

Self-healing Materials

Fundamentals, Design Strategies, and Applications

Edited by
Swapan Kumar Ghosh



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Preface

Scientists have altered the properties of materials such as metals, alloys, polymers, and so on, to suit the ever changing needs of our society. As we entered into the twenty-first century, search of advanced materials with crack avoidance and long-term durability is on high priority. The challenge for material scientists is therefore to develop new technologies that can produce novel materials with increased safety, extended lifetime and no aftercare or a very less amount of repairing costs. To stimulate this interdisciplinary research in materials technology, the idea of compiling a book came to my mind in 2005. When I contacted one of the pioneer scientists in this field he remarked that it is too early to write a book on such a topic. His opinion was right because the field of material science and technology is rapidly advancing and it would be worth to wait few more years to include the latest updates. Thus this book is compiled when the field of self-healing materials research is not matured enough as it is in its childhood.

The title *Self-healing Materials* itself describes the context of this book. It intends to provide its readers an upto date introduction of the field of self-healing materials (broadly divided into four classes—metals, polymers, ceramics/concretes, and coatings) with the emphasis on synthesis, structure, property, and possible applications. Though this book is mainly devoted to the scientists and engineers in industry and academia as its principle audience, it can also be recommended for graduate courses.

This book with its nine chapters written by international experts gives a wide coverage of many rapidly advancing fields of material science and engineering. The introductory chapter addresses the definition, broad spectrum of strategies, and application potentials of self-healing materials. Chapter 2 summarizes the recent advances in crack healing of polymers and polymer composites. Self-healing in most common polymeric structures occurs through chemical reactions. However, in the case of ionic polymers or ionomers healing follows a different mechanism. This is the subject of Chapter 3. Corrosion causes severe damages to metals. Encapsulated corrosion inhibitors can be incorporated into coatings to provide self-healing capabilities in corrosion prevention of metallic substrates. This is dealt in Chapter 4. Ceramics are emerging as key materials for structural applications. Chapter 5 describes the self-healing capability of ceramic materials. Concrete is the

most widely used man made materials for structural applications. The possibility of introducing self-healing function in cements is the key subject of Chapter 6. Self-healing in metals is dealt in Chapter 7 while its subsequent Chapter 8 provides an insight of self-healing phenomenon in metallic alloys. The last chapter of this book describes the developments of a model to predict the effects of distributed damages and its subsequent self-healing processes in fiber reinforced polymer composites.

I hope the above mentioned chapters will deliver the readers useful information on self-healing material developments. I am grateful to the contributing authors of this book for their assistance to make this project a success. I would also like to thank the whole Wiley-VCH team involved in this project. Though, last but not least, I would like to dedicate this book to my wife Anjana and son Subhojit for their constant support and encouragement in this venture.

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September 2008

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1

Self-healing Materials: Fundamentals, Design Strategies, and Applications

Swapan Kumar Ghosh

1.1

Introduction

Self-healing materials are no more an illusion and we are not far away from the days when manmade materials can restore their structural integrity in case of a failure. For example, the cracks in buildings can close on their own or the scratches on car bodies can recover their original shiny appearance by itself. Indeed, this is what everyone can see in case of the natural healing of wounds and cuts in living species. Virtually, all materials are susceptible to natural or artificial degradation and deteriorate with time. In the case of structural materials the long-time degradation process leads to microcracks that causes a failure. Thus, repairing is indispensable to enhance reliability and lifetime of materials. Though scientists are inspired by the natural process of blood clotting or repairing of fractured bones, incorporating the same concept into engineering materials is far from reality due to the complex nature of the healing processes in human bodies or other animals [1–6]. However, the recent announcement from Nissan on the commercial release of scratch healing paints for use on car bodies has gained public interest on such a wonderful property of materials [7].

1.2

Definition of Self-healing

Self-healing can be defined as the ability of a material to heal (recover/repair) damages automatically and autonomously, that is, without any external intervention. Many common terms such as self-repairing, autonomic-healing, and autonomic-repairing are used to define such a property in materials. Incorporation of self-healing properties in manmade materials very often cannot perform the self-healing action without an external trigger. Thus, self-healing can be of the following two types:

- autonomic (without any intervention);

- nonautonomic (needs human intervention/external triggering).

