for a range of properties (Eqs. (1)–(4)). This approach has been commonly adopted as discussed in later sections, and has been used as the basis for a non-property-specific method of comparing "healing efficiency" (Eq. (5)) of different self-healing polymeric systems

$$R(\sigma) = \frac{\sigma_{\text{healed}}}{\sigma_{\text{initial}}} \quad (1)$$

$$R(\varepsilon) = \frac{\varepsilon_{\text{healed}}}{\varepsilon_{\text{initial}}} \quad (2)$$

$$R(E) = \frac{E_{\text{healed}}}{E_{\text{initial}}} \quad (3)$$

$$R(I) = \frac{I_{\text{healed}}}{I_{\text{initial}}} \quad (4)$$

$$\text{Healing efficiency} = 100 \times \frac{\text{Property value}_{\text{healed}}}{\text{Property value}_{\text{initial}}} \quad (5)$$

where $R$, $\sigma$, $\varepsilon$, $E$ and $I$ represent the recovery ratios relating to fracture stress, elongation at break, fracture energy and molecular parameters, respectively.

This review briefly describes the fracture mechanics of polymeric materials and the traditional methods of repairing damage in these materials to provide the context for our focus of highlighting major advancements in design and development of self-healing polymeric materials during the last 15 years. Tables 1 and 2 provide summaries of these developments. It can be seen that both molecular and structural approaches were investigated for self-healing of thermoplastic and thermoset materials although the research interests have been shifted to

Table 1
Developments in self-healing polymers

| Matrix | Healing type | Healing method | First report of method | Best efficiency achieved | Test method | Healing conditions |
|---|---|---|---|---|---|---|
| Thermoplastic | Molecular | Molecular interdiffusion (thermal) | 1979 [67] | 120% [67] | Fracture toughness | 7–8 min at 115 °C |
| | | Molecular interdiffusion (solvent) | 1990 [44] | 100% [44] | Fracture toughness | 4–5 min at 60 °C |
| | | Reversible bond formation | 2001 [91] | 100% [94] | Puncture closure | <1 min at −30 °C |
| | | Recombination of chain ends | 2001 [82] | 98% [88] | Tensile strength<br>Molecular weight | 600 h at Ambient<br>600 h at Ambient |
| | | Photo-induced healing | 2004 [77] | 26% [77] | Flexure strength | 10 min at 100 °C |
| | | Living polymer | 2005 [95] | – | – | – |
| | Structural | Nanoparticle healing | 2004 [99] | Impeded Crack Growth [102] | Visual inspection | Ambient |
| Thermoset | Molecular | Chain re-arrangement | 1969 [189] | 100% [187]<br>100% [189] | Visual inspection<br>Fracture toughness | 10 min at ambient<br>150 °C |
| | | Thermally reversible crosslinks | 2002 [170] | 80% [169] | Fracture toughness | 30 min at 115 °C then 6 h at 40 °C |
| | | Ion-mediated healing | 2006 [13] | 75% [13] | Tensile strength | 12 h at ambient |
| | Structural | Microencapsulation approach | 1997 [120,121,162] | 213% [135]<br>93% [127]<br>14% [136] | Fatigue resistance<br>Fracture toughness<br>Tensile strength | Ambient<br>24 h at Ambient<br>24 h at ambient then 24 h at 80 °C |
| | | Thermoplastic additives | 2005 [184] | 65% [186] | Impact strength | 1 h at 160 °C |
| | | Healing via passivation | 1998 [202] | – | – | – |
| | | Memory shape alloy | 2002 [195] | – | – | – |
| | | Healing via swelling | 2005 [201] | – | – | – |

Table 2
Developments in self-healing polymer composites

| Host matrix | Healing type | Healing method | First report of method | Best efficiency achieved | Test method | Healing conditions |
|---|---|---|---|---|---|---|
| Thermoset composites | Structural | Microencapsulation approach | 2001 [163] | 80% [122,163]<br>19% [136] | Fracture toughness<br>Tensile strength | 48 h at 80 °C<br>24 h at Ambient then 24 h at 80 °C |
| | | Thermoplastic additives | 1999 [183] | 100% [183]<br>30% [186] | Flexure strength<br>Tensile strength<br>Visual | 10 min at 120 °C<br>10 min at 120 °C<br>2 h at 130 °C |
| | | Hollow-fiber Approach | 1996 [109] | 93% [114] | Flexure strength | 24 h at Ambient |

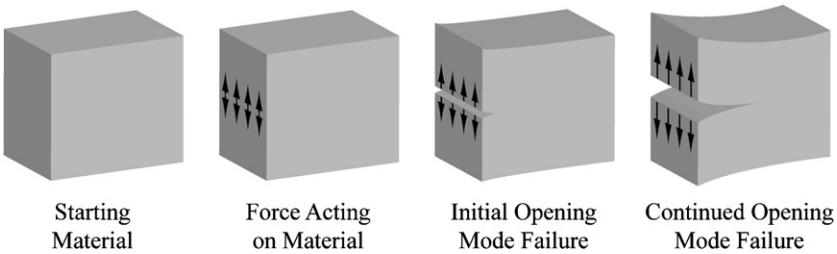


Fig. 1. Mode 1 opening failure in a material [1].

thermoset-based systems in recent years. We will also describe and discuss the different approaches proposed to prepare and characterize the self-healing systems, the methods for evaluating self-healing efficiencies, the applicability of the concepts to composites and structural components, and the challenges and future research opportunities.

## 2. Fracture mechanics of polymeric materials

Although thermal, chemical and other environmental factors can cause damage in polymers, impact and cyclic fatigue associated failures are receiving the most attention for structural applications of polymeric materials [15]. Both of these failure mechanisms proceed via crack propagation, with a monotonic load experienced during impact-type incidents and cyclic loads experienced during fatigue. Crack propagation [16–18] and the mechanics [19,20] associated with these failures in polymeric materials have been modeled and researched extensively.

For a crack to propagate, the energy released during cracking must be equal to, or larger than the energy required to generate new surfaces on the material [1,21]. Although new models for crack propagation are still being developed [22,23], most crack propagation modeling is based on a parameter called the ($K_I$) [24,25]. During crack opening-type failure growth (mode I in Fig. 1), $K_I$ is related to crack depth, material/crack geometry and the applied stresses. As the applied stress and crack geometry change during monotonic or cyclic loading, a critical stress intensity factor ($K_{IQ}$) is reached and then crack growth occurs. During an impact damage incident (consisting of a monotonic load) the extent of crack propagation is related to the maximum stress intensity factor ($K_{IMax}$) experienced. During fatigue-type damage crack propagation is related to both $K_{IMax}$ and the change in $K_I$ during cycling ($\Delta K$) [26]. In order to heal cracked polymers, the fractured surfaces need to be resealed or alternatively crack growth must be impaired.

Fig. 2 demonstrates a number of methods to retard crack growth [24,27]. Basically, crack growth retardation occurs when energy is dissipated within the loaded material without extending an existing crack. Intrinsic crack growth retardation can be achieved through selection of appropriate monomer and curing agent system [28,29], varying the ratio of curing components [30–32], or use of additives or

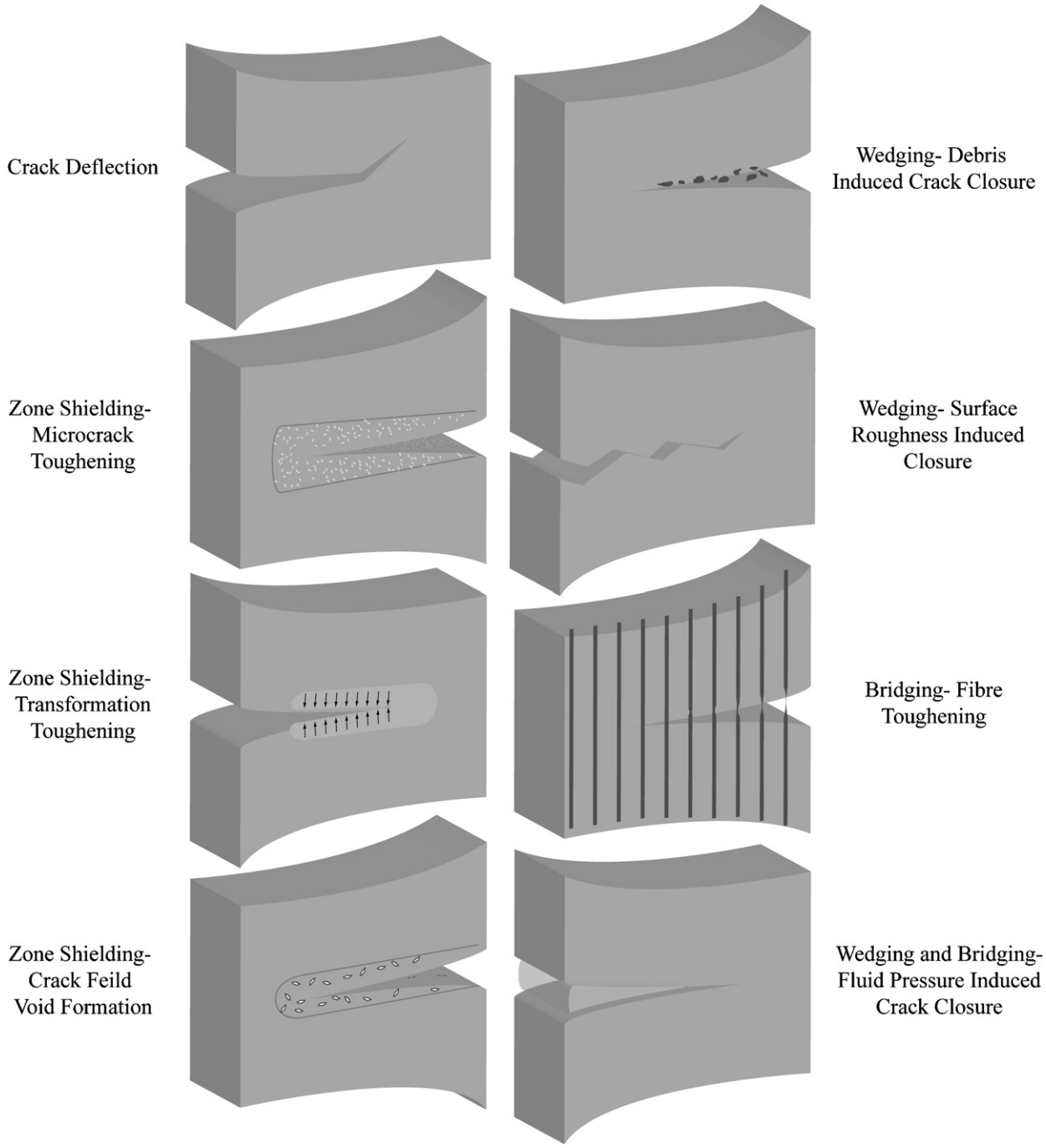


Fig. 2. Extrinsic mechanisms of crack growth retardation [24].

modifiers [33–35]. These intrinsic approaches to crack growth retardation provide alternative avenues for stress relief within the original structure, and they are generally used to improve the intrinsic properties of the virgin materials rather than to heal-damaged components.

Extrinsic crack growth retardation mechanisms are used as the primary method of repairing damage in both the traditional and the self-healing techniques. This generally involves dissipation of energy away from the propagating crack tip via a mechanical change behind the crack tip. Additives can act

as intrinsic toughenes, and as extrinsic toughenes when they are stretched or compressed in the void behind the crack tip [36]. A more common extrinsic toughening mechanism is that of patching, where a cracked surface is covered or filled with a rigid material. Patching can provide bridging- and wedging-type mechanical support for the damaged material, retarding crack propagation and restoring structural integrity to the polymer composite. Existing techniques for producing self-healing polymeric materials that utilize extrinsic toughening mechanisms are the focus of this review.

## 3. Traditional repair methods for polymeric materials

### 3.1. Repair of advanced composites

Traditional methods for healing or repairing advanced composites include welding, patching, and *in-situ* curing of new resins.

#### 3.1.1. Welding

Welding enables the rejoining of fractured surfaces (closing cracks) or fusing new materials to the damaged region of the polymer composite. It relies on formation of chain entanglements between two contacting polymer surfaces [37] and is designed to reinstate the original physical properties of the damaged area [14,38]. During welding, the two polymer surfaces pass through a series of transitions including surface rearrangement, surface approach, wetting and then diffusion [14,39]. Once these processes have been completed and entanglement of the polymer chains has occurred, the two surfaces are fused together and the repair is complete. Factors such as welding temperature [40,41], surface roughness [7,42], chemical bonding between the surfaces [43] or the presence of solvents [44,45] directly affect the rate and extent of repair that can be achieved. Although welding is most commonly used on thermoplastic materials, its application to thermosets was explored by Chen et al. [46] with thermally re-workable thermosets and by Stubblefeild et al. [47] with the use of the pre-impregnated patches (prepreg). Chen et al. [46,48,49] used cycloaliphatic epoxies containing tertiary ester linkages to produce resins that can be degraded thermally and then reworked. Although other re-workable epoxies had been reported elsewhere [50,51], the use of tertiary ester linkages enables reworking at relatively low temperatures [46]. Experiments on these epoxies are yet to be explored beyond the degradation processes [48], however reworking of these systems may include their use in polymer composite welding applications. Stubblefeild et al. [47] employed virgin materials for joining composite pipes. The thermally cured resins containing both continuous and chopped fibers were applied to the pipes, wrapped in shrink tape to produce a join resembling a patching-type repair.

#### 3.1.2. Patching

Patching repairs differ from the welding repairs in that they involve the covering or replacing of the damaged material with a new material. The new material can be attached via mechanical fastening or adhesive bonding in order to provide additional mechanical strength to the damaged region. Patching repairs may be achieved by direct attachment of superficial patches [52], removal of the damaged material followed by attachment of superficial patches [53] or, removal of damaged material followed by insertion of replacement material and superficial patches [54]. The extent of property recovery as a result of the repair is dependent upon factors such as the interface between the patch and the original material [55], the presence/orientation of reinforcing fibers [56,57], and the thickness of the patch [53,58].

#### 3.1.3. In-situ curing of new resin

A third method of repairing polymers and polymer composites is that of *in-situ* curing of a new resin. This technique is similar to patching, in that the new material is used to reinforce the mechanical strength. In fact, some patching techniques involve direct addition of the uncured resin to an excavated section of the original polymer [55–57]. The uncured resin diffuses into the damaged component and deepens the adhesive region that holds the patch in place [59]. However, relatively little attention has been given to this repair mechanism, with the few published papers available reporting mixed results [60–62].

### 3.2. Repair of thermoplastics

The methods for thermoplastic repair include (i) fusion bonding through resistance heating, infrared welding, dielectric and microwave welding, ultrasonic welding, vibration welding, induction welding and thermobond interlayer bonding, (ii) adhesive bonding and mechanical fastening such as riveting [63–66].

Fusion bonding and adhesive bonding/mechanical fastening work in essentially the same way as do welding and patching repairs, respectively.

The traditional methods for repairing both advanced composites and thermoplastics are costly, time consuming, and require reliable detection techniques and a skilled work force. They are mainly applicable to the repair of external and accessible damages instead of the internal and invisible microcracks. The development of self-healing polymeric materials is expected to fill this technological gap.

## 4. Self-healing of thermoplastic materials

Self-healing of thermoplastic polymers can be achieved via a number of different mechanisms and is a well-known process [67]. A detailed description of these approaches is given below.

### 4.1. Molecular interdiffusion

Crack healing of thermoplastic polymers via molecular interdiffusion has been the subject of extensive research in the 1980s. The polymers investigated cover amorphous, semi-crystalline, block copolymers, and fiber-reinforced composites. It has been discovered that when two pieces of the same polymer are brought into contact at a temperature above its glass transition ($T_g$), the interface gradually disappears and the mechanical strength at the polymer–polymer interface increases as the crack heals due to molecular diffusion across the interface. The healing process was examined at atmospheric pressure or in vacuum, for healing times ranging from minutes to years, and at healing temperatures above the $T_g$ of the polymers that typically varied from $-50$ to $+100\,^{\circ}C$.

Jud and Kausch [67] studied the effect of molecular weight and degree of copolymerization on the crack healing behavior of poly(methyl methacrylate) (PMMA) and PMMA–poly(methoxy ethylacrylate) (PMEA) copolymers. The self-healing ability of the copolymers was tested by clamping and heating these samples in which the fractured surfaces (of single-edge notched and compact tension specimens) were brought together and held for set periods of time. Various experimental parameters were investigated, which included the time between fracturing and joining of the fractured surfaces, the healing time, the healing temperature and the clamping pressure. It appeared that a temperature of $5\,^{\circ}C$ higher than the $T_g$ and a healing time of over 1 min were required to produce healing greater than that could be attributed to simple surface adhesion. An increase of the time between fracture initiation and self-healing of the fractured surfaces was found to significantly inhibit healing, dropping optimum property recovery from 120% to 80%. Visual healing of the fracture surfaces was found to occur before a significant recovery in strength was achieved, with the inter-diffusion of numerous chain segments (rather than entire chains) being reported as the most likely healing mechanism.