Here, in this review, different types of healing processes are considered as self-healing in general. Currently, self-healing is only considered as the recovery of mechanical strength through crack healing. However, there are other examples where not only the cracks but also small pinholes can be filled and healed to have better performance. Thus, this review addresses recovery of different types of properties, of materials.

1.3 Design Strategies

The different types of materials such as plastics/polymers, paints/coatings, metals/alloys, and ceramics/concrete have their own self-healing mechanisms. In this chapter, different types of self-healing processes are discussed with respect to design strategies and not with respect to types of materials and their related self-healing mechanisms as they are considered in the other chapters of this book. The different strategies of designing self-healing materials are as follows:

- release of healing agent
- reversible cross-links
- miscellaneous technologies
 - electrohydrodynamics
 - conductivity
 - shape memory effect
 - nanoparticle migration
 - co-deposition.

1.3.1 Release of Healing Agents

Liquid active agents such as monomers, dyes, catalysts and hardeners containing microcapsules, hollow fibers, or channels are embedded into polymeric systems during its manufacturing stage. In the case of a crack, these reservoirs are ruptured and the reactive agents are poured into the cracks by capillary force where it solidifies in the presence of predispersed catalysts and heals the crack. The propagation of cracks is the major driving force of this process. On the other hand, it requires the stress from the crack to be relieved, which is a major drawback of this process. As this process does not need a manual or external intervention, it is autonomic. The following sections give an overview of different possibilities to explore this concept of designing self-healing materials.

1.3.1.1 Microcapsule Embedment

Microencapsulation is a process of enclosing micron-sized particles of solids, droplets of liquids, or gases in an inert shell, which in turn isolates and protects them from the external environments [8–11]. The inertness is related to the reactivity of the shell to the core material. The end product of the microencapsulation process is termed as *microcapsules*. It has two parts, namely, the core and the shell. They may have spherical or irregular shapes and may vary in size ranging from nano- to microscale. Healing agents or catalysts containing microcapsules are used to design self-healing polymer composites. Early literature [12, 13] suggests the use of microencapsulated healing agents in a polyester matrix to achieve a self-healing effect. But they were unsuccessful in producing practical self-healing materials. The first practical demonstration of self-healing materials was performed in 2001 by Prof. Scot White and his collaborators [14]. Self-healing capabilities were achieved by embedding encapsulated healing agents into polymer matrix containing dispersed catalysts. The self-healing strategy used by them is shown in Figure 1.1.

In their work, they used dicyclopentadiene (DCPD) as the liquid healing agent and Grubbs' catalyst [bis(tricyclohexylphosphine) benzylidene ruthenium (IV) dichloride] as an internal chemical trigger and dispersed them in an epoxy matrix. The monomer is relatively less expensive and has high longevity and low viscosity. Figure 1.2 shows a representative morphology of encapsulated DCPD and Grubbs' catalyst [15–18].

When DCPD comes into contact with the Grubbs' catalyst dispersed in the epoxy resin a ring opening metathesis polymerization (ROMP) [19, 20] starts and a highly cross-linked tough polycyclopentadiene is formed that seals the crack (Figure 1.3).

The low viscosity of the monomer helps it to flow into the crack plane. The authors have demonstrated that as much as 75% of the recovery of fracture toughness compared to the original specimen can be achieved [17]. The same authors later used encapsulated catalyst instead of encapsulated monomer healing agent [21]. Monomers such as hydroxyl-functionalized polydimethylsiloxane (HOPDMS) and polydiethoxysilane (PDES) were added to vinyl ester matrix where they stay as microphase-separated droplets. The polyurethane microcapsules containing the catalyst di-*n*-dibutyltin dilaurate (DBTL) is then dispersed in the matrix. Upon rupture of these capsules the catalyst reacts with the monomer and polycondensation reaction of the monomers takes place. Keller *et al.* [22] have designed polydimethylsiloxane (PDMS)-based self-healing elastomers using two different types of microcapsules, namely, a resin capsule and an initiator capsule. The size of microcapsules on the self-healing efficiency was also investigated by White *et al.* [23].