A number of researchers [14,68,69] subsequently proposed various models to explain the phenomenon of crack healing at the thermoplastic interface such as the reptation model of chain dynamics developed by de Gennes [70], and later Doi and Edwards [71]. In particular, Wool and O'Connor [14] suggested a five stages model to explain the crack healing process in terms of surface rearrangement, surface approach, wetting, diffusion and randomization (Fig. 3). Kim and Wool [72] also presented a microscopic theory for the diffusion and randomization stages. Kausch and Jud [73] observed that the development of the mechanical strength during the crack healing process of glassy polymers is related to interdiffusion of the molecular chains and subsequent formation of molecular entanglements. The research carried out by Wool et al. [74,75] confirmed that the phenomena of crack healing in the thermoplastics occur most effectively at or above the $T_g$ of these materials. Research in this area slowed down since the beginning of the 1990s.

Utilizing thermoplastics chain mobility with a minimal application of heat, Lin et al. [44] studied crack healing in PMMA by methanol treatment from 40 to 60 °C. The authors found that the tensile strength of PMMA treated by methanol can be fully recovered to that of the virgin material. The extent of the healing defined by the recovery of tensile strength is found to depend on wetting and diffusion. The presence of methanol facilitates both processes as a result of reducing the $T_g$ and promoting diffusion of the polymer chains across the interface. A subsequent study [45] examined ethanol-induced crack healing in PMMA in a similar manner to the methanol work for comparison purpose. It is observed that the crack-healing process in the presence of ethanol is similar to that of methanol in terms of the plasticization effect and

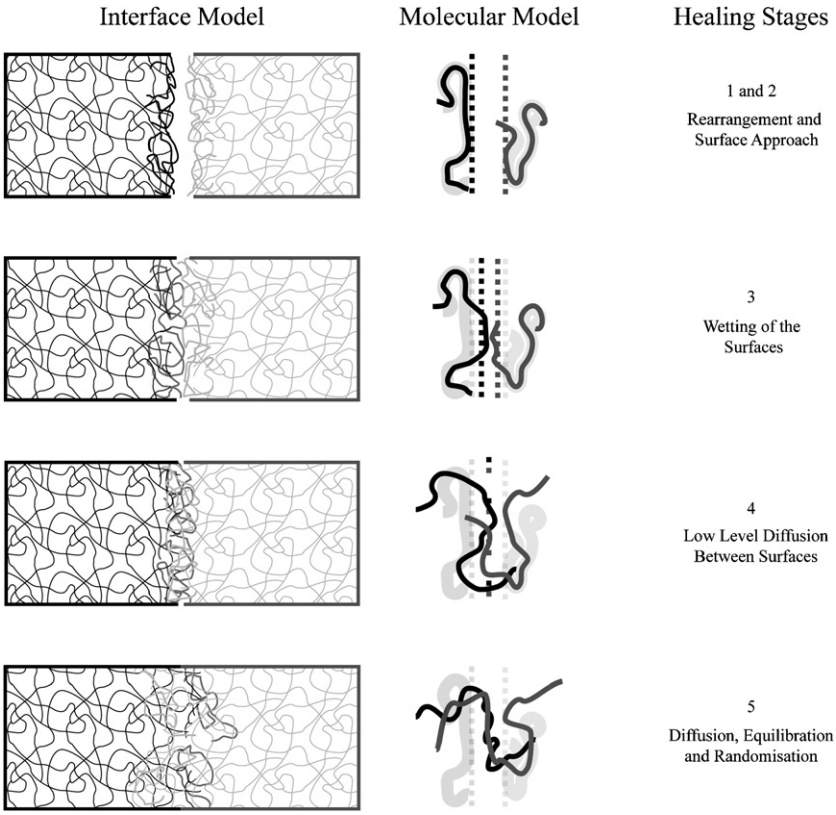


Fig. 3. Mechanisms involved in self healing via molecular interdiffusion [14,72].

the reduction of the $T_g$. However, ethanol causes excessive plasticization and swelling in the PMMA matrix, leading to incomplete recovery of the mechanical strength.

In a couple of recent publications, Boiko et al. [40] used tensile test to determine the healing at the PET and PS interfaces, studying the joining of the virgin rather than fractured surfaces. It was shown that virgin PET/PET, and PET/PS joints experienced only low levels of adhesion even after 15 h treatment at 18 °C over their $T_g$. Yang and Pitchumani [76] studied interfacial healing of carbon-reinforced polyether–ether–ketone (PEEK) and polyether–ketone–ketone (PEKK) under non-isothermal conditions. After different processing times, the strength of the thermally bonded plates was compared with their ultimate shear strength. All of the systems tested reached 100% efficiency and a model was proposed for the non-isothermal healing of the thermoplastic surfaces, but this model appears to be more applicable to polymer processing than repair.

### 4.2. Photo-induced healing

The first example of photo-induced self-healing in PMMA was reported by Chung et al. [77]. The photochemical [2 + 2] cycloaddition of cinnamoyl groups was chosen as the healing mechanism since photo-cycloaddition produced cyclobutane structure [78] and the reversion of cyclobutane to the original cinnamoyl structure readily occurs in a solid state [79] upon crack formation and propagation. The feasibility of this concept was tested by blending a photo-cross-linkable cinnamate monomer, 1,1,1-tris-(cinnamoyloxymethyl) ethane (TCE) with urethane dimethacrylate (UDME), triethyleneglycol dimethylacrylate (TEGDMA)-based monomers, and a visible-light photoinitiator camphorquinone (CQ) (Fig. 4). The mixture was polymerized into a very hard and transparent film after irradiation for 10 min with a 280 nm light source. Healing of the fractures in these films was achieved by re-irradiation for 10 min with a light of $\lambda > 280$ nm. The healing was shown to only occur upon exposure to

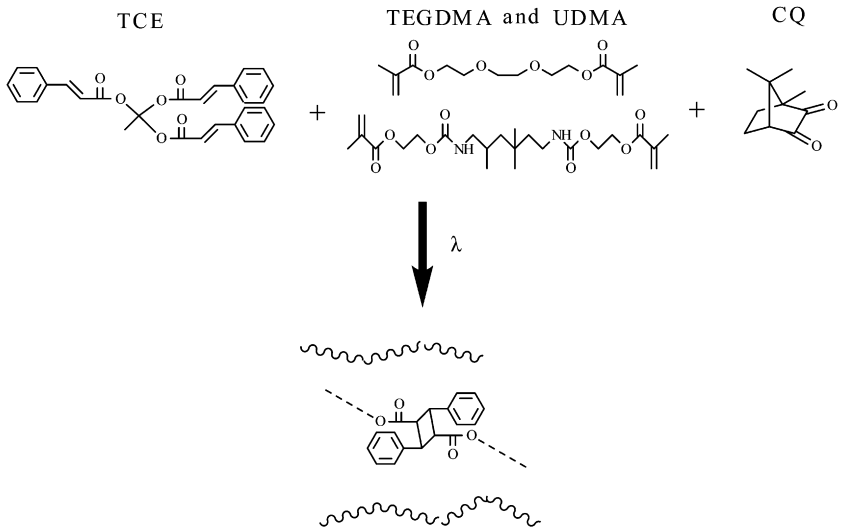


Fig. 4. Route to producing photo-healable PMMA as reported by Chung et al. [77,223].

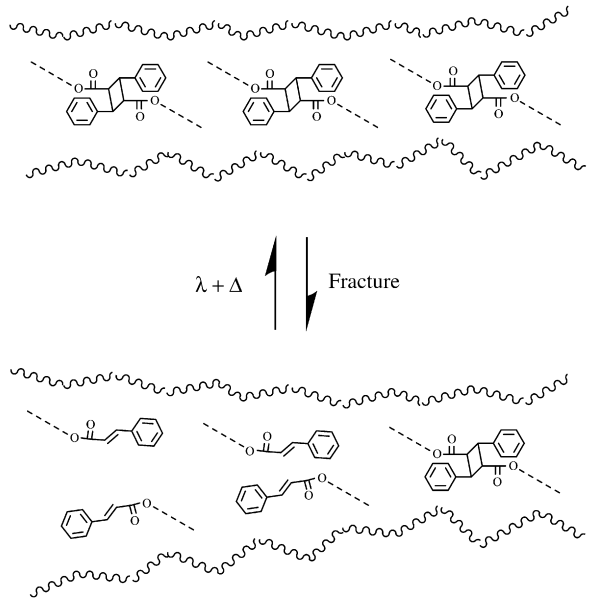


Fig. 5. Mechanism of fracture and repair of photo-induced healing in PMMA [77].

the light of the correct wavelength, proving that the healing was light initiated. Healing efficiencies in flexural strength up to 14% and 26% were reported using light or a combination of light and heat (100 °C). A mechanism of fracturing and healing was proposed (Fig. 5). In this particular system, however, healing was limited to the surfaces being exposed to light, meaning that internal cracks or thick substrates are unlikely to heal.

### 4.3. Recombination of chain ends

Recombination of chain ends is a relatively new technique proposed to heal structural (strength loss) and molecular (chain scission) damages in certain thermoplastics. This approach relies on neither constrained chain confirmations to promote site-specific chain scission nor an external source of energy such as UV light as discussed above.

Takeda et al. [80,81] has shown that some engineering thermoplastics prepared by condensation reactions such as polycarbonate (PC), polybutylene terephthalate (PBT), polyether–ketone (PEK), and PEEK, can be healed by a simple reaction that reverses the chain scission. Polyphenylene ether (PPE) was employed as a model system for investigating this self-healing behavior by Imaizumi et al. [82] in 2001. The authors observed that the self-healing reaction of this polymer did occur in the solid state, and a series of events was identified prior to and during the healing process. These events include (i) occurrence of chain cleavage due to degradation; (ii) diffusion of oxygen into the polymer materials; (iii) re-combination of the cleaved chain ends by the catalytic redox reaction under oxygen atmosphere and in the presence of copper/amine catalyst; and (iv) water discharge as a result of the self-healing reaction.

As such, the kinetics of the self-healing reaction was found to depend on factors such as oxygen concentration and mobility of the polymer chain (affected by the concentration of the plasticizer). It was also observed that the speed of the healing reaction decreases with an increase of the reaction time due to a reduction of the polymer chain mobility with increasing molecular weight as the reaction progresses and a gradual decrease of available hydroxyl (OH) end groups as they are consumed by the recombination reaction. The healing efficiency of this specific system was not discussed in the paper.

The recombination of chain ends approach has also been investigated for healing of the PC suffering from thermal, UV or hydrolysis degradations [83–87]. The feasibility of the healing process was found to depend on the type of end groups present, which is in turn affected by the synthesis method of the PC. It has been reported [88] that although the repair of the standard PC prepared by bisphenol-A and phosgene was not feasible, the use of sodium carbonate ($Na_2CO_3$) as a healing agent for the PC prepared by ester exchange of a diester carbonate and a hydroxyl compound (Fig. 6) was successful. Healing efficiencies up to 98% in tensile strength and molecular weight recovery were achieved after a healing period of more than 600 h. Self-healing of hydrolysis scissored chains in the PC occurred through recombination of the phenolic end groups and the phenyl end groups and was accelerated by the presence of a small amount (0.1 ppm) of $Na_2CO_3$ (Fig. 7). This healing mechanism is only applicable to a certain type of thermoplastics capable of recombining chain ends via a specific reaction mechanism. This limits the range of polymers and applications to which this technology can be applied.

### 4.4. Self-healing via reversible bond formation

The chain mobility in thermoplastics can also be used to heal fractures at ambient temperatures by inclusion of reversible bonds in the polymer matrix. This provides an alternative approach to the UV light or catalyst-initiated healing of the covalent bonds as discussed in the previous sections, and utilizes hydrogen or ionic bonds to heal damaged polymer networks.

#### 4.4.1. Organo-siloxane

A system exhibiting molecular self-healing via reversible bond formation was patented by Harreld et al. [89] in 2004. The self-healing materials described were relating to the production of polypeptide–polydimethylsiloxane copolymers (Fig. 8) in which the silicon-based primary polymeric networks were grafted or block copolymerized with a secondary network of crosslinking agents (such as peptides). The secondary crosslinking components comprise polymer domains with intermediate-strength crosslinks formed via hydrogen and/or ionic bonding. The intermediate-strength crosslinks provide a good overall toughness to the material while allowing for self-healing due to the possibility of reversible crosslinking. Healing was initiated when the fractured surfaces came in contact either through physical

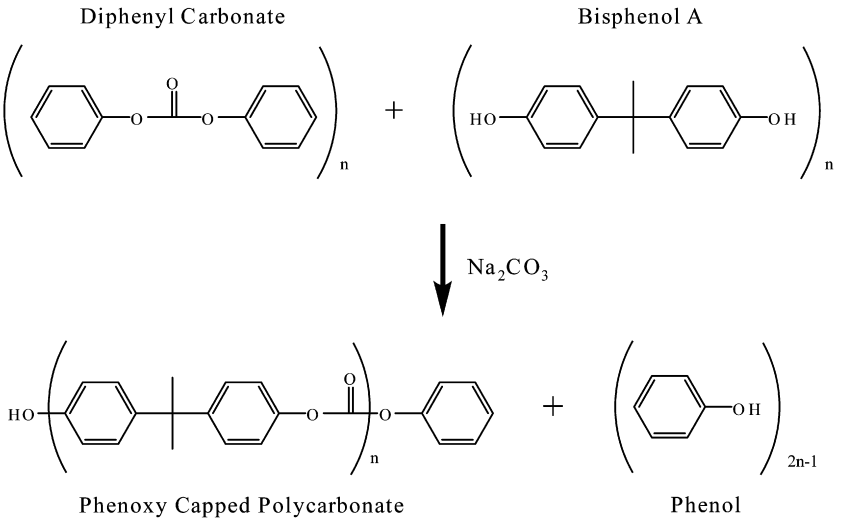


Fig. 6. Reaction mechanism for self-healing PC production [88].

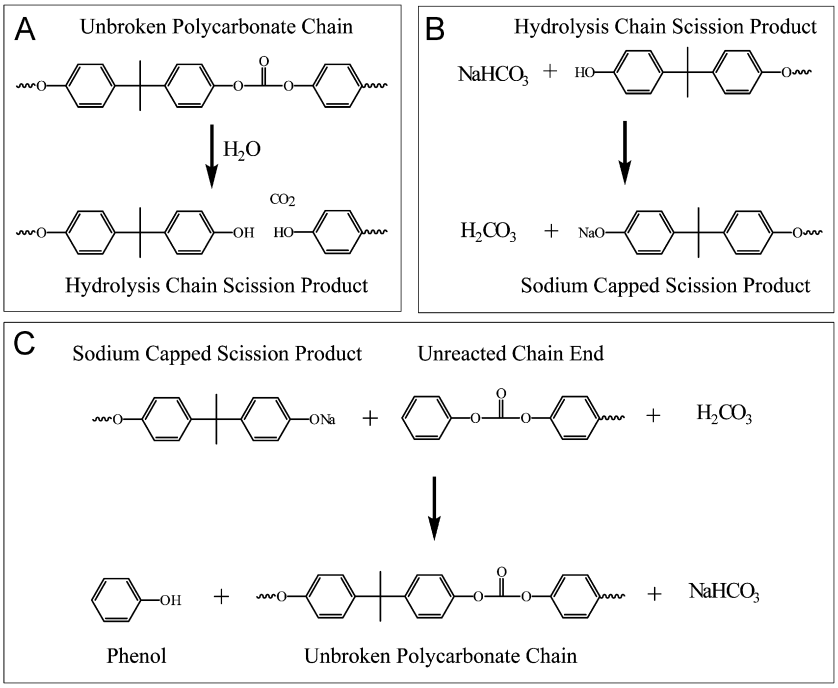


Fig. 7. (A) chain scission (B) healing initiation and (C) healing completion reactions in self-healing PC as proposed by Takeda et al. [81,88].

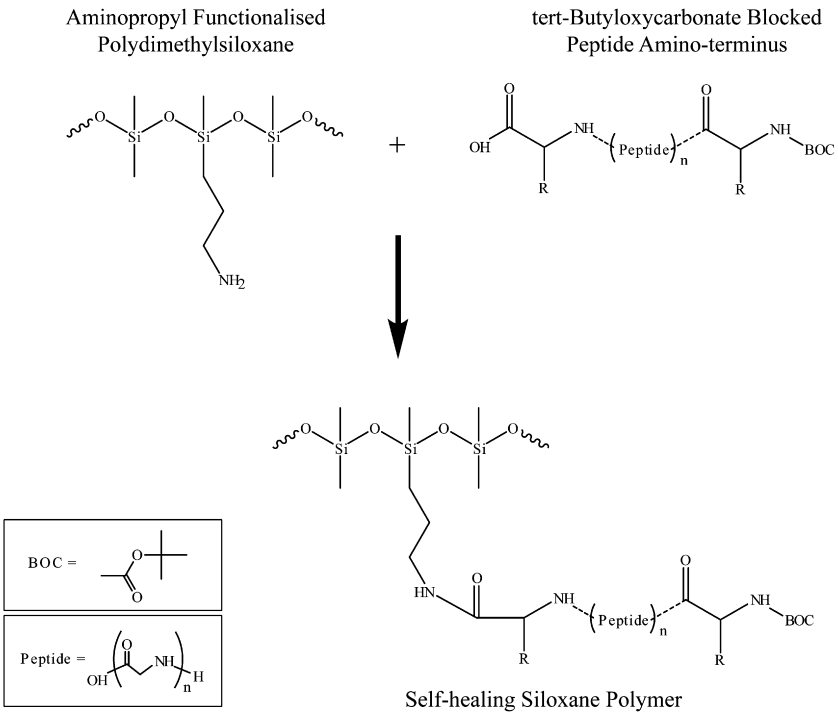


Fig. 8. A production route for self-healing organo-siloxane polymers [89].

closure or via solvent-induced chain mobility. This self-healing approach is similar to that described by Chung et al. [77] in terms of specific chemical linkages being used to enable the healing. However, the Harreld et al. [89] system was not based on covalently bonded chains so healing could take place in the absence of energy such as UV light. Although relatively few experimental details were published, permanent rejoining reportedly occurred either immediately or after several minutes when the fractured surfaces were pressed together. It was claimed that the healing times could be adjusted by varying the structure of the polymer, the degree of crosslinking, or the strength of the crosslinks.

#### 4.4.2. Ionomers

Ionomers are defined as polymers comprising less than 15 mol% ionic groups along the polymer backbone [90]. These polymers have existed since the 1960s; the exploration of their self-healing behavior has only been initiated in recent years. In particular, the self-healing ability of poly(ethylene-*co*-methacrylic acid) (EMAA)-based ionomers (structure shown in Fig. 9) following high-speed impact was investigated [91,92] along with proposals of possible healing mechanisms. While it is recognized that the existing EMAA ionomers with self-healing properties are not suitable for some applications, it is hoped that suitable ionomers could be synthesized or modified by fillers or fibers based on a better understanding of the associated healing phenomenon.

In 2001, Fall [91] examined the self-healing response upon high-speed impact for the following samples containing none or various extent of ionic contents:

- *Nucrel® 925*: EMAA random polymer with 5.4 mol% methacrylic acid (MA).
- *Surlyn®*: EMAA random polymer with 5.4 mol% MA, and has been neutralized with a sodium cation. Surlyn® 8940 has 30% of the 5.4 mol% MA groups neutralized with sodium and Surlyn® 8920 has 60% of the 5.4 mol% MA groups neutralized with sodium.
- *React-A-Seal®*: An ionomer based on Surlyn® 8940, and is marketed for its ability to self-heal upon high-speed impact.

All of the above samples were found to exhibit a certain degree of self-healing behavior even though Nucrel® 925 does not contain any ionic groups. The healing was reported to occur almost instantaneously following projectile puncture. Another important point to note is that the self-healing phenomenon taking place in the EMAA materials is not a small crack but a circular hole of several mm in diameter. While reptation motions may lead to interdiffusion of polymer surfaces, they would certainly not dictate the large-scale motions required to bring the surfaces back together in the case of puncture healing in the EMAA material. Fall [91] proposed that the ionic content and its order–disorder transition was the driving force behind the healing process. It has been hypothesized that the self-healing response was related to ionic aggregation and melt flow behavior of these copolymers. Healing was expected to occur if sufficient energy was transferred to the polymer upon impact, heating the material above its order–disorder transition resulting in disordering of the aggregates. During the post-puncture period, the ionic aggregates have the tendency to reorder and patch the hole. Such a hypothesis cannot explain the observed healing in Nucrel® 925 given the lack of ionic aggregates in this sample although the author attributed it to the existence of a weak aggregation. Therefore, questions remain in relation

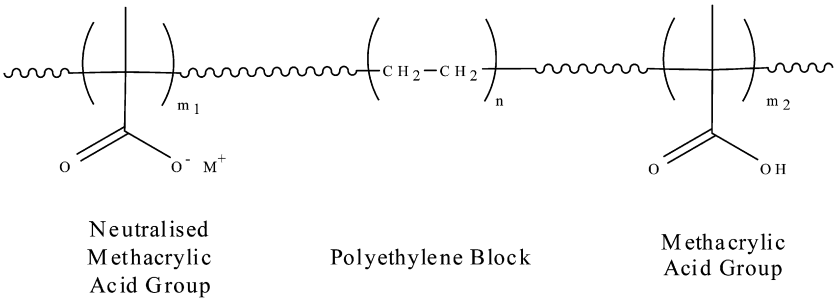


Fig. 9. Structure of a partially neutralized random EMAA ionomers where $M^+$ can be sodium, potassium, zinc, copper or an iron cation [224].

to the reason behind the unexpected healing behavior of Nucrel® 925, which possesses no ionic content.

Research in self-healing ionomers has been continued by Kalista [92,93] who used the EMAA samples listed above, carbon nanotube-filled EMAA composites, and low-density polyethylene (LDPE) for comparative purposes. A number of techniques were used to elucidate the self-healing mechanism involved. These included differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), peel tests, controlled projectile tests, and quantification of healing response by a pressurized burst test. When tested at room temperature, all samples except LDPE, exhibited the self-healing behavior including the base copolymer Nucrel® 925. The lack of self-healing in LDPE suggests that the existence of the ionic functionality and/or the polar acid groups in the EMAA polymers is essential to achieving self-healing. This, together with the self-healing response observed with Nucrel® 925 implies that the polar acid groups are responsible for the self-healing response displayed by these materials.

Of further interest was the discovery that testing the samples at 70 °C hindered rather than helped the healing response [92]. This unexpected phenomenon was thought to be caused by the impact energy being dissipated faster at the elevated temperature without leaving sufficient time for the elastic response of the localized molten polymer to close the puncture. Healing of ballistic impacts in ionomers is also limited at the low temperatures (−25 °C) during which the localized melting around the impact site is significantly reduced [94]. Further research by Kalista and Ward [92,94] led to the proposition that healing was due to the addition of the MA component to the polyethylene structure instead of the ionic attraction. The two main requirements necessary for achieving the self-healing behavior include the need for the puncture event to produce a local melt state in the polymer and for that molten material to have sufficient melt elasticity to snap back and close the hole (Fig. 10).

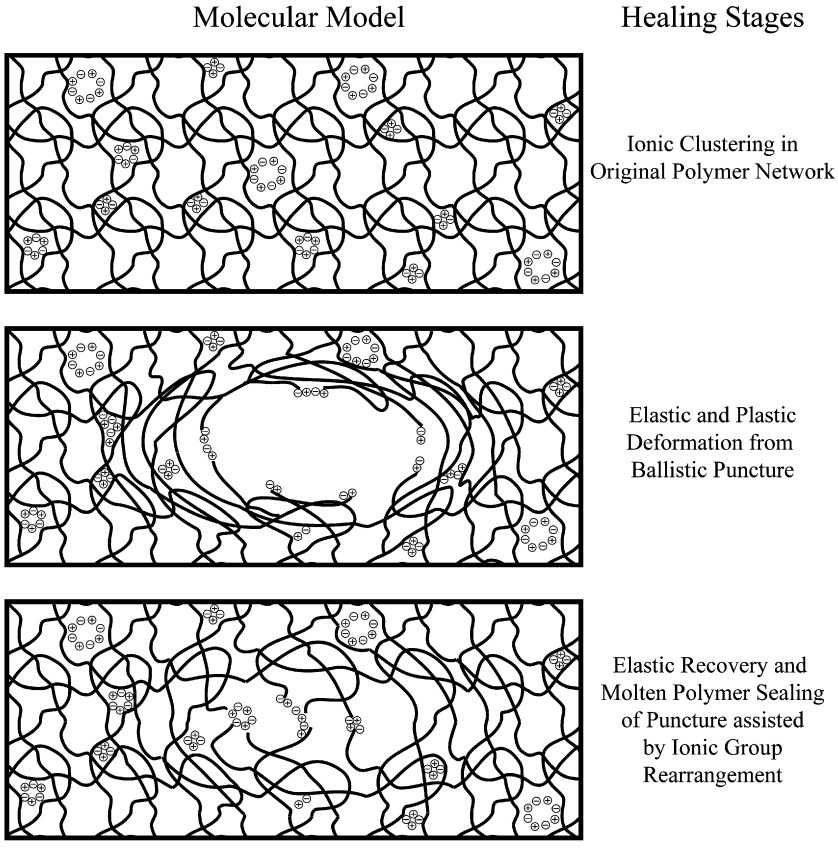


Fig. 10. Theoretical healing mechanism in ionomers [91,92,94].

Although not suitable for healing at elevated temperatures, these self-healing ionomers represent a class of self-healing material that is capable of undergoing repeated healing events at a single damage site without any added healing agents.

### 4.5. Living polymer approach

For the purpose of providing protection against damage mechanisms unique to space applications such as ionizing radiation damage, the development of self-healing polymeric materials using living polymers as the matrix resins has been proposed [95]. These authors suggested preparing living polymers with a number of macroradicals (polymer chains capped with radicals). The living polymers can be theoretically synthesized by either ionic polymerization or free radical polymerization during which the polymer chains grow without chain transfer and termination (Fig. 11) [96–98]. As a consequence, the chain ends of the living polymers are equipped with active groups capable of resuming polymerization if additional monomer is added to the system. The free radical living polymerization is likely more suitable for this purpose considering the high reactivity and stringent conditions required for the ionic living polymerization.

In this approach, the degradation of the material upon exposure to ionization or UV radiation is potentially prevented because of possible recombination reactions between the new free radicals generated and the macroradicals on the chain ends. Such a molecular scale healing process is controlled by the diffusion rate of the macroradicals, which is in turn affected by the $T_g$ of the polymer. Below $T_g$, the diffusion rate of the macroradicals in the condensed state is low, resulting in a slow healing process. The electron spin resonance (ESR) data indicated that such polymers should be capable of providing self-healing capabilities at temperatures up to 127 °C.

Although Chipara and Wooley [95] demonstrated the living polymer approach in a PS matrix, it may also be applicable to thermosets. Such a self-healing system does not require the addition of catalysts in the polymer, and may provide protections for space materials against various degradation environments. However, the concept requires further investigation in terms of working conditions required to prevent premature deactivation of the living radicals and the applicability of the concept to different polymer matrices, etc. It is proposed that such a molecular healing process can be combined with the inclusion of microencapsulated monomers (as described in Section 5.2) to provide a multi-scale self-healing system. As the polymer chains remain active, the release of the monomer in the event of a crack is expected to restart the polymerization process and heal the microcracks.

### 4.6. Self-healing by nanoparticles

Using nanoparticles to repair cracks in polymeric materials is an emerging, but nonetheless interesting approach to creating self-healing materials. This technique is different in that it does not involve breaking and rejoining of polymer chains, as do the self-healing technologies described previously, but rather uses a dispersed particulate phase to fill cracks and flaws as they occur.

As a first attempt to demonstrate self-healing in polymers by nanoparticles, Lee et al. [99] integrated computer simulations with micromechanics to demonstrate that the addition of nanoparticles to multilayer composites yields a self-healing system. This type of polymer–nanoparticle composite actively

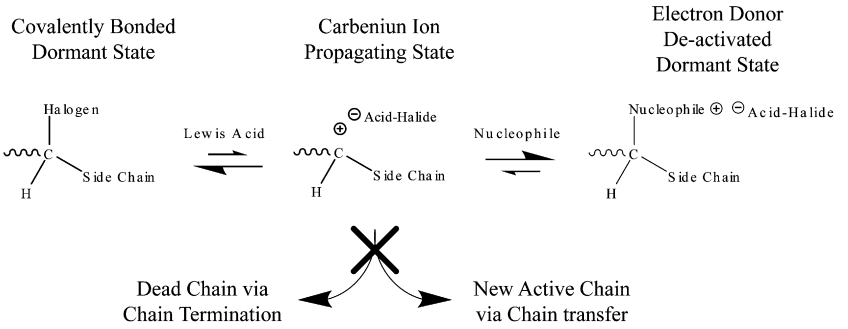


Fig. 11. Mechanism of a living polymerization showing dormant and active state transformation of the polymer without termination or chain transfer [96].

responds to the damage and can potentially heal itself multiple times as long as the nanoparticles remain available within the material. A related publication [100] applied molecular dynamics and lattice spring simulations to model the feasibility of applying nanocomposite coatings to repair nanoscale defects on a surface. The modeling results indicate that nanoparticles have a tendency to be driven towards the damaged area by a polymer-induced depletion attraction, and that larger particles are more effective than small particles for migrating to the damaged region at relatively short time scales. Once particle migration has occurred, the system can then be cooled down so that the coating forms a solid nanocomposite layer that effectively repairs the flaws in the damaged surface.

Some aspects of the above computer simulations were confirmed by Gupta et al. [101], who experimentally demonstrated the migration and clustering of the embedded nanoparticles around the cracks in a multilayered composite structure. The example involves a 50-nm-thick silicon oxide ($SiO_2$) layer deposited on top of a 300-nm-thick PMMA film embedded with 3.8 nm CdSe/ZnS nanoparticles. The migration of the nanoparticles towards the cracks in the brittle $SiO_2$ layer is dependent on the enthalpy and entropic interactions between the PMMA matrix and the nanoparticles. Cross-sectional transmission electron microscopy (TEM) analyses revealed that the nanoparticles were uniformly and preferentially segregated at the interface of PMMA and $SiO_2$ layer when they were surface modified by a polyethylene oxide (PEO) ligand. After a crack is produced in the brittle $SiO_2$ layer, fluorescence microscopy showed that the nanoparticles have migrated towards and clustered around the crack surface, confirming the prediction of the computer simulations [99,100]. The phenomenon of self-healing by nanoparticles has been explained [102] by the polymer chains close to the nanoparticles being stretched and extended, driven by the tendency to minimize nanoparticles–polymer interactions via segregation of the nanoparticles in the crack and pre-crack regions (Fig. 12). In contrast to the findings from the computer simulations [100], the experimental results [101] suggested that the nanoparticles are more effective than the larger particles for healing because they diffuse faster than the larger ones.

One of the key enabling requirements for this type of auto-responsive healing technique relies on the ability to functionalize the surface of the nanoparticles with suitable ligands, similar to that described by Glogowski et al. [103]. Further research and development of this concept is required to confirm the occurrence of healing by the nanoparticles clustered around the cracks in thick substrates, and to develop understanding on the characteristics and durability of the nanoparticles filled cracks.

## 5. Self-healing of thermoset materials

The search for self-healing thermoset materials coincides with these materials being more and more widely used in structural applications. These applications generally require rigid materials with a thermal stability that most thermoplastics do not possess. The rigidity and thermal stability of thermosets comes from their crosslinked molecular structure, meaning that they do not possess the chain mobility so heavily utilized in the self-healing of thermoplastics. As a result of their different chemistry and molecular structure, the development of self-healing thermosets has followed distinctly different routes.

The most common approaches for autonomic self-healing of thermoset-based materials involve incorporation of self-healing agents within a brittle vessel prior to addition of the vessels into the polymeric matrix. These vessels fracture upon loading of the polymer, releasing the low viscosity self-healing agents to the damaged sites for subsequent curing and filling of the microcracks. The exact nature of the self-healing approach depends on (i) the nature and location of the damage; (ii) the type of self-healing resins; and (iii) the influence of the operational environment.

### 5.1. Hollow fiber approach

Dry and Sottos [8,104–110] pioneered the concept of releasing healing chemicals stored in hollow fibers to repair damage. This concept has been initially applied to cementitious materials to alter the cement matrix permeability, repair cracks, prevent corrosion, and as sensors for remedial actions [104–108,110]. The feasibility of this approach was subsequently extended to polymeric materials [8,109].