Recently, White *et al.* has reported the synthesis of self-healing polymer composites without the use of catalysts [24]. Following these reports [25–30], a large number of research groups around the globe have involved actively in this radical field. Yin *et al.* recently reported the use of a latent curing agent, $\text{CuBr}_2(2\text{-MeIm})_4$, instead of

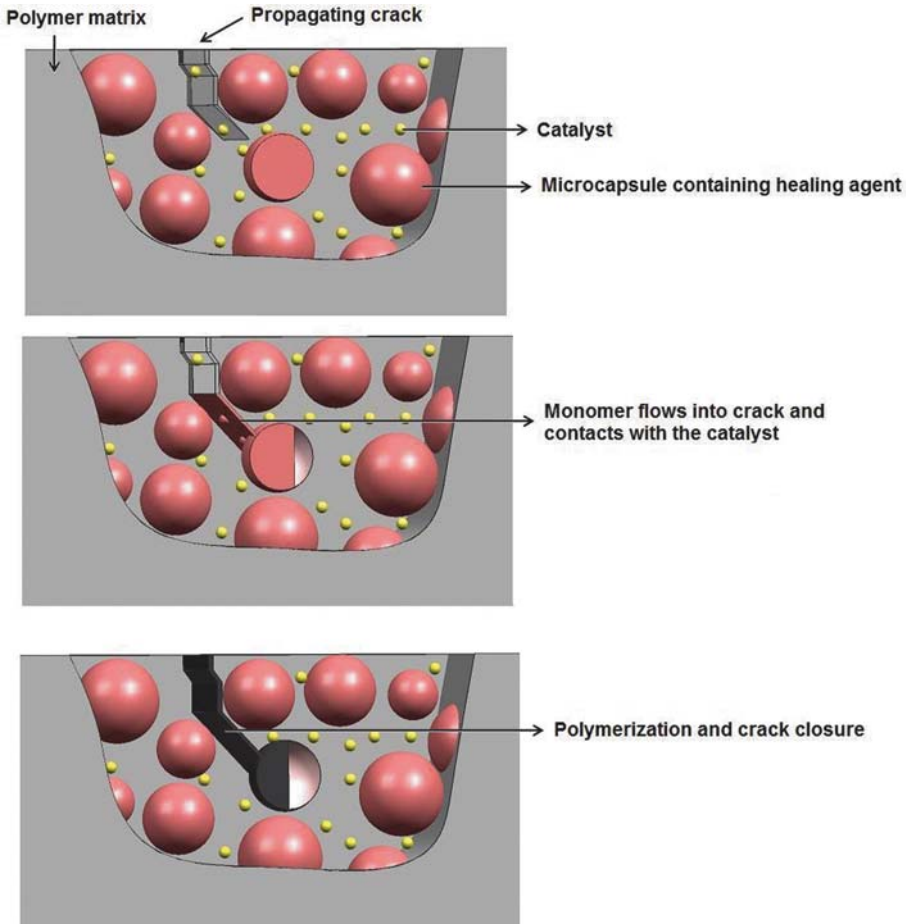


Fig. 1.1 Schematic representation of self-healing concept using embedded microcapsules.

solid phase catalyst, to design self-healing materials using ROMP reactions [31]. More detailed discussion on self-healing polymer composites designed through healing agent-based strategy can be found in Chapter 2 of this book.

The critical factors that influence the microencapsulation-based self-healing approach to produce an effective self-healing material are summarized in Table 1.1.

1.3.1.2 Hollow Fiber Embedment

Microcapsule-based self-healing approach has the major disadvantage of uncertainty in achieving complete and/or multiple healing as it has limited amount of healing agent and it is not known when the healing agent will be consumed entirely. Multiple healing is only feasible when excess healing agent is available in the matrix after the first healing has occurred. Thus, to achieve multiple healing in composite materials, another type of reservoir that might be able to deliver larger