#### 5.1.1. Manufacture and characterization

In the hollow fiber approach, healing takes place when the healing agent was released from the hollow fibers to fill internal flaws and then cure

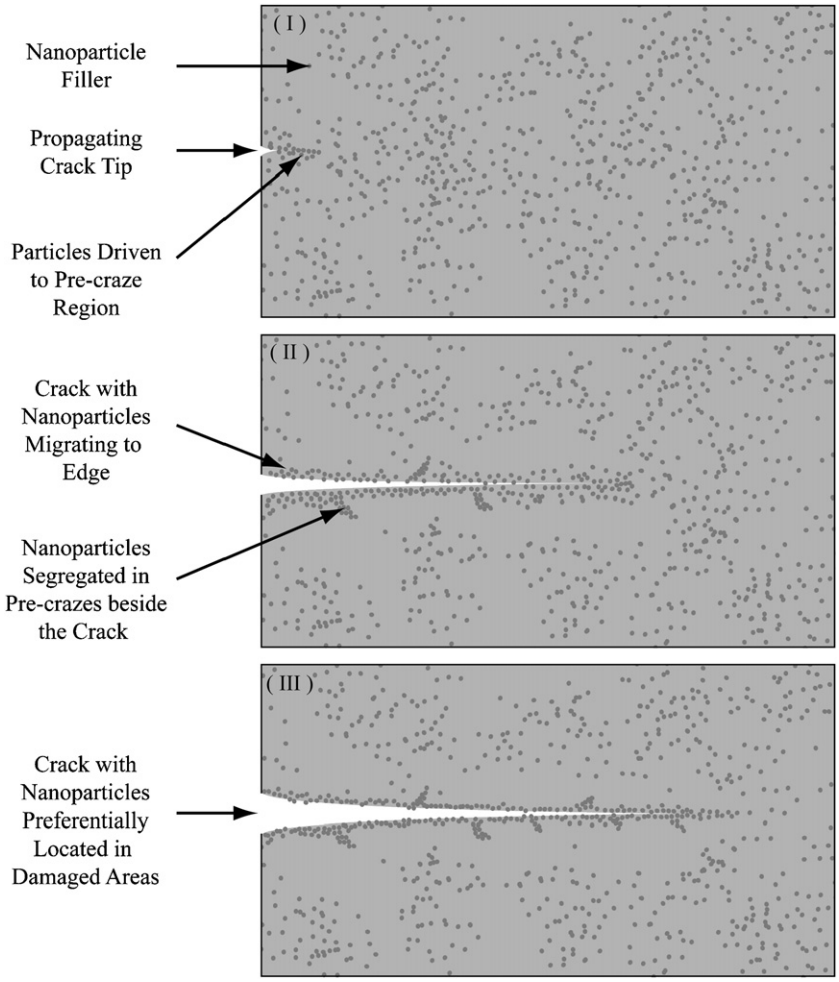


Fig. 12. Schematic diagram of nanoparticle movement during crack growth in thermoplastics.

*in situ* (Fig. 13). Different embodiments of the concept used one part cyanoacrylate or two part epoxy healing agents in conjunction with reinforcing metal wire or glass bead, respectively. Healing in both cases occurred in at least two-third of the samples after repeated exposure to impact and bending tests followed by 8–12 months of healing period. A patent relating to this concept was granted in 2006 [111].

A similar approach was pursued by Motuku et al. [112] in 1999 to study the low impact response of self-healing composite laminates containing hollow repairing tube and solid reinforcing S-2 glass fabric in epoxy and vinyl ester matrices. The effect of different parameters such as the type of storage tubing materials, the number and spatial distribution of the repair tubes as well as the type of healing agents (vinyl ester 411-C50 or EPON-862 epoxy) were investigated. Unidirectional laminates containing one, two, or three repair tubes were successfully manufactured by a vacuum-assisted resin transfer moulding process. Amongst the different tubing materials evaluated, the glass tubing (e.g. borosilicate glass and flint glass) were preferred over the copper and aluminum tubing because their incorporation did not affect the impact failure behavior of the laminates within the energy range considered, and they were broken at the low-energy levels where barely visible damage occurred. The results suggest that the number and spatial distribution of the repair tubes influence the microstructure and impact response of the self-healing laminates. An increase of distance between the repairing tubes and the use of smaller diameter tubes appeared to eliminate the void problem occurred during the manufacturing process. Since the glass tubes used for storing

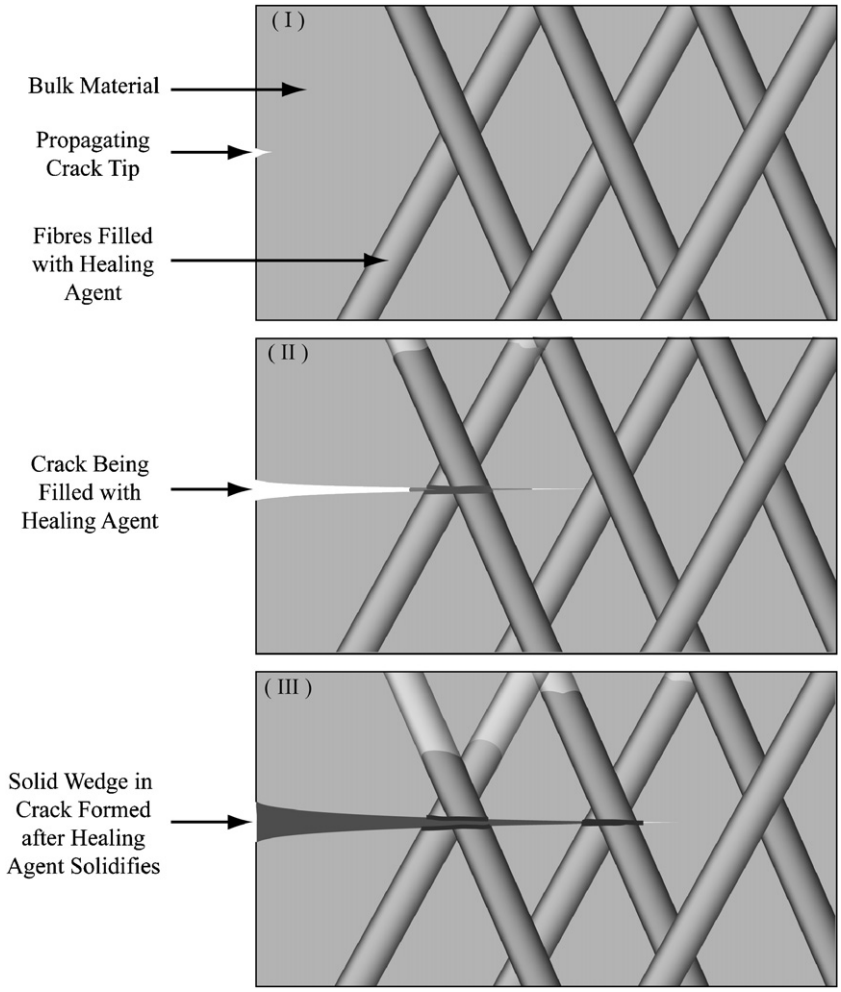


Fig. 13. Concept of healing mechanism in hollow fiber-based self-healing composites [111].

healing chemicals in the work were relatively large in diameter (up to 1.15 mm) in comparison to that of the reinforcing fibers (12 μm) in the laminates, it was suspected that they might cause undesirable stress concentration, resulting in initiation of failure within the composite structure.

In 2001, Bleay et al. [113] developed a self-healing epoxy composite using smaller hollow glass fibers (with external diameter of 15 μm and internal diameter of 5 μm) to function as structural reinforcement and as containers for self-healing chemicals (cyanoacrylate or epoxy) and X-ray opaque dye. The presence of the healing resin in the hollow fiber core did not cause an adverse effect on the impact behavior of the composites. However, the filling and release of the healing chemicals from the fine hollow fibers proved to be problematic, even with a specially developed vacuum-assisted capillary action technique. Filling with the one-part cyanoacrylate resin was not successful because the curing rate of the healing resin was faster than its diffusion rate resulting in the ends of the hollow fibers being blocked. Filling with the two-part epoxy healing system was more feasible although a significant reduction of the resin viscosity was required prior to the filling. This was achieved by heating the chemicals and the composite panels to 60 °C and adding up to 40% acetone into the resin. Since total removal of the solvent from the composite is difficult, there is a chance of bubble formation in the composite during curing. Practical implementation of this approach, particularly in the case of large components, may represent a challenge considering the need to heat up the component and to remove the solvent. Due to the difficulties experienced, the authors recommended the use of larger

hollow glass fibers with an external diameter of 40–60 μm and an internal diameter of 50 μm to avoid some of the manufacturing problems.

Research into producing self-healing composites based on the hollow fiber method was continued by Bond and associates [12,114–117] in recent years. They proposed to use epoxy-based healing agents and UV dye containing hollow fibers as a multi-functional component for structural reinforcement, self-healing, and *in-situ* damage detection. The idea was to tailor the self-healing systems for the specific application by varying the self-healing chemicals, and the number and the position of the healing agent containing hollow fiber layers within the laminate stacks. Pang and Bond [114] used an in-house facility to produce hollow glass fibers of 60 μm external diameter and 50% hollow fraction. The self-healing system under investigation comprised unidirectional hollow glass fibers incorporated into a conventional E-glass/epoxy laminate. Uncured epoxy resin and hardener were chosen as the healing agents, with or without the presence of a UV dye for detection purpose. These were infiltrated into the hollow fibers with the epoxy residing within the 0° layers and the hardener within the 90° layers, respectively. A subsequent study [116] showed that the specimens containing 4-ply of filled hollow glass fibers in a 16 ply E-glass/epoxy laminate could be readily fabricated using the autoclave process.

### 5.1.2. Assessment of self-healing efficiency

The initial study by Dry and co-workers [8] was focused on investigating the mechanism of chemical release from a single repair fiber embedded in a polymer matrix. Controlled cracking of the repair fiber and release of the healing chemicals were achieved by applying a polymer coating to the surface of the repair fiber. Through appropriate choice of coating stiffness and thickness, it was possible to control how and when a repair fiber would fail and consequently release its self-healing chemicals. The release of chemicals into cracks was observed by optical microscopy and photoelasticity. Fiber pull out test was employed to examine the ability to re-bond fibers whereas impact test was used to confirm the ability to fill the cracks. Dry [109] further verified the concept in glass bead-reinforced epoxy composites, and confirmed that the extent of damage within the composite would rupture the 100 μl glass pipettes filled with epoxy resin and hardener separately as the healing agents. However, no specific values of healing efficiency were reported in these initial studies.

Motuku et al. [112] confirmed the release and transport of a liquid dye together with an uncured vinyl ester resin as healing agent into the damaged areas by optical microscopic inspection. However, the healing resin was not cured after release and the mechanical properties after self-healing were not provided.

Bleay et al. [113] enclosed a X-ray opaque dye and the epoxy healing agent in small hollow fibers (15 μm) to improve damage detection. The method was capable of showing the damaged area as indicated by the ingress of the dye into the damaged zone after impact. Healing efficiency assessed by impact test was negligible (approximately 10%) even after exposing the specimens to a combination of heat (60 °C) and vacuum.

In later developments, Pang and Bond [114] subjected the test pieces to impact fracture and to various healing regimes. Filling and release from the hollow fibers remained a challenge with some of the hollow fiber cores being blocked during the specimen preparation. Nevertheless, the freshly prepared self-healing laminates were capable of restoring 93% of flexural strength subsequent to the impact damage. However, the self-healing ability was shown to significantly deteriorate over time, and the specimens lost their healing ability after 9 weeks period. The deterioration was believed to have been caused by the presence of the acetone and the UV dye in the healing agent system.

Healing efficiency tests on specimens containing 4-ply of filled hollow glass fibers in a 16 ply E-glass/epoxy laminate [116] revealed that repair of internal matrix cracking and delamination was accomplished throughout the thickness of the laminates using a two-part epoxy resin (Cycom 823) as the healing agent. This healing agent was specifically chosen to suit the temperature profile of a low earth orbit condition of 90 min at $\pm 100$ °C given the healing materials developed were intended for space applications. However, a 16% reduction in the initial flexural strength was recorded as a result of incorporating the hollow fibers into the E-glass/epoxy laminates. The proposed explanation was that the presence of the larger hollow fibers (60 μm) caused localized crushing of the hollow fibers under the impact site.

Bond et al. also tested the effect of heating on the healing efficiency of the self-healing composites [12,116,118]. The epoxy-based healing system was

found to cure faster upon heating, causing a reduction of healing efficiency to less than 89% due to insufficient time available to disperse the healing agent [116] within the polymer matrix before it started to cure. Although these reduced healing efficiencies are still higher than those reported previously, the damage being healed in these composites had not reached the point of critical failure in the material. Under the testing conditions used by Bond and associates, the composites without any healing agents also had healing efficiencies up to 87% [115], meaning that the highest efficiency achieved in this work actually represent a 10% improvement with respect to the damaged sample without the presence of the healing agent.

While conceptually interesting, the introduction of large hollow fibers in a brittle matrix was shown to achieve a certain level of healing at the expense of the intrinsic mechanical properties of the systems due to stress concentrations [119]. In addition, the hollow fiber concept may not be suitable for healing on a smooth surface due to large diameters of the fibers. Further improvement of the performance and manufacturing ability of this interesting concept is required to make it industrially viable. These include:

- Methods to fill and seal hollow fibers.
- Investigate the feasibility of using alternative hollow fibers such as carbon nanotubes for better performance and compatibility with graphite fibers and carbon fibers containing composite laminates.
- Different sealing agents.
- Development of healing agents to suit different matrices.
- The shelf-life and economics of the chemicals need to be analyzed for practical applications.
- Develop ''re-healing'' capable systems, which provide high strength and high reactivity only when required.
- Effective filling and placing of the hollow fibers in large-scale applications.
- The sealing effectiveness after damage remains to be investigated.

### 5.2. Microencapsulation approach

The microencapsulation approach is by far the most studied self-healing concept in recent years. Table 3 summarizes the type of self-healing systems investigated in the literature, and it is noticed that the self-healing system based on living ring-opening metathesis polymerization (ROMP) has attracted most of the research attentions. This particular approach involves incorporation of a microencapsulated healing agent and a dispersed catalyst within a polymer matrix [120–122]. Upon damage-induced cracking, the microcapsules are ruptured by the propagating crack fronts resulting in release of the healing agent into the cracks by capillary action (Fig. 14). Subsequent chemical reaction between the

Table 3
Literature summary of self-healing chemicals investigated for the microencapsulation approach

| Self-healing agent | Catalyst | Self-healing reaction | Reference |
|---|---|---|---|
| Dicyclopentadiene (DCPD) | Bis(tricyclohexylphosphine) benzylidine ruthenium (IV) dichloride (Grubbs' catalyst) | Ring-opening metathesis polymerization | [9,125–127,130–136,142,143,163,164,218,226] |
| 5-Ethylidene-2-norbornene (ENB) | Bis(tricyclohexylphosphine) benzylidine ruthenium (IV) dichloride (Grubbs' catalyst) | Ring-opening metathesis polymerization | [142] |
| DCPD/ENB blends | Bis(tricyclohexylphosphine) benzylidine ruthenium (IV) dichloride (Grubbs' catalyst) | Ring-opening metathesis polymerization | [143] |
| Mixture of hydroxyl end-functionalised polydimethylsiloxane (HOPMDS) and polydiethoxysiloxane (PDES) | Di-*n*-butyltin dilaurate | Polycondensation | [148] |
| Epoxy | Amine | Polycondensation | [129,227,228] |
| Styrene-based system | Cobalt naphthenate, dimethylaniline | Radical polymerization | [121,162] |

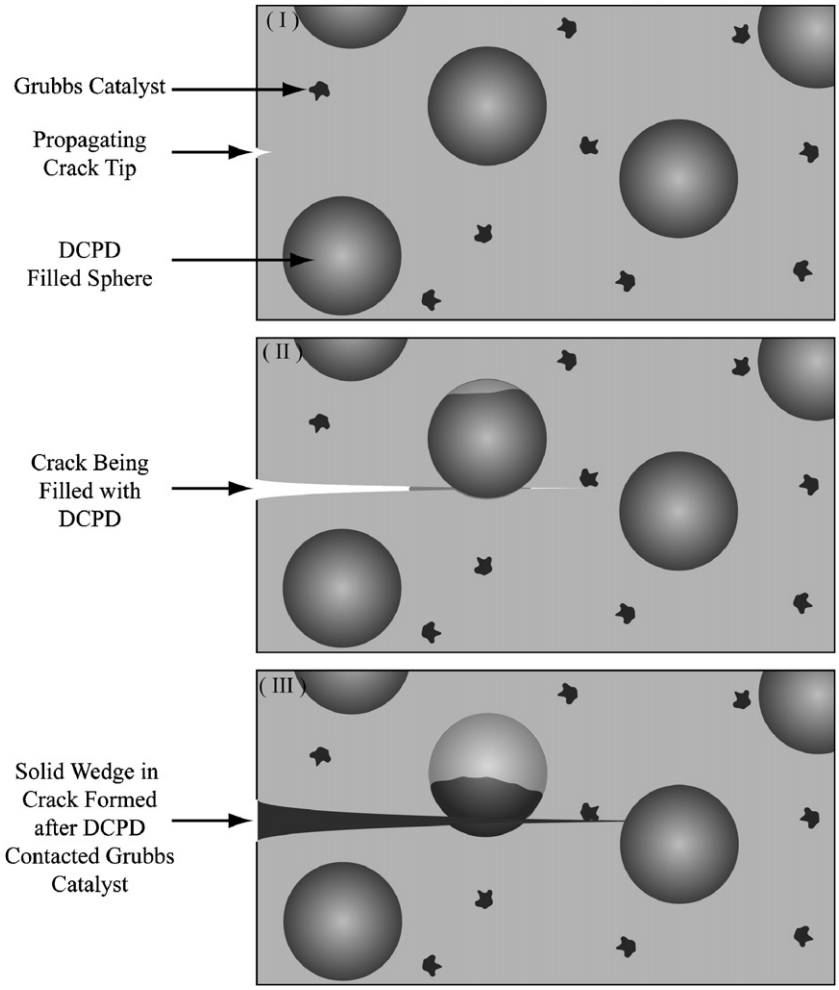


Fig. 14. Microencapsulation self-healing concept [132].

healing agent and the embedded catalyst heals the material and prevents further crack growth. There are some obvious similarities between the microencapsulation and hollow fiber approaches, but the use of microcapsules alleviates the manufacturing problems experienced in the hollow fiber approach.