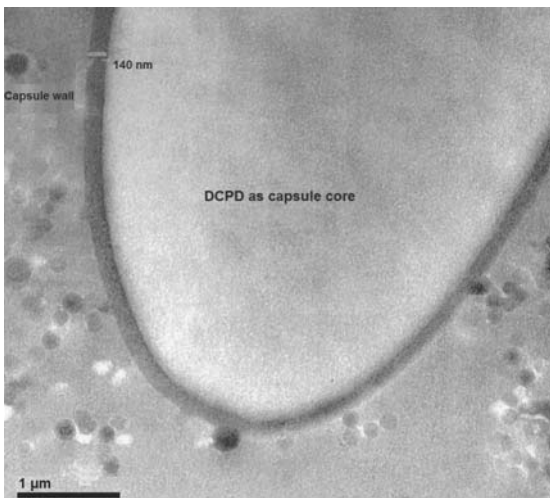
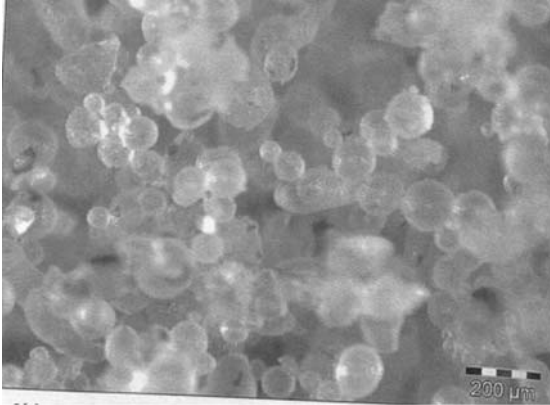


Fig. 1.2 Light microscopic picture of encapsulated DCPD and Grubb's catalyst. (Reprinted with permission from [18].)

amount of liquid healing agent was developed by Dry and coworkers [12, 32, 33]. However, they have achieved only limited success using their approach. Later, large diameter capillaries were embedded into resins by Motuku *et al.*, but the trials were unsuccessful as well [34]. Belay *et al.* have used smaller hollow glass fibers (Hollex fibers) filled with resin [35]. Composites system formulated on the basis of these filled glass fibers were unable to deliver the resin into the crack owing to the use of high viscous epoxy resins, and curing was also not good.

Bond and coworkers later developed a process to optimize the production of hollow glass fibers [36] and used these fibers as the container for liquid healing agents and/or dyes [37–41]. These borosilicate glass fibers' have diameter ranging from 30 to 100 μm with hollowness of 55% (Figure 1.4).

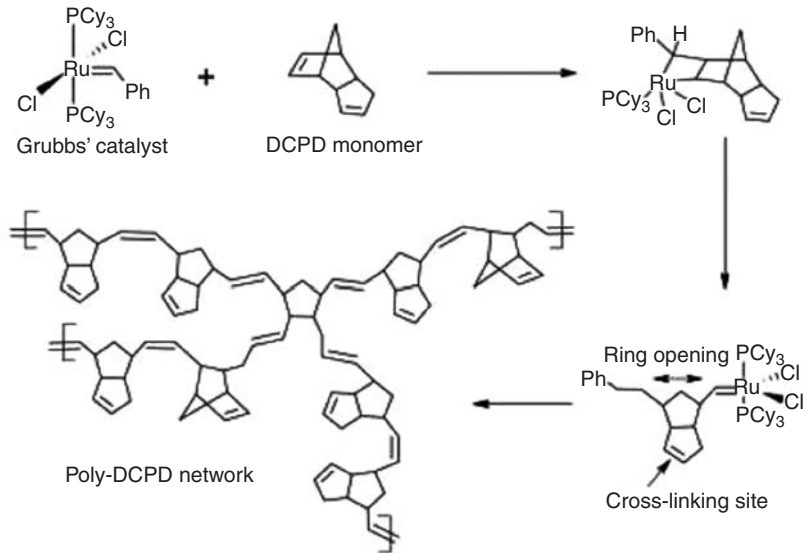


Fig. 1.3 Ring opening metathesis polymerization of DCPD. (Adapted from [19].)

Table 1.1 Important factors for developing microcapsule-based self-healing materials.