The microencapsulation approach is also potentially applicable to other brittle material systems such as ceramics and glasses [9]. Although the feasibility of the technology has been mainly tested in epoxy matrices, other matrices such as polyester and vinyl ester have also been investigated. Unlike the hollow fiber approach, Kumar and Stephenson [123] claimed that the microencapsulation approach could be used for producing self-healing coating systems. These coatings were produced by incorporation of self-healing microcapsules (60–150 μm in diameter) in order to control the spalling of lead dust and protect the underlying substrate from damage.

#### *5.2.1. Manufacture and characterization of self-healing microcapsules*

The most successful and extensively investigated self-healing system comprises the ROMP of dicyclopentadiene (DCPD) with Grubbs' catalyst. The synthesis and characterization of the DCPD/Grubbs catalyst system has recently been reviewed [124], and their use as a self-healing agent has been reported [9,125–127]. This system supposedly provides a number of advantages such as long shelf life, low monomer viscosity and volatility, completion of polymerization at ambient conditions in several minutes, low shrinkage upon polymerization, and

formation of a tough and highly crosslinked crack filling material [9]. Repairs made using the ROMP of DCPD/Grubbs' catalyst supposedly form living poly(DCPD) chain ends capable of continuously growing as more monomer is added. If a new monomer is supplied at any time to the end of the chain, further ROMP occurs and the chain extends making it possible to achieve multiple healings simply by replenishing the supply of the DCPD monomer. However, no detailed study has been reported at this stage to demonstrate this particular aspect of the technology.

Microencapsulation in this type of system is required to protect either the healing agent or the catalyst, or both, making the selection and manufacturing of effective self-healing microcapsules the first step towards a successful application of this concept. A suitable self-healing system should be (i) easily encapsulated; (ii) remains stable and reactive over the service life of the polymeric components under various environmental conditions; and (iii) respond quickly to repair damage once triggered. The resulting microcapsules need to possess sufficient strength to remain intact during processing of the polymer matrix, rupture (rather than de-bond) in the event of the crack, capable of releasing the healing agent or catalyst into the crack, and have minimal adverse affects on the properties of the neat polymer resin or reinforced composite.

Microencapsulation of DCPD by a urea-formaldehyde (UF) shell has been carried out by *in-situ* polymerization in an oil-in-water emulsion. Brown and associates [125] systematically studied the influence of process variables such as agitation rate, temperature, and pH on diameter, shell wall thickness, surface morphology and content of the microcapsules. Their results showed that microcapsules with average diameter of 10 to1000 μm could be produced by varying the agitation rate between 200 and 2000 rpm. The mean diameter of the microcapsules reduced as the agitation rate increased. SEM inspection revealed that the shell wall thickness was relatively independent of the manufacturing parameters, and it varied between 160 and 220 nm. Another publication by the same group [128] suggested that microcapsules in this range of shell thickness were suitable for self-healing application because they were sufficiently robust to survive handling and manufacture of the self-healing polymers while still being susceptible to rupture under microcracks for the release of the healing chemicals. During the microencapsulation process, UF nanoparticles were found to form and deposit on the microcapsule surface producing a rough surface morphology. While surface roughness of the microcapsules may enhance mechanical adhesion with the polymer matrix, it is also possible to prevent the deposition of the UF nanoparticles on the microcapsule surface by increasing the DCPD core–water interfacial area. Elemental analysis performed on microcapsules immediately after manufacturing and drying indicated that the microcapsules contained 83–92 wt% DCPD and 6–12wt% UF. However, the DCPD content in the UF microcapsules decreased by 2.3 wt% after 30 days exposure at ambient conditions possibly due to diffusion and leakage of the DCPD out of the UF shell. From a practical point of view, a systematic study is thus required to understand the rate and extent of such reduction under the service conditions of the self-healing components. This may involve variation of the shell wall thickness or the type of microencapsulation shell material.

Evaluation of thermal stability of DCPD/Grubbs catalyst systems by DSC indicated that the thermal decomposition of the Grubbs' catalyst occurred above 120 °C [122]. The UF encapsulated DCPD began to decompose at processing temperatures higher than 170 °C [129]. This means that the DCPD/Grubbs' catalyst-based self-healing system is not suitable for application in high performance structural composite systems where the manufacturing temperatures of the components are likely to be higher than 120 °C.

The DCPD/Grubbs' catalyst systems investigated in various studies typically used DCPD-filled microcapsules with average diameters of 50–460 μm, shell wall thickness of 240 nm, encapsulated DCPD loading of 10–25 wt%, and Grubbs catalyst content of 2.5 wt% or 5 wt% [130–136]. The Grubbs' catalyst is a fine purple powder with a tendency to agglomerate. Availability of active catalyst for crack healing was affected by factors such as the order of mixing, the type of matrix resin, type of curing agent, the catalyst particle size, and the amount of catalyst added [128]. It was suggested that the highest healing efficiency was obtained with 180–355 μm catalyst particle size [128]. Jones et al. [126] showed that the morphology of the Grubbs' catalyst affected its dissolution kinetics, thermal stabilities and resistance to deactivation by the amine-curing agent contained in the epoxy matrix. These characteristics can be used to tailor the catalyst's properties for specific self-healing applications. The smaller catalyst crystals were found to

dissolve faster in the DCPD monomer. Despite this, they do not provide any better healing capability than the larger size catalyst because the smaller size catalysts (sub-micrometer) are more susceptible to deactivation upon exposure to the amine curing agents such as diethylenetriamine (DETA) contained in the epoxy matrix [137–140]. Therefore, the key to achieving optimal healing efficiency is to balance the competing effects of better catalyst protection during fabrication with the larger crystals and faster dissolution in the DCPD healing agent with the smaller crystals.

Rule and co-workers [127] proposed to encapsulate Grubbs' catalyst by wax to overcome the deactivation problem. This was achieved by a hydrophobic congealable disperse phase encapsulation process already established in pharmaceutical applications [141]. The average diameters of the wax encapsulated catalyst ranged from 50 to 150 μm. Analysis by *in-situ* $^{1}$H NMR confirmed that the encapsulated Grubbs' catalyst was protected against deactivation by the DETA curing agent, retaining 69% of its reactivity. The authors also claimed that the encapsulated catalyst was more uniformly dispersed throughout the epoxy matrix although it is difficult to envisage how the hydrophobic wax is compatible with the more hydrophilic epoxy matrix.

Further attempts were made to improve the performance of the self-healing system by replacing DCPD with 5-ethylidene-2-norbornene (ENB) [142] or blending ENB with DCPD [143]. Microencapsulation of ENB was also achieved by *in-situ* polymerization of urea and formaldehyde. This system was supposed to overcome some of the limitations of the DCPD including the low melting point, and the need to use a large amount of catalysts. It is recognized that DCPD is capable of forming a crosslinked structure with high toughness and strength [144–146] whilst ENB polymerizes to a linear chain structure and may possess inferior mechanical properties. However, ENB is known to react faster in the presence of a lower amount of Grubbs' catalyst, has no melting point, and produces a resin with a higher $T_g$ [142,147]. Hence, a blend of DCPD with ENB was believed to provide a more reactive healing system with acceptable mechanical properties, making it more suitable for practical use. However, the authors did not investigate the fracture behavior and healing efficiency of such self-healing systems.

Cho et al. [148] chose to develop a completely different healing system using di-*n*-butyltin dilaurate (DBTL) as the catalyst and a mixture of HOPDMS and PDES as the healing agent. The polycondensation of HOPDMS with PDES is alleged to occur rapidly at room temperature in the presence of the organotin catalyst even in open air [149,150]. The authors suggested that this system possessed a number of important advantages over the DCPD/Grubbs catalyst system such as:

- The healing chemistry remains stable in humid or wet environments.
- The chemistry is stable at an elevated temperature (>100 °C), enabling healing to occur in thermoset systems processed at higher-temperatures.
- The healing chemicals are widely available and comparatively low in cost.
- The concept of phase separation of the healing agent simplifies processing, as the healing agent can be simply mixed into the polymer matrix.

In this particular system [148], the catalyst was encapsulated instead of the siloxane-based healing agent, both of which were simply phase-separated in the vinyl ester matrix (VE) (Fig. 15). Polyurethane microcapsules containing a mixture of DBTL catalyst and chlorobenzene were formed (prior to

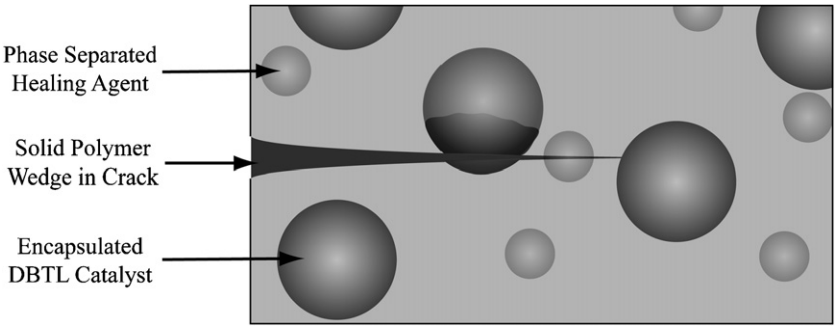


Fig. 15. Schematic of microencapsulation system reported by Cho et al. [121].

embedding in the matrix) through interfacial polymerization [151,152]. The average diameter of these microcapsules varied from 50 to 450 μm, and could be controlled by changing the stirring rate during the polymerization process. The low solubility of the siloxane-based polymers enables the HOPDMS–PDES mixture and the encapsulated catalyst to be directly blended with the VE matrix, forming a distribution of stable phase-separated droplets and protected catalyst. Addition of an adhesion promoter such as methylacryloxypropyl triethoxysilane to the matrix was necessary to optimize the healing efficiency due to improved bonding between the healing agent and the matrix. Despite the potentially more stable healing agent, this system actually achieved a healing efficiency value of 46%, which is lower than the 75–90% reported for the DCPD/Grubbs' catalyst-based healing system [9,128].

In another alternative self-healing system, Jung [121] employed polyoxymethylene urea as a storage container for the self-healing agent in a polyester matrix. The best healing results were obtained with a styrene-based system containing 1.3 wt% cobalt naphthenate, 1.3 wt% dimethylaniline (DMA), and 0.01 wt% *para*tertbutylcatechol (TBC). However, it is unclear as to whether the healing agents were actually encapsulated. It was also reported that this system would have little practical use because of the limited shelf life of the healing chemicals. Characterization of Jung's system [121] using optical techniques (optical microscope, SEM and high speed video imaging) confirmed the rupture of the microcapsules, and subsequent release and transport of their contents into an approaching crack. Establishment of good interfacial adhesion between the microspheres and the matrix was critical for initiating the self-healing although this led to a decrease of the composite toughness. In comparison to the neat polyester resin, the fracture toughness of the self-healing samples was increased at the expense of the stiffness of the material.

Another variation to the traditional microencapsulation approach was patented by Skipor et al. [153] who described the concept of attaching catalyst molecules to the exterior of the microcapsules filled with the healing agent (Fig. 16A). The positioning of the catalysts near the healing agent release site was claimed to potentially improve the overall healing efficiency. A second patent [154] was published a year later in which Skipor et al. proposed an improved approach that eliminated the need for a catalyst by crosslinking the healing agent directly with the damaged surfaces (Fig. 16B).

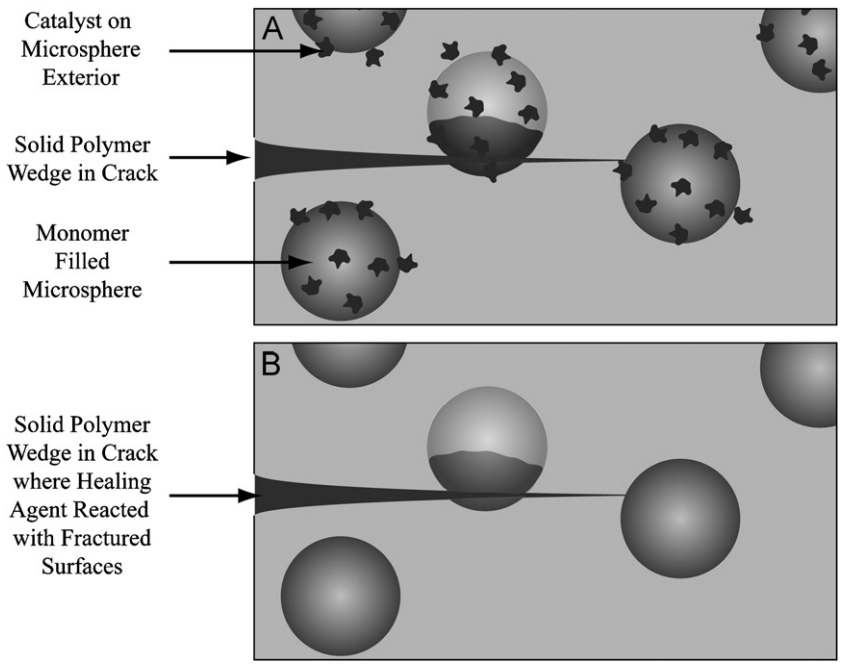


Fig. 16. Schematics of healing mechanisms in non-traditional microencapsulation approaches presented by (A) Skipor et al. [153] and (B) Scheifers et al. [154].

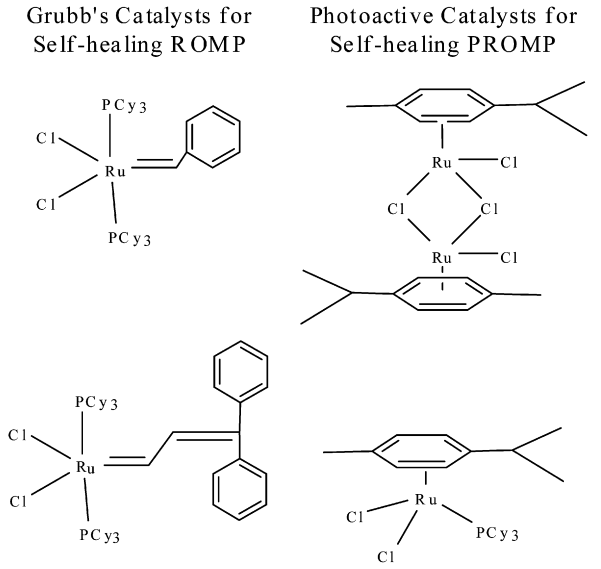


Fig. 17. Ruthenium-based catalysts used in ROMP and PROMP reactions [155].

Limited experimental details and no healing efficiency data were provided in both cases, but the two patents represent the continued development of new variations on the microencapsulation approach.

A final variation on the microencapsulation approach uses photo-activated catalysts instead of the traditional Grubb's catalyst. The concept of photo-induced healing is potentially attractive because the reaction takes place under ambient conditions and is generally fast, simple and environmentally friendly. In 2002, Sriram [155] suggested a self-healing system based on photo-induced ring opening metathesis polymerization (PROMP) of norbornene (NBE) or DCPD, as a complementary process to the free radical ROMP. This work (Fig. 17) was motivated by several potential advantages over the conventional free radical ROMP approach in that the catalyst can be easily synthesized in large quantities, and the PROMP reaction is extremely fast ($<5$ min) with a minimum change in volume. The occurrence of PROMP of DCPD and NBE at room temperature was confirmed by $^{1}$H NMR analysis. However, Sriram did not report the production of any self-healing composites using this technique.

### 5.2.2. *Mechanical property and processing considerations*

The addition of microencapsulated healing agent or catalyst in a polymer matrix can potentially change its mechanical properties and processing characteristics. The extent of this change depends on the volume fraction of the additives, the level of interfacial interaction, and the inherent properties of the additives. For a self-healing concept to be viable, the healing performance should be achieved without compromising the overall processing and mechanical properties of the polymer matrix.

In epoxy matrices [130], modulus and ultimate strength were both reported to decrease with increasing the loading of the DCPD microcapsules. These trends are similar to those obtained with other microcapsule [121,156–161] and rubber [156,157] modified systems. However, research has shown that the epoxy resin could be significantly toughened (up to 127% of the original value) at 15 wt% loading of the DCPD microcapsules [9,85] and, to a less extent, by the addition of the catalyst phase [128]. The concentration of the DCPD microcapsules at which the maximum toughness occurs depends strongly on the microcapsule diameter with the smaller microcapsules exhibiting a maximum toughness at lower concentrations. The toughness improvement of the epoxy matrix achieved with the DCPD microcapsules was evidenced by the increased hackle marking and subsurface microcracking as observed by SEM [128] although this increase has not been translated into toughening of the corresponding laminates. It is suggested that this may be achievable through refinement of the manufacturing and processing techniques [134]. In another publication [9], the average critical load for the self-healing samples containing microcapsules and Grubbs' catalyst was 20% higher than that of the neat epoxy, indicating that the addition of the DCPD microcapsules also increased the inherent toughness of the epoxy resin. On the other hand, the addition of more than 3 wt% Grubbs' catalyst appeared to reduce the fracture toughness of the epoxy matrix although a higher healing efficiency value was obtained at these high catalyst loadings [128].

Trends similar to those seen in epoxy resins were also observed in a polyester matrix [162]. The elastic modulus of the composite was found to decrease with an increase of the volume fraction of the DCPD microcapsules. The fracture toughness of the composite determined by a tapered double-cantilever beam (DCB) test showed a maximum toughness occurring at a 10% microcapsule concentration. An investigation of different surface treatments of the DCPD microcapsules on the composite toughness

suggested that an increased adhesion between the microcapsules and the matrix was detrimental for the composite fracture toughness although this was favorable for promoting rupture of the microcapsules in the event of a crack.

Beyond the effects discussed above, an increase of the microcapsules or catalyst content reduces the processability of these composites due to the increase of resin viscosity [128]. Further consideration to the processing conditions must also be given to minimize rupture of the microcapsules during mixing or mould filling stages of self-healing composite production.

Subsequent application of a self-healing polymer matrix has been investigated in woven laminate systems by taking advantage of the large resin rich areas between the interlacing of undulating warps and fill yarns. These interstitial areas may serve as natural sites for storage of the healing agent microcapsules (50–100 μm in diameter) since their presence will not disrupt the inherent undulation of the fiber tow. Depending on the architecture of the weave and the fiber volume fraction, a large number of microcapsules can be potentially stored in the interstitial regions without significantly changing the bulk material properties of the composite. Self-healing of composite laminate is fundamentally more difficult than self-healing of neat resin. Although resin micro-crack is expected to be healed similarly, the presence of the woven fiber reinforcement increases the number of possible damage modes and the complexity of the healing process. The architecture of the woven cloth imposes a more tortuous crack path than would be expected from the neat resin alone, or with unidirectional composites constructed of the same materials.

Self-healing in E-glass/epoxy plain weave specimens was demonstrated by embedding Grubbs' catalyst (1.75 wt%) into the matrix and injecting DCPD monomer into the fracture plane [163]. To demonstrate the ability to achieve multiple healing with the DCPD/Grubbs' catalyst system, a self-activated DCB specimen was tested four times in succession while injecting pure DCPD into the delamination plane each time. The level of recovery of fracture toughness compared to the virgin loading was between 50% and 60% of the peak load. The incorporation of the catalyst into the epoxy matrix led to a slight decrease in the toughness and potentially unstable crack propagation due to the existence of many large catalyst clusters in the matrix resin.

#### 5.2.3. Assessment of self-healing efficiency

Self-healing efficiencies in neat epoxy- and fiber-reinforced epoxy laminates, and to a lesser extent in polyester and vinyl ester matrices, have been assessed by tensile, fracture, and fatigue tests. Each of these tests assesses different performance characteristics of the self-healing systems.

*5.2.3.1. Self-healing efficiency assessed by tensile test.* Sanada et al. [136] studied the healing of interfacial de-bonding in neat epoxy and unidirectional carbon fiber-reinforced epoxy composites using tensile testing. Preparation of the self-healing fiber-reinforced composites was carried out by dipping and coating the carbon fiber strands with an epoxy mixture containing 30 wt% DCPD microcapsules and 2.5 wt% Grubbs' catalyst. The coated fibers were then impregnated with the epoxy matrix resin. The maximum healing efficiency assessed after a healing period of 48 h at room temperature was 14%. SEM inspection of the fracture surfaces of the healed specimens indicated that the low healing efficiency achieved was due to incomplete release and insufficient coverage of the DCPD healing agent on the fracture plane. It was proposed that higher healing efficiencies could be achievable by controlling the surface roughness and diameter of the microcapsules [125]. On the other hand, the self-healing fiber-reinforced composites tested in tension perpendicular to the fibers exhibited interfacial de-bonding as the dominant mode of failure. The maximum healing efficiency achieved with these specimens was 19%. The presence of the fibers seemed to modify the stress state around the microcapsules resulting in a higher percentage of the microcapsules being broken and released into the fracture plane.

Limited study on self-healing of polyester resin has been carried out by making tensile coupons, fracturing them in the gage section, and repairing manually using the styrene-based healing system [162]. Approximate 75% of the original strength was recovered after repair with 1.3 wt% cobalt naphthenate, 1.3 wt% DMA, and 0.01 wt% TBC. The use of cobalt and DMA initiators was necessary to obtain this level of repair. Without the initiators, the diffusion rate of the styrene into the polyester network was so high that very little styrene was left at the crack surface after 24 h. The presence of the initiators increased the reaction rate and resulted in 100% crack filling. Alternatively, high-molecular-weight polystyrenes were incorporated

into the self-healing chemicals to reduce the diffusion rate of styrene into the polyester matrix. It is unclear as to whether the styrenic healing agents were actually encapsulated and embedded in the polyester matrix (or injected into flaws), however a healing efficiency of 40% was reported with a healing system comprising 23 wt% PS ($M_w = 250{,}000$), 0.01 wt% TBC, and 76.99 wt% styrene.

*5.2.3.2. Self-healing efficiency assessed by fracture test.* Manual injection of the healing agent and fracture testing was used to prove that the ROMP of DCPD worked as a healing technique in neat epoxy [128,133] and fiber-reinforced epoxy composites [134,163]. The healing efficiencies in terms of fracture toughness ranged from 75% [9] to 90% [128] in neat epoxies and from 7% [133] to 66% [135] in fiber-reinforced epoxies.

Fracture toughness healing efficiencies have been assessed in accordance to a previously established protocol [9,128]. In this test a tapered double-cantilever beam (TDCB) specimen is completely fractured under mode I loading. The sample geometry allows the determination of the mode I fracture toughness of the specimen from elastic modulus, geometrical shape information, and peak load obtained during a fracture test. Crack healing efficiency, $\eta$, is defined as the ability of a healed sample to recover fracture toughness [14]:

$$\eta = K_{\text{IC healed}}/K_{\text{IC virgin}} \tag{6}$$

where $K_{\text{IC virgin}}$ and $K_{\text{IC healed}}$ represent the fracture toughness of the virgin and healed samples respectively.

Successful self-healing has been demonstrated for neat epoxy resin comprising 5–25 wt% microencapsulated DCPD monomer and 2.5 wt% Grubbs catalyst. White et al. [9] reported recovery of 75% of the virgin fracture load for a self-healing epoxy composite distributed with Grubbs' catalyst and DCPD microcapsules. This corresponded to an average healing efficiency of 60%. Brown et al. [128] determined and optimized the amount of time required for recovering the toughness of epoxy matrix by performing fracture tests on healed specimens at time intervals ranging from 10 min to 72 h after the initial fracture event. No measurable recovery of mechanical properties occurred until 25 min, which closely corresponded to the gelation time of the poly(DCPD) at room temperature [164]. The recovery of mechanical properties reached steady-state values within 10 h after the initial crack event. The correlation between the healing efficiency and the healing time was also observed in previous work with self-healing thermoplastics [14,67,73]. As a result of the optimization, 90% recovery of the virgin fracture toughness was achieved. A further systematic study carried out by Brown et al. [130] investigated the effect of the microcapsule size and loading on the healing efficiency of the neat epoxy matrix. The concentration of Grubbs' catalyst was kept constant at 2.5 wt% whereas the average diameters of the DCPD microcapsules varied between 50, 180, and 460 μm, and the loading of the microcapsules changed from 5 to 25 vol%. The maximum healing efficiency for 180 μm DCPD microcapsules occurred at a low concentration (5 vol%) whereas in the case of the sample containing 50 μm DCPD microcapsules, a high healing efficiency only occurred at a higher microcapsule concentration (20 vol%) since more microcapsules were required to deliver the same volume of DCPD healing agent to the fracture plane. In both cases, over 70% recovery of virgin fracture toughness was obtained through careful selection of DCPD microcapsule concentration.

Kessler and White [164] studied the chemical kinetics of the DCPD/Grubbs' healing system and showed that the degree of cure reaction was affected by the catalyst concentration and healing temperature. The experiments were performed with known amounts of Grubbs' catalyst dissolved in DCPD. The effective concentration of catalyst was dependent on the availability of the exposed catalyst on the fracture plane as well as the rate of dissolution of the catalyst in the DCPD monomer. Even with large amounts of catalyst exposed on the fracture plane, the effective concentration of Grubbs' catalyst in the DCPD healing agent may be relatively low if the rate of dissolution of the catalyst is slow.

In an attempt to avoid deactivation of the Grubbs' catalyst by the amine curing agent and to achieve a better dispersion of the catalyst in the epoxy matrix, Rule et al. [127] encapsulated the Grubbs' catalyst with paraffin wax to provide an insoluble protective layer. Fracture samples were prepared and tested with 5 wt% DCPD microcapsules and the amount of the catalyst in the microcapsules was varied from 0% to 2.5%, corresponding to 0 wt% to 1.25 wt% of catalysts in the epoxy samples. The self-healing induced with the catalyst microcapsules exhibited nonlinear elastic behavior due to plasticization of poly(DCPD) by the wax. As such, the critical fracture toughness protocol described in Eq. (6) cannot be employed.

The authors thus defined the healing efficiency as the internal work (or strain energy) of the healed sample divided by the internal work of the virgin sample, each normalized by the new surface area generated upon fracture. Under this assumption, a maximum average healing efficiency of 93% was reported with 0.75 wt% catalysts loading. The healing in this case only occurs when DCPD is released into the crack plane and if it dissolves the wax to release the catalyst, and then polymerizes. Hence it is necessary to carry out a rigorous analysis of fracture properties after healing to better understand the role of wax on the performance and durability of this self-healing system.

Fracture testing was also used to assess healing efficiencies of the HOPDMS- and PDES-based system [148]. A maximum healing efficiency of 46% was achieved with the sample containing 12 wt% PDMS, 4 wt% methylacryloxypropyl triethoxysilane (adhesion promoter), and 3.6 wt% DBTL microcapsules (catalyst). This relatively low healing efficiency was attributed to the significantly lower stiffness and fracture toughness of the PDMS in comparison with that of the vinyl ester matrix. Despite an expected better stability of this particular healing chemistry in humid/wet environment, exposure of the fractured sample to water during the healing process led to reductions of healing efficiency (25%) with respect to the samples healed in air.

Kessler and White [122,163] initiated fracture testing studies on self-healing epoxy laminates reinforced with woven E-glass fabric. They focused on healing of the interlaminar fracture damages in the woven laminates because the interlaminar fracture delamination often occurred due to low energy impact or manufacturing defects. Healing efficiency of the laminates healed *in situ* was assessed by the DCB testing, giving a healing efficiency of 20% [163] which was considerably less than the healing efficiency of 51–67% obtained with the manually catalysed specimens. This discrepancy of healing efficiencies was attributed to the different rate and degree of polymerization of the self-healing systems between the *in-situ* healing and the manually catalysed specimens.

Epoxy and cyanoacrylate-based healing agents were also investigated in self-healing epoxy matrix reinforced with woven E-glass fabric [163] (using a manual injection method). Results of these tests showed average healing efficiencies of 12% for epoxy and 122% for the cyanoacrylate healing agent respectively. The healing efficiency obtained with the poly(DCPD)-based healing system lies somewhere between the epoxy and cyanoacrylate healing agents.

The self-healing behavior of satin weave and plain weave laminate specimens were tested by Kessler and White [122,163]. The satin weave specimens exhibited lower healing efficiencies, with values ranging from 0 to 10%. The dominant mode of fracture for these specimens was interfacial failure, resulting in very little of the catalyst directly exposed to the fracture plane. It was postulated that *in-situ* polymerization of the healing agent in the satin weave specimens was either very slow or non-existent.

On the other hand, the plain weave specimens possessed large interstitial areas where Grubbs' catalyst was directly exposed to the fracture plane. Several factors affecting the healing efficiency of the self-healing laminates were identified [163]. The healing agent must bond both to the glass fabric and the epoxy matrix in order to achieve complete repair. It was proposed that further improvement of healing efficiency is possible by either treating the fiber surface with a suitable coupling agent, or by choosing a more compatible healing agent/fiber system. The healing efficiency was also affected by both the rate and degree of polymerization of the healing agent system, in such a way that it must be sufficiently fast to prevent diffusion of the monomer away from the fractured regions into the matrix.

Further research [122,134] has been extended into self-healing in carbon fiber-reinforced epoxy laminates, and demonstrated autonomous healing of delamination at room temperature. Width-tapered DCB specimens were manufactured by compression moulding of woven carbon fiber prepregs in an epoxy matrix. The central layers where the delamination was introduced were filled with 20 wt% DCPD microcapsules and 5 wt% of Grubbs' catalyst. Freshly fractured specimens were clamped shut with a modest pressure and allowed to heal at room temperature for 48 h. Upon retesting, the healing efficiency was up to 45%. By elevating the healing temperature to 80 °C, the healing efficiency increased to over 80%. An increase of healing temperature appeared to increase the overall healing efficiency of the self-healing material as a result of increased rate of polymerization and the degree of cure for the healing system. While experiments on the self-healing epoxy resin have shown 90% recovery at room temperature [128], the structural laminates described in this paper contain a high

thermal mass of reinforcing fibers and a lower mass fraction of self-healing matrix. Both can lead to a lower local temperature at the crack face where healing is initiated, contributing to a slightly lower healing efficiency. Other contributing factors to the lower healing efficiency include an increased interlaminar thickness and poor catalyst dispersion. The average thickness of the central layers was almost 60% higher than the outer layers which did not contain catalysts and DCPD microcapsules. The increased thickness of the interlaminar region led to a lower toughness. Further improvement of the laminate toughness and healing efficiency is possible by lowering the catalyst concentration and improving the dispersion of the catalyst prior to laminate lay-up.

*5.2.3.3. Self-healing efficiency assessed by fatigue test.* Characterization of fatigue response is more complex than monotonic fracture because it depends on a number of factors such as the applied stress intensity range, the loading frequency, the ratio of applied stress intensity, the healing kinetics, and the rest periods employed [135]. The investigation considered successful healing as the recovery of stiffness lost due to damage induced by cyclic loading rather than changes in crack-growth rate or absolute fatigue life. Epoxy resins containing the DCPD/Grubbs' catalyst system were subjected to cyclic loading and examined [133,135]. The mechanisms for retardation and repair of a fatigue damage were firstly assessed by manual injection of the healing agent into the fractured surfaces [133] before *in-situ* healing was investigated [135]. The fatigue-crack propagation behavior of the self-healing epoxy was evaluated using the protocol outlined by Brown et al. [128]. The fatigue-healing efficiency is defined by fatigue life-extension,

$$\eta = (N_{\text{healed}} - N_{\text{control}})/N_{\text{control}} \quad (7)$$

where $N_{\text{healed}}$ is the total number of cycles to failure for a self-healing sample and $N_{\text{control}}$ is the total number of cycles to failure for a similar sample without healing.

During the crack growth under fatigue (cyclic) loading, the competition between crack propagation and kinetics of polymerization of the healing agent dictates the ultimate performance of a self-healing polymer system [126]. A slow growing fatigue crack can be completely arrested during the loading process, whilst a fast growing fatigue crack may require rest periods to achieve significant life extension [135]. Assessment of retardation and repair of a fatigue damage via manual injections used DCPD mixed with 2 g/l of Grubbs' catalyst as a healing system [133]. The results showed that crack-tip shielding by a self-healing polymer wedge yielded a temporary crack arrest and extended the fatigue life by more than 20 times. Such fatigue-crack retardation was achieved by artificial crack closure induced by the formation of a polymerized healing agent (DCPD) wedge at the crack tip, preventing a full crack-tip unloading. Moreover, the successful crack closure was independent of the adhesive strength of the interface. Crack closure from the polymer wedge continued to retard crack growth long after the crack started to propagate through the healed region. The success of these mechanisms for retarding fatigue crack growth demonstrates the potential for *in-situ* healing of fatigue damage.

Brown et al. [135] continued the investigation into *in-situ* healing of the fatigue damage of epoxy samples with 20 wt% 180 μm DCPD microcapsules and 2.5 wt% Grubbs' catalyst. Significant crack arrest and life-extension resulted when the *in-situ* healing rate was faster than the crack-growth rate. In the cases when the crack grew too rapidly, carefully timed rest periods were required to achieve a prolonged fatigue life. Otherwise, the fatigue life-extension was nearly zero. Under low-cycle fatigue conditions, the fatigue life-extension achieved for *in-situ* self-healing epoxy with a rest period varied from 73% to 118%. In the case of the high-cycle fatigue conditions ($N_{\text{healed}} > 10{,}000$), total fatigue life-extension of the samples was reported to range from 89% to 213%.