Parameters	Influencing factors
Microcapsule	<ul style="list-style-type: none"> Healing agent must be inert to the polymer shell Longer self life of the capsules Compatibility with the dispersion polymer medium Weak shell wall to enhance rupture Proximity to catalyst Strong interfacial attraction between polymer matrix and capsule shell wall to promote shell rupture
Monomer	<ul style="list-style-type: none"> Low viscous monomer to flow to the crack upon capillary action Less volatility to allow sufficient time for polymerization
Polymerization	<ul style="list-style-type: none"> Should be fast Stress relaxation and no cure induced shrinkage Room temperature polymerization
Catalysts	<ul style="list-style-type: none"> Dissolve in monomer No agglomeration with the matrix polymer
Coatings	<ul style="list-style-type: none"> Incorporation of microcapsules should have very less influence on physicomechanical properties of the matrix Coating thickness must be larger than the microcapsule size No clustering of catalysts or microcapsules in the matrix polymer Less expensive manufacturing process
Healing	<ul style="list-style-type: none"> Must be faster Multiple

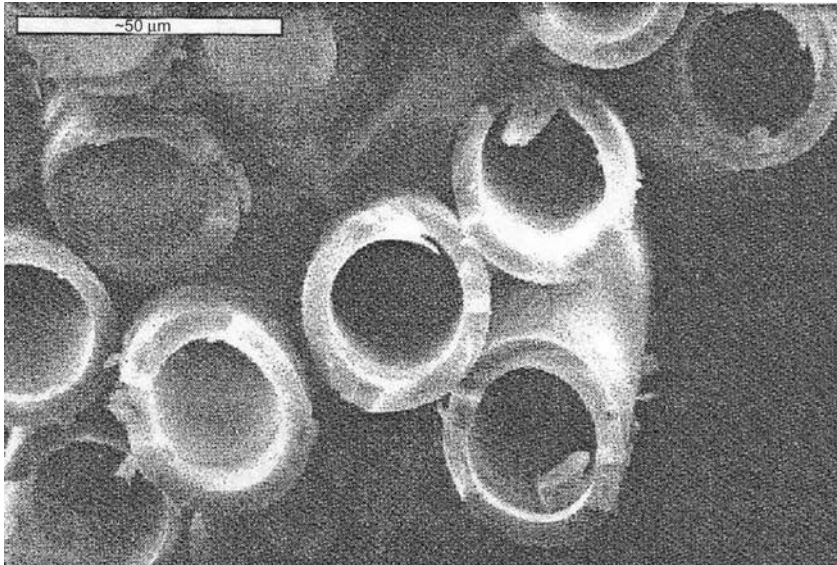


Fig. 1.4 Optical micrographs of hollow glass fibers.
(Reprinted with permission: Dr. J. P. Bond, University of Bristol, UK.)

Bond and coworkers have employed a biomimetic approach and fabricated composites with bleeding ability. Hollow fibers containing uncured resin or hardener (mixed with UV fluorescent dye for visual inspection) were prepared and plied to achieve a special layered up ($0^\circ/90^\circ$) structure in the matrix (epoxy resin) in combination with conventional glass fiber/epoxy system. Hollow fiber-based self-healing strategy is shown in Figure 1.5.

They have demonstrated that composite panels prepared using hollow fibers containing repairing agents can restore up to 97% of its initial flexural strength. The release and infiltration of fluorescent dye from fractured hollow fibers into the crack plane was also demonstrated. This approach of self-healing material design offers certain advantages, which are as follows:

- higher volume of healing agent is available to repair damage;
- different activation methods/types of resin can be used;
- visual inspection of the damaged site is feasible;
- hollow fibers can easily be mixed and tailored with the conventional reinforcing fibers.

Besides the above advantages, this approach has the following disadvantages as well:

- fibers must be broken to release the healing agent;
- low-viscosity resin must be used to facilitate fiber infiltration;
- use of hollow glass fibers in carbon fiber-reinforced composites will lead to CTE (coefficient of thermal expansion) mismatch.
- multistep fabrication is required.