In summary, the application of DCPD/Grubbs' catalyst healing system for repairing fatigue damage has been investigated on a number of occasions [165–168] and had achieved healing efficiencies up to 213% [135]. The tests revealed that healing and crack growth retardation readily takes place in the low stress fatigue condition. In contrast to this, healing in high stress fatigue-type failures only takes place if periods of rest are included in the fatiguing cycles, allowing healing agent setting while the fatigue crack is held open [135]. The full potential of the technology will be realized subsequent to further research to overcome some technical issues such as restricted availability of healing agent at the damage site, limited environmental stability of healing agents, potential issues with transferability to fiber-reinforced composites, immobility of healing

agents at low temperatures, shelf life of the healing agents, and healing multiple fractures in the same location.

### 5.3. Thermally reversible crosslinked polymers

This self-healing concept involves the development of a new class of cross-linked polymer capable of healing internal cracks through thermo-reversible covalent bonds. The mechanical properties of this type of polymers were comparable to those of the epoxy resins and the other thermoset resins commonly used in fiber-reinforced composites. Therefore, this type of polymer may be used to fabricate fiber-reinforced polymer composites for structural applications. The use of thermally reversible crosslinks to heal thermosets eliminates the need to incorporate healing agent vessels or catalysts in the polymeric matrix although heat is now needed to initiate the healing. In fact, preferential rupturing of the reversible bonds in these systems is similar to that used by Chung et al. [77] in the photo-induced healing in thermoplastics (discussed in Section 4.2). Since application of heat is a necessary part of this healing mechanism (both triggering and assisting the healing process), there are questions as to whether these materials may be classified as autonomic healing. However, the authors [169–172] argued that it should be considered a self-healing material, particularly when the healing agent and the heat source are integrated into the system. A patent relating to this technology was published by Wudl and Chen [172] in 2004, just after Harris and Rajagopalan [171] published a patent using a similar system to produce thermally mendable golf balls in 2003.

The exploration of a thermally reversible reaction such as the Diels–Alder (DA) reaction for self-healing application has been pioneered by Chen et al. [169,170]. They described a "re-mendable" material capable of offering multiple cycles of crack healing. This approach also offers advantages over the popular microencapsulation approach because it eliminates the needs for additional ingredients such as catalyst, monomer or special treatment of the fracture interface. The first generation of a highly cross-linked and transparent polymer was synthesized as described in Fig. 18 via the DA cycloaddition of furan and maleimide moieties, and the thermal reversibility of the chemical bonds is accomplished via the retro-DA reaction [173]. Solid state reversibility of the cross-linking structure via DA and retro-DA reactions was tested and confirmed by subjecting the polymerized films to different heating and quenching cycles, and analyzing the corresponding chemical structure by solid state $^{13}C$ NMR.

Healing in the thermally reversible crosslinked polymers depends upon the fracture and repair of the specific covalent bonds. It is proposed that the bond strength between the furan and maleimide moieties is much lower than that of the other covalent bonds, meaning the retro-DA reaction should be the main pathway for crack propagation. Since the inter-monomer linkages formed by the DA cycloaddition are disconnected upon heating to 120 °C then reconnected upon cooling, the self-healing process does not occur at a temperature lower than 120 °C. Quantification of the healing efficiency by fracture tests shows that it was about 50% at 150 °C, and 41% at 120 °C. Multiple healing at or near the same interface was also observed although the critical load at fracture of the third cracking was about 80% of the second. This drop in mechanical properties from the second to the third healing process was attributed to the healed region

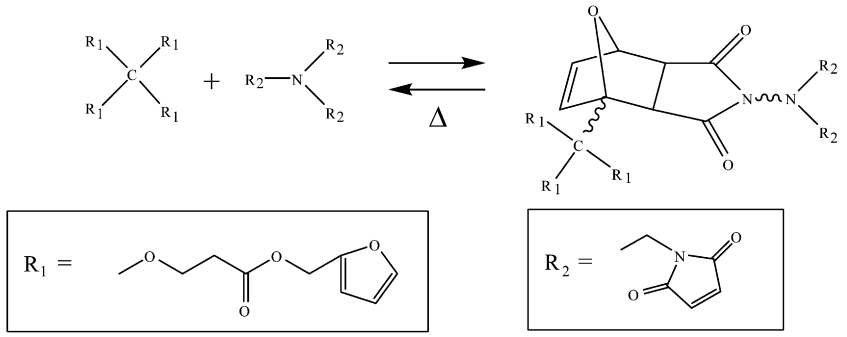


Fig. 18. Crosslinking agents and thermally reversible crosslinking mechanism in self-healing polymers proposed by Chen et al. [170].

having different mechanical properties than the original material.

Further progress was made by the same group of researchers [169] to develop a second generation of this type of polymers. In comparison with the first generation, the second generation polymers are harder, colorless, transparent at room temperature, and do not require solvent for the polymerization process. Healing efficiency of these polymers was assessed using the procedure discussed in Section 5.2.3.2 and involved a heating—quenching cycle of 115 °C for 30 min, following by cooling at 40 °C for 6 h. The healing efficiency was about 80% for the first crack healing process, and 78% for the second one. This indicates that the second-generation polymers provide further improvement of the healing efficiencies with added advantages in processing and appearance. However, it is recognized that the healing efficiency values reported by these authors were intended for relative comparison within their series of studies, rather than for absolute comparisons with the other self-healing technologies. More quantitative experiments should be undertaken in the future to determine the absolute values of healing efficiency considering the value of critical load can be influenced by factors such as crack length and crack bluntness.

A recent development using the DA reaction healing mechanism integrated arrays of conductive electromagnetic elements, such as copper wires and copper coils, into the fiber-reinforced composites [174]. This makes it possible to heal internal damage in the composites through application of mild heat and restore the material by means of thermoreversible covalent bonds. However, the healing process was only monitored qualitatively as shown by the disappearance of the crack after the samples had been treated for at least 6 h above 80 °C under nitrogen protection. The authors mentioned that quantitative measurements of the healing efficiency are yet to be undertaken. Other issues worth investigation include the effect of incorporating the copper wires on the mechanical properties, fracture behavior, corrosion resistant, long-term durability of the fiber-reinforced composites, and the potential problems caused by mismatch of thermal coefficient between the metal components and the advanced fibers.

The applicability of self-healing polymers using DA reactions in advanced composite production was further explored in recent contributions by Liu et al. [175,176]. These researchers employed epoxy precursors to prepare multifunctional furan and maleimide monomers. These monomers appear to possess the desirable characteristics of the traditional epoxy resins such as solvent and chemical resistance, low melting point, and solubility in a number of organic solvents. These characteristics enable them to be processed in a similar fashion to the epoxy resins. The self-healing behavior of these polymers thermally treated at 120 °C for 20 min and at 50 °C for 12 h was only visually confirmed.

An alternative approach to the Diels–Alder (DA) reaction was suggested by Otsuka et al. [177–182] who employed 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) containing alkoxyamine derivatives as junctions between the polymer segments, polymer chains and polymer grafts. When subjecting to heating, the TEMPO containing alkoxyamine junctions disconnect and then reconnect with both similar and dissimilar sites. The authors initially incorporated these junctions into development of linear polyesters [180] but have since produced a range of adjustable polymer matrices including polyurethanes [181] and crosslinked methacrylic esters [178]. There is potential to use this type of thermally reversible crosslink instead of the DA reagents for self-healing purpose. It should be noted that the practicability of the current embodiment of the technology needs to be improved since the healing reaction only takes place under extreme conditions (anisole solution maintained at 100 °C for 24 h).

### 5.4. Inclusion of thermoplastic additives

The use of thermoplastic additive as self-healing agent for thermoset matrices was first reported by Zako and Takano [183] in 1999. Using thermoplastic additives instead of thermally reversible crosslinks enables the original polymer matrix to remain unaltered during incorporation of the healing capability, as well as providing solidifiable crack filler capable of re-bonding fracture surfaces. The feasibility of this technology was demonstrated using up to 40 vol% of thermoplastic epoxy particles (average diameter of 105 μm) in a glass fiber-reinforced epoxy composite. Upon heating the particles melted, flowed into internal cracks or flaws and healed them (Fig. 19). Healing efficiency in this system was evaluated in terms of stiffness recovery by static three-point bending test and tensile fatigue test. The tensile specimen was fatigued until the stiffness decreased by 12.5%. The test was stopped

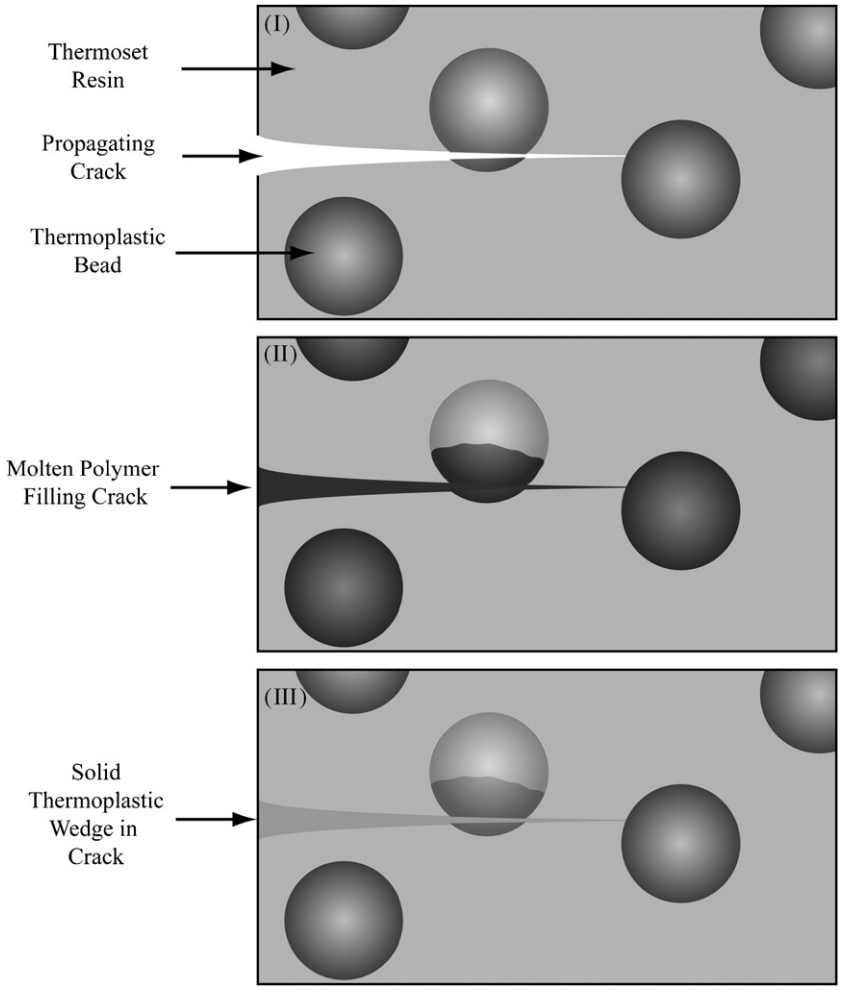


Fig. 19. Concept of healing mechanism in thermoplastic bead-based self-healing composites [183].

and the crack was healed by application of heat, which triggered flow and subsequent polymerization of the embedded particles. The fatigue test was resumed with almost full recovery of stiffness. Both tensile and three-point bend tests indicated that the self-healing composites managed to recover 100% of its stiffness from the initial damage when the samples were heated at 120 °C for 10 min. Although the feasibility of this concept is proven in terms of stiffness recovery, other important characteristics of the healing composites such as strength and fracture toughness need to be investigated to realize its full potential. Considering the potential issues associated with heating thicker components without causing excessive heat to the surface, the authors proposed to investigate the use of $CO_2$ laser or semiconductor laser for providing localized heat to the damaged spot as one of their future research efforts.

A second embodiment of this healing mechanism was patented by Jones and Hayes in 2005 [184] who suggested to use a "solid solution" of thermoplastic and thermoset polymers instead of the two phase system described above for self-healing fiber-reinforced composites. It was specified that the matrix should contain 10–30 wt% of a thermoplastic polymer. The healing efficiency determined by compact-tension test is defined as the critical stress concentration factor ($K_{IQ}$) or strain energy release factor ($G_Q$) of the healed specimen over those of the original specimen. Factors affecting the healing efficiency include:

- Compatibility of the two polymers as indicated by the solubility parameters: the thermoplastic healing agent should be miscible with the thermoset polymer, but does not chemically react with it at ambient temperature. This means that

the thermoplastic preferably forms a homogeneous solution with the thermoset matrix both before and after cure.

- $T_g$ *of the polymers*: The $T_g$ of thermoplastic and thermoset polymer need to be similar so that the thermoplastic melts above ambient temperature but not so high to cause thermal decomposition of the thermoset.
- *Molecular weight distribution of the thermoplastic*: Low-molecular-weight polymer diffuses faster resulting in quicker healing whilst high-molecular-weight polymer provides better mechanical properties. Hence, there is a need to balance rapid healing and good healed mechanical properties.
- *Healing temperature employed*: Since the healing process is thought to be diffusion in nature, the healing temperature is expected to influence the healing rate and efficiency.

The healing efficiency of epoxy containing up to 25 wt% of polybisphenol-A-*co*-epichlorohydrin (PBE) has been investigated at healing temperatures from 100 to 140 °C [184,185]. The healing efficiency assessed by compact tension fracture test improved with the increase of healing temperature. This trend was attributed to increased diffusion rate of the thermoplastic healing agent across the fracture surfaces at the higher temperature, allowing greater entanglements and molecular interdiffusion between the two fracture surfaces. An increase of the healing temperature beyond 140 °C resulted in substantial loss in dimensional stability of the specimen, possibly due to thermal decomposition of the polymer. The thermoplastic additives have also been employed as healing agents for glass fiber-reinforced epoxy composites [185,186]. Multiple impact-healing cycles were used to test composites containing 7–10% PBE. These samples were assessed visually, and 30–50% healing efficiency was reported. This seems to be lower than that reported by Zako and Takano [183]. It should however be recognized that the two cases may not be directly comparable considering the test methods used for assessment of healing efficiencies and the matrix resins were different.

### 5.5. Chain rearrangement

Healing of thermosets has also been shown to achieve by rearranging polymer chains at ambient or elevated temperatures. Similarities exist between this technology and thermoplastic molecular interdiffusion technologies. Chain rearrangement occurring at ambient temperature heals cracks or scratches via interdiffusion of dangling chains [187] or chain slippage in the polymer network [188]. These two ambient temperature modes of healing eliminate the need for heating cycles during healing that were required for the thermoplastic additives or the thermally reversible crosslinks approach.

The first report of healing via chain rearrangement in thermoset resins was published in 1969 [189]. Fractured epoxy resins made from diglycidyl ether of bisphenol-A (DGEBA), nadic methyl anhydride (NMA) and benzyl dimethylamine (BDMA) were shown to repeatedly heal when heated to above 150 °C. Healing was assessed visually and by double torsion fracture testing; each resulted in a 100% healing efficiency over multiple fracture events. When subjecting to different thermal treatments, the healing process was independent of the healing temperature or the presence of un-reacted monomer, but only occurred when the epoxy was heated above its $T_g$ (120 °C). Healing was attributed to Micro-Brownian motion of the polymer chains with local flow enabling good interfacial bonding and the restoration of the original surface contours.

In 2007, Yamaguchi et al. [187] reported the first self-healing thermoset based on molecular interdiffusion of dangling chains. These self-healing polymers consisted of a polyurethane network made using a tri-functional polyisocyanate, polyester-diol and a dibutyl-tin-dilaurate catalyst. The authors varied reagent ratios to manipulate the crosslink density and therefore the number of dangling chain ends. Healing was assessed visually by checking slit closure of cut specimens over time. Using the correct reagent ratios enabled healing to occur rapidly (10 min) once the cut surfaces were brought in contact with each other. It was concluded that weakly gelled polymers (just beyond the critical point) were capable of healing via the entanglement of dangling chain ends (Fig. 20). The interdiffusion of dangling chains were also found to contribute to healing in epoxies [189], and in polyurethane with initiator residues forming loose chain ends [190]. Yamaguchi et al. [187] proposed to do more tests including mechanical property evaluation on this type of self-healing system.