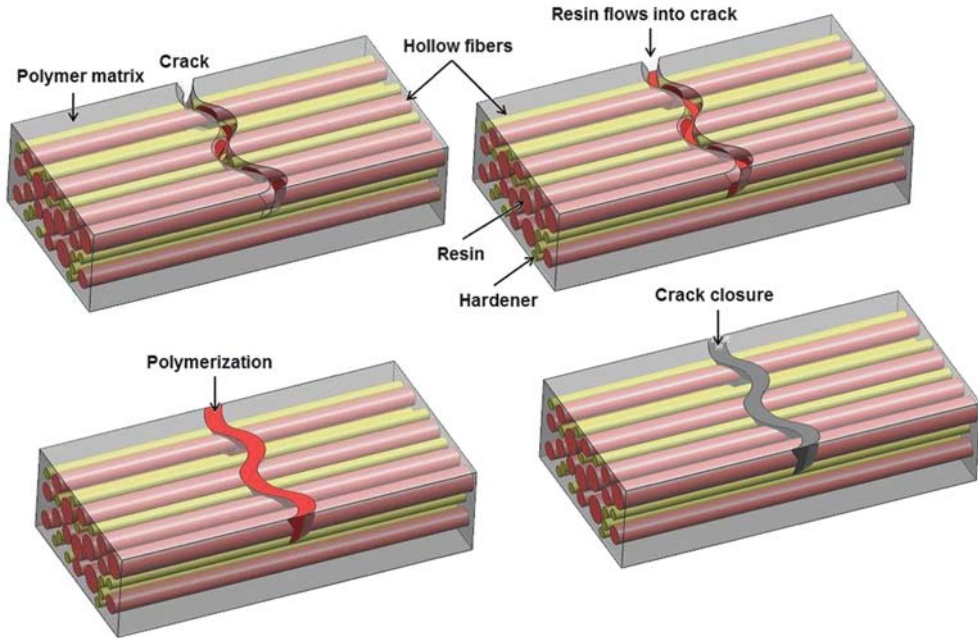


Fig. 1.5 Schematic representation of self-healing concept using hollow fibers.

Recently, Sanada *et al.* have shown the healing of interfacial debonding in fiber-reinforced polymers (FRPs) [42]. They have dispersed microencapsulated healing agent and solid catalyst in the coating layer on the surface of the fibers.

1.3.1.3 Microvascular System

To overcome the difficulty of short supply of a healing agent in microcapsule-based self-healing concept, another approach similar to biological vascular system of many plants and animals was explored by White *et al.* [43, 44]. This approach relies on a centralized network (that is microvascular network) for distribution of healing agents into polymeric systems in a continuous pathway. The fabrication process is complex and it is very difficult to achieve synthetic materials with such networks for practical applications. In this process, organic inks are deposited following a 3D array and the interstitial pores between the printed lines are infiltrated with an epoxy resin. Once the polymer is cured, the fugitive ink is removed leaving behind a 3D microvascular channel with well-defined connectivity. Polymeric systems with microvascular networks were prepared by incorporating chemical catalysts in the polymer used to infiltrate the organic ink scaffold (Figure 1.6). Upon curing the polymer and removing the scaffold, the healing agent is wicked into the microvascular channels. Several researchers reported such fabrication processes and related self-healing capabilities [45–48].

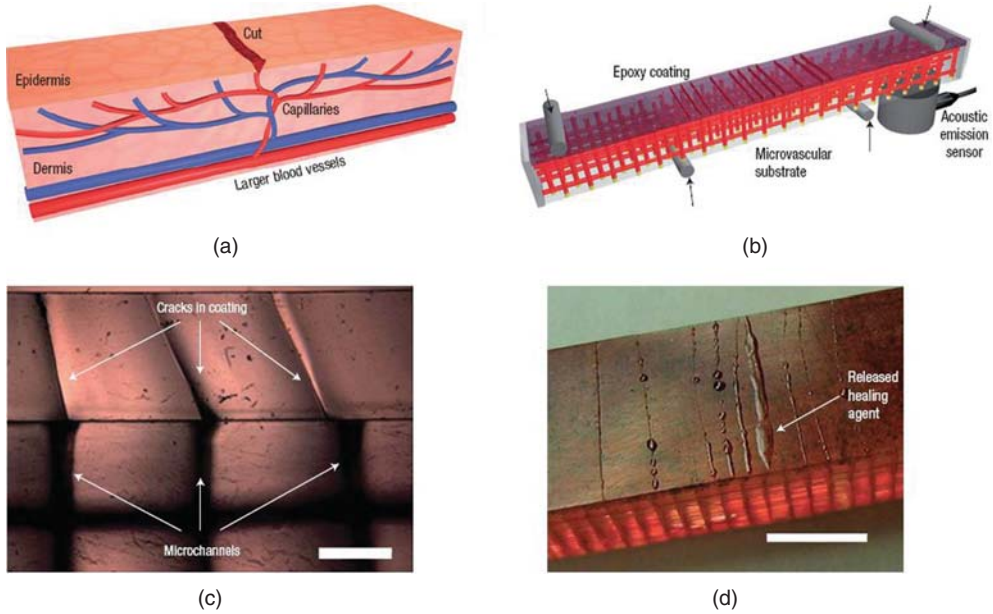


Fig. 1.6 Schematic showing self-healing materials with 3D microvascular networks. (a) Schematic diagram of a capillary network in the dermis layer of skin with a cut in the epidermis layer. (b) Schematic diagram of the self-healing structure composed of a microvascular substrate and a brittle epoxy coating containing embedded catalyst in a four-point bending configuration monitored with an acoustic-emission sensor.

(c) High-magnification cross-sectional image of the coating showing that cracks, which initiate at the surface, propagate toward the microchannel openings at the interface (scale bar = 0.5 mm). (d) Optical image of self-healing structure after cracks are formed in the coating (with 2.5 wt% catalyst), revealing the presence of excess healing fluid on the coating surface (scale bar = 5 mm). [Reprinted with permission from Ref. 44.]

1.3.2

Reversible Cross-links

Cross-linking, which is an irreversible process, of polymeric materials is performed to achieve superior mechanical properties, such as high modulus, solvent resistance, and high fracture strength. However, it adversely affects the refabrication ability of polymers. Moreover, highly cross-linked materials have the disadvantage of brittleness and have the tendency to crack. One approach to bring processability to cross-linked polymers is the introduction of reversible cross-links in polymeric systems [49–51]. In addition to refabrication and recyclability, reversible cross-links also exhibit self-healing properties. However, reversible cross-linked system does not show self-repairing ability by its own. An external trigger such as thermal, photo, or chemical activation is needed to achieve reversibility, and thereby the self-healing ability. Thus, these systems show nonautonomous healing phenomenon. In the following sections, different approaches that are considered to bring reversibility in cross-linked polymeric materials are discussed.

1.3.2.1 Diels–Alder (DA) and Retro-DA Reactions

Major classes of thermally reversible polymers are made using Diels–Alder (DA) reactions. Examples of this category include cross-linking of furanic polymers with maleimide or polymers containing maleimide pendants at low temperature. Retro-DA reaction occurs at elevated temperatures to debond the chemical linkages of formed networks and to reverse the cross-linking process [52]. DA reactions ($4 + 2$ cycloadditions) are the most studied thermally controlled covalent bond formation. Though there are several reports available on reversible reactions, Wudl and coworkers were the first to implement this strategy to design thermally remendable polymers [53, 54]. The first polymer ($3M + 4F = \text{polymer } (3M4F)$) they synthesized (Figure 1.7) showed a strength recovery of 53% [55]. Later, they have reported improved system with mechanical strength recovery of 83%. Since their discovery, several other research groups around the globe have further contributed to this exciting field of research [56–61].

Liu *et al.* have adapted a modified Wudl's approach in their work [57]. They have synthesized multifunctional furan and maleimide compounds using epoxy compounds as precursors (Figure 1.8). These precursors induce advantageous characteristics of epoxy resins, such as solvent and chemical resistance, thermal and electrical properties, and good adhesion in the final cured polymer. Besides that, the modified furan and maleimide monomers become soluble in most common organic solvents such as acetone, methanol, ethanol, and tetrahydrofuran. The use of solvents, such as acetone, with low-boiling temperature is beneficial, as curing of the matrix can be avoided in the solvent removal stage.