Ho [188] published a patent describing water-based self-healing polyurethane formulations containing siloxane and/or fluorinated segments. Self-healing in this case was defined as the extent of deformed or marred surfaces returning to its original appearance. The self-healing behavior was

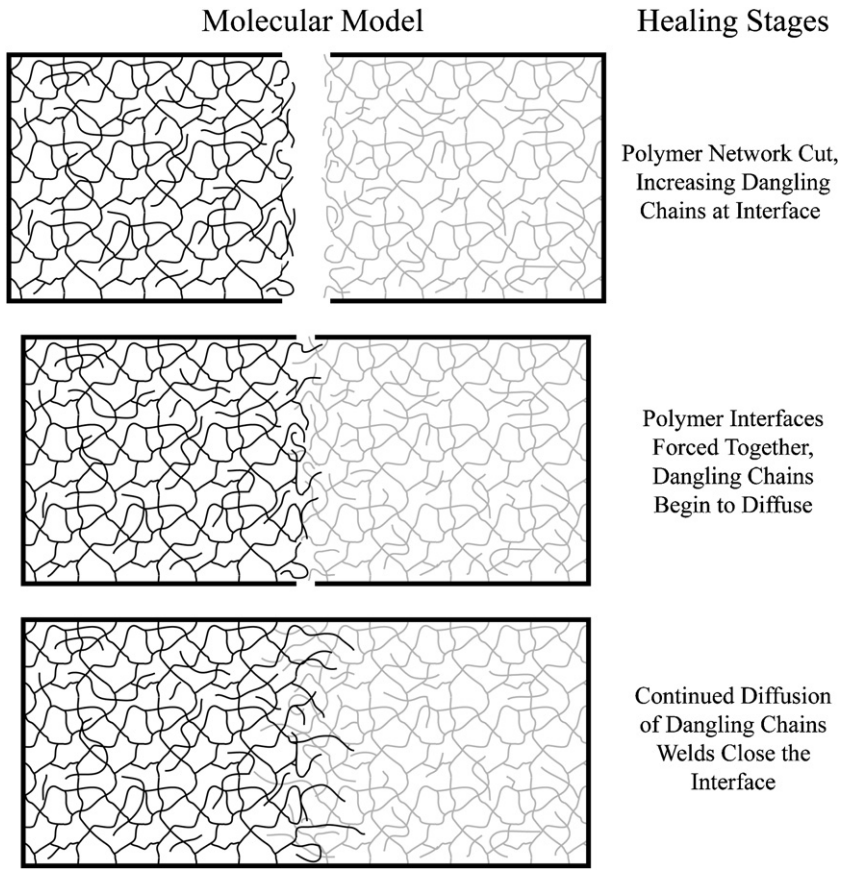


Fig. 20. Healing of a crosslinked network via dangling chain entanglement.

attributed to a so-called ''chain slippage'' phenomenon during which the siloxane segments and the polyurethane segments expelled each other due to their incompatibility and the large differences in their surface tensions. More specifically, the polyurethane needs to comprise 2–20 wt% of siloxane or fluorinated segments to provide self-healing ability and suitable outdoor durability. The inventors claimed that shallow scratches on these polymers completely disappeared over a time frame of 2 min to 14 days, citing the above-mentioned ''chain slippage'' of siloxane segments within polyurethane as the healing mechanism. The healing was found to occur only at a temperature above 10 °C, and the rate of healing depends on factors such as the temperature, the depth of the scratch, and the composition of the formulation.

### 5.6. Metal-ion-mediated healing

Self-healing via metal-ion-mediated reactions was developed for repair of lightly crosslinked hydrophilic polymer gels [13,191,192]. This technology involves rearrangement of crosslinked networks (similar to those discussed in Section 5.5), however this change occurs as metal-ions are absorbed from an aqueous solution and then incorporated into the hydrogel. The metal-ion-mediated healing of hydrogels is distinct from self-healing systems discussed above because the ''healed'' material has an entirely different structure and set physical properties from the ''un-healed'' material, making comparisons between the systems difficult.

The self-healing hydrogels [13] contain flexible hydrophobic side chains with a terminal carboxyl group and undergo healing at ambient temperature through the formation of coordination complexes mediated by transition-metal ions. A series of monomers made by reacting amino acids with acryloyl chloride were tested [191,192], but a gel based on acryloyl-6-amino caproic acid (A6ACA) was studied extensively [13] (production method shown in Fig. 21). Healing of the gels was undertaken by placing dried pieces of the gels together in

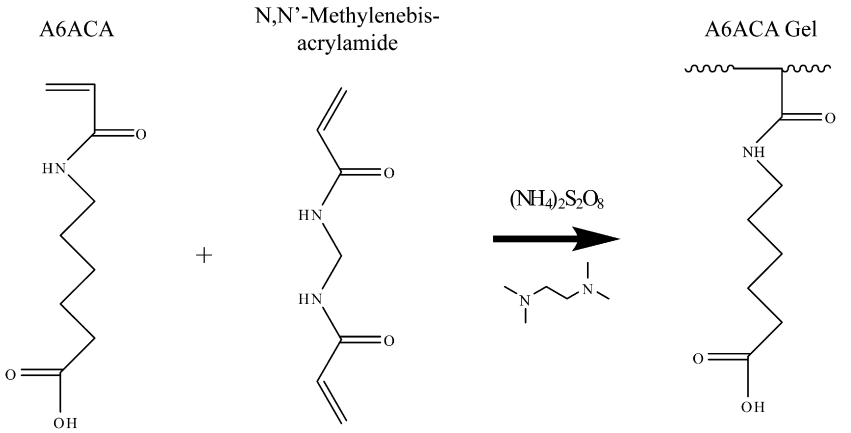


Fig. 21. Reaction used to produce self-healing hydrogels [13,225].

a dilute aqueous solution of 0.1 M $CuCl_2$ at ambient temperature. Tensile tests of the gels were performed as a function of healing period of 2, 6, and 12 h. Although the tensile strength of the healed gels increased with time and achieved up to 75% strength recovery after 12 h healing, 100% recovery to the original strength was not achieved. This is due to the occurrence of fracture along the weld line, which was weaker than the intrinsic strength of the gels. The factors affecting the healing ability include the metal-binding capacity of the gel, the nature of the complexation, and the ability to deform under stress.

### 5.7. Other approaches

A number of other approaches have been undertaken during the development of self-healing thermosets including the use of shape memory alloys, passivating additives and water absorbent matrices. These approaches can be separated from those discussed in previous sections as they do not repair structural defects, but address other properties such as surface smoothness or permeability. The focus of these technologies on non-structural repairs makes comparison with traditional self-healing polymers difficult. However, these approaches represent novel developments opening avenues to alternative applications of self-healing polymeric systems.

#### 5.7.1. Self-healing with shape memory materials

A method of producing "self-healing surfaces" based on the use of shape memory materials was patented in 2004 by Cheng et al. [193]. They described the complete recovery of dented or scratched surfaces by heating (to 150 °C) and then cooling the materials. Although the examples described are restricted to nickel–titanium alloys [193–195], shape memory polymers such as those described by Lendlein and Kelch [196] can also be used. This technology is likely to require heating for the healing to occur and is applicable to repair surface scratches. Other self-healing technologies involving shape memory alloys were also reported, however they either involved non-polymeric systems [197,198] or were used to assist other repair processes rather than complete the repair itself [199,200].

#### 5.7.2. Self-healing via swollen materials

Easter [201] developed a low-cost cable capable of self-healing damage through expansion action of the water-absorbable materials surrounding the conductor. The water-absorbable material can be located in any one of many layers covering the cable. When the cable is damaged and water ingress reached the water-absorbable composition, the water-absorbable material expands and fills in any voids, punctures or cracks present, thus sealing the damage in the cable. The water-absorbable material is comprised of either water-absorbable filler such as sodium bentonite or polyethylene oxide dispersed in a non-water-absorbable polymer such as polyisobutene or polyisoprene, or a water-absorbable polymer, i.e. polyethylene vinyl chloride or polyacrylic resins. The healing efficiency was not discussed in the patent. It is also worth noting that this self-healing mechanism is only effective for repairing damage when water is present in the environment.

A more detailed study is required to determine (i) the threshold amount of water for triggering the healing, and (ii) the effect of water content on the self-healing response and the extent of healing achieved.

### 5.7.3. Self-healing via passivation

In 1998, Sanders et al. [202] published a patent describing a flexible polymer barrier coating that automatically healed damages caused by exposure to UV radiation, oxygen, and in particular atomic oxygen in low earth orbit environment. The self-healing polymer layer is an organo-silicon material, which operates by providing silicon to react with oxygen from the environment to form a $SiO_x$ compound that condenses on defects, encapsulating impurities and filling the voids, cracks and other flaws. This self-healing structure can be used by itself or applied on top of a UV-sensitive substrate for instance. In one embodiment, the self-healing polymeric coating was applied to the base material followed by a layer of silicon-oxide. The silicon-based self-healing polymer is claimed to react with oxygen and undergo passivation when any damages in the silicon-oxide occur, repairing any cracks, pinholes or flaws in the UV barrier.

## 6. Modeling

Theoretical modeling and utilization of computational design tools to predict properties of self-healing materials are still in early stages. The modeling effort relates to self-healing of thermoplastics and various aspects of thermoset materials; however, a particular emphasis has been placed on the microencapsulation approach in the most recent publications.

Modeling of self-healing thermoplastics was first reported in the 1980s [14,72] to provide a basis for understanding the processes of damage as well as healing in these materials. The model describes healing in polymers in which mechanical properties, e.g., stress, strain, modulus, and impact energy, were related to time, temperature, pressure, molecular weight, and constitution of the material. Five stages of crack healing were presented as (i) the surface rearrangement stage initiates diffusion function; (ii) the approach stage controls the mode of healing; (iii) the wetting stage affects wetting distribution function; (iv) the diffusion stage is considered the most important stage where recovery of mechanical properties occur; (v) the randomization stage involves complete loss of memory of the crack interface. Although it is claimed that many of the theoretical predictions are supported by experimental data for single crack healing and processing of pellet resin, it appears that this model is mostly suitable for thermoplastic rather than thermoset materials because the chain mobility of the former is more likely to fit into the five stages healing model.

With the focus of the self-healing materials development shifting towards thermoset-based systems in recent years, the emphasis of latest modeling efforts have also been placed on various aspects of these self-healing materials. As part of the initial concept development, micro-mechanical modeling was used to study the effects of geometry and properties of the healing agent filled microcapsules on the mechanical triggering process for the healing [9,120,121]. The aspects investigated were thickness of the microcapsule wall, the toughness and the relative stiffness of the microcapsules, and the strength of the interface between the microcapsule and the matrix. Rupture and release of the microencapsulated healing agent were experimentally confirmed by optical and scanning microscopy observations, in agreement with the modeling prediction.

The modeling effort performed by Barbero et al. [203] extended continuum damage mechanics into continuum damage healing mechanics to model the irreversible healing process. This led to development of a numerical model of damage, plasticity, and healing for fiber-reinforced polymer composites. As a first step towards setting up a numerical modeling framework, Privman et al. [204] employed Monte Carlo simulations to model the dependence of a gradual formation of fatigue damage and its manifestation in polymer composite, and its healing by nanoporous fiber rapture and release of healing chemical. The results indicated that with the proper choice of the material parameters, effects of fatigue can be partially overcome and degradation of mechanical properties can be delayed. However, the simple continuum modeling adopted in the study of Privman et al. [204] cannot address the details of the morphological material properties and transport characteristics of the healing chemicals. In response to this problem, Maiti and Geubelle [23] adopted a numerical model based on the cohesive finite elemental technique to study the effect of fatigue crack closure in a self-healing material originally reported by White et al. [9]. The cohesive modeling has been successfully employed to study the crack propagation under cyclic loading [22,205–207].

A detailed study [23] of fatigue crack propagation in self-healing polymers has identified two key effects responsible for crack retardation: the crack bridging effect associated with the adhesion of the healing agent to the crack flanks, and the crack closure effect associated with the solid wedge formed by the deposited polymer behind the crack. The model allows for quantification of the relevant parameters such as applied load levels, wedge distance to the crack tip and wedge stiffness, which suggest that the inserted wedge shields the crack tip by reducing the effective stress intensity factor, thus retarding the crack growth. The model is also discussed in the context of self-healing polymers where the wedge effect is associated with the polymerization of the healing agent. However, this study assumes an instantaneous healing, in contrast to the experimental observations that rest periods on the fatigue response were required to achieve healing. A subsequent study [208] extended the capability of the modeling by combining a novel molecular dynamics simulation with cohesive modeling. This approach takes into consideration of the cure kinetics and the mechanical properties as a function of the degree of cure, and the resultant information is input into the continuum-scale models. The incorporation of healing kinetics in the model allows for a detailed study of the effect of a rest period on the crack retardation behavior, showing different regimes of crack retardation depending on the relative magnitudes of these characteristics time scales. The results of the modeling indicate that the presence of a rest period always increases the characteristic time for crack propagation and helps in crack retardation, in line with the experimental observations.

## 7. Conclusions

Research into self-healing polymeric materials is an active and exciting field. Beyond a strong interest of both academic and commercial researchers in the hollow fiber and microencapsulation approaches to self-healing polymer development, new types of self-healing technology have been emerging at an increasing rate over the last decade. Methods of incorporating self-healing capabilities in polymeric materials can now effectively address numerous damage mechanisms at molecular and structural levels. Activities in the field not only focus on mechanical and chemical approaches to improving the durability of materials but also involve new damage detection technique incorporated *in situ* the materials. Research in this field over the last 5 years has led to the development of new polymers, polymer blends, polymer composites and smart materials although none of these are commercially viable at present due to structural/chemical instabilities of the healing systems or use of expensive additives, etc.

Besides the most studied hollow fiber and microencapsulation approaches, technologies using thermally initiated healing (such as molecular interdiffusion, thermally reversibly crosslinks and thermoplastic additives) provides alternative pathway for self-healing polymer developments amongst the others. These technologies have a greater potential to provide multiple healing capabilities over extended time frames. Current developments are moving towards development and optimization of microvascular healing agent delivery networks [209–211] and healing agent filled nanocapsules that may be used in conjunction with these microvascular networks [212]. In reviewing recent developments of self-healing polymeric materials it is evident that significant advancements have been made toward the production of genuinely self-healing materials suitable for structural and other commercial applications.

## 8. Insights for future work

To date, the development of self-healing polymeric materials has been largely based on mimicking of biological healing. Despite the significant advancements made using biomimetic approach, there is still a long way to go before even the simplest biological healing mechanism can be replicated within these synthetic materials.

One immediate difference between biological and these synthetic healing mechanisms is that biological systems involve multi-step healing solutions. For example, healing in vertebrates and invertebrates is based on a ''patch then repair'' mechanism, even though the actual healing processes are significantly different. Human healing processes also rely on fast forming patches to seal and protect damaged skin before the slow regeneration of the final repair tissue [213]. In contrast to these mechanisms, all of the self-healing concepts discussed above attempt to complete healing in a single step either through *in-situ* curing of a new phase or a permanent re-sealing of newly exposed surfaces. The closest that the synthetic healing has come to a multi-step

healing process has been through the use of monomer mixtures by Liu et al. [143], where *in-situ* polymerization of a reinforcing wedge included a secondary and slower formation of a rigid polymeric component. It is expected that the introduction of multi-step healing processes will further improve the performance of the new self-healing polymeric materials.

A second difference in the dimensionality of the biological and synthetic healing systems resides in the multi-mechanistic approach used by the biological systems. Even the simplest biological systems use multiple healing mechanisms simultaneously. The healing process used by damaged cells involves a chaotic coalescence of lipids to block the hole [214] and then forms a purse-string-like structure to pull the edges of the hole closer together [215]. The repair mechanisms for bone [216], tendons [217] and skin [213] in humans are also based on a multi-mechanistic approach, involving initial inflammatory responses in conjunction with the regeneration of the damaged material. However, in synthetic healing either wedging or bridging is used as the sole repair mechanism despite the availability of numerous other crack growth retardation mechanisms such as crack surface sliding and zone shielding [24]. It could be argued that the addition of healing agent filled microcapsules to the epoxy matrix has increased the fracture toughness via crack growth retardation mechanisms such as crack pinning [121,130], however these improvements contribute to the intrinsic toughness of the composites rather than acting as a repair mechanism. Through the development of self-healing concept that deliberately uses multiple repair mechanisms, improved healing efficiencies and system robustness are likely to be achieved.

In addition to the development of a broader range of healing mechanisms, changes in the nature of the healing agents may be used to improve existing self-healing systems. Limitations of existing self-healing materials such as working temperatures and healing agent lifespan have already been identified [218] and are being addressed to produce self-healing composites that work in more extreme environments [116]. Further developments in healing agents may also include biomimetic fillers enabling an improved bending and buckling resistance with the use of sandwich-type cellular agents [219], enhancement of surface adhesion using branched fibrous agents that possess higher pullout energies [220], or improvement of healing consistency with self-assembling agents [221,222]. Whether achieved through the use of possible multistage/multi mechanistic healing methodologies or via evolutionary improvement of the existing methodologies, it is certain that continuous development of self-healing composites will produce a new generation of structural materials. It is anticipated that the field of self-healing will someday evolve beyond the current methods to procedures that use biomimetic healing abilities with incorporation of a circulatory system that continuously transports the necessary chemicals and building blocks of healing to the damaged sites.

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