Equal amounts of the modified monomers were dissolved in acetone to produce a homogeneous solution. Then, the solvent was removed and the film was heated

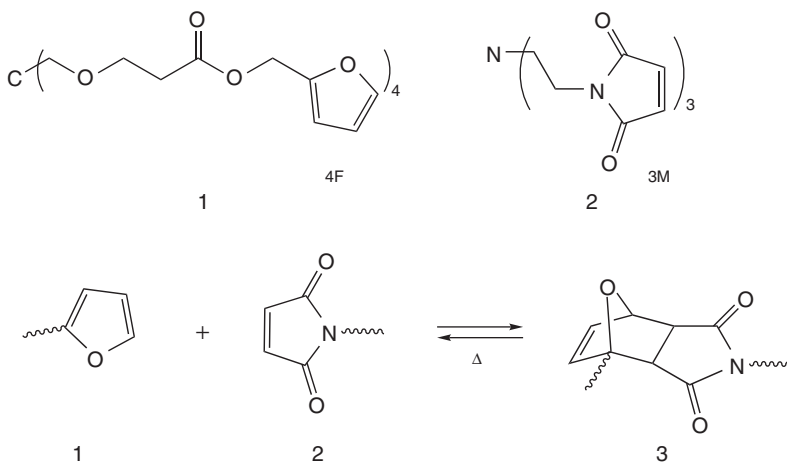


Fig. 1.7 Schematic showing formation of highly cross-linked polymer (3M4F) [polymer 3] using a multi-diene (four furan moieties, 4F) [monomer 1] and multi-dienophile (three maleimide moieties, 3M) [monomer 2] via DA reactions [adapted from Ref. 55].

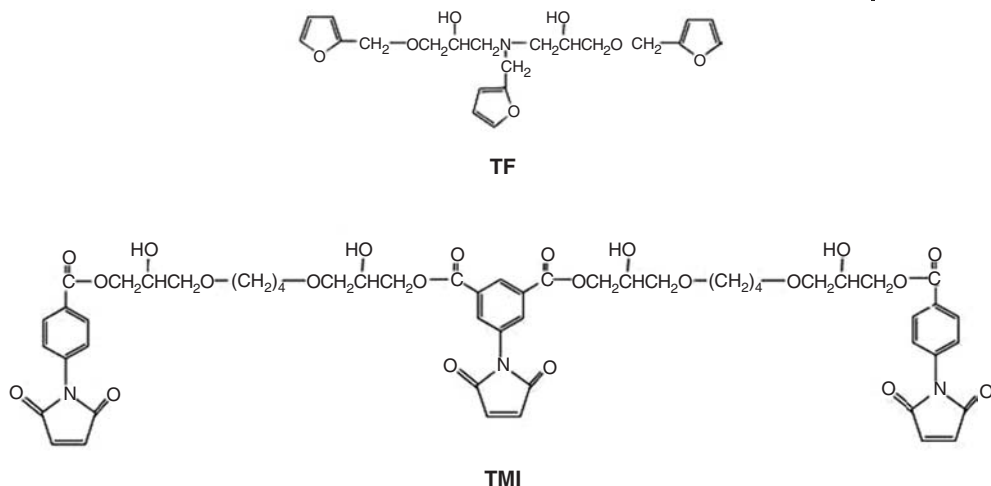


Fig. 1.8 Chemical structure of functionalized maleimide and furan monomers [adapted from Ref. 57].

in an oven for 12 h at 50 °C. A solid film was produced as the cross-linking between trimaleimide (TMI) and trifuran (TF) takes place via maleimide and furan groups through DA reactions (Figure 1.9). The debonding (retro-DA) occurred upon heating the sample at 170 °C for 30 min.

The self-repairing property of TMI–TF cross-linked material was investigated by morphological analysis using Scanning Electron Microscopic (SEM) techniques (Figure 1.10). The cross-linked material shows a smooth and planar surface as-prepared Figure 1.10a. Figure 1.10b shows a notch made on the surface of the sample by knife-cutting. The cut sample was then thermally treated at 120 °C for 20 min and at 50 °C for 12 h (Figure 1.10c). At higher temperature, debonding (retro-DA) occurred and the polymer chains reformed at this temperature. DA reactions (bonding of polymer chains) take place again at lower temperatures and the cross-linked structure is reformed. A complete repairing was obtained by treating the sample at 50 °C for 24 h (Figure 1.10d).

Later Lu *et al.* have synthesized polymers-based maleimide-containing polyamides and a tri-functional furan compound [58]. The prepared adduct shows good thermoreversibility and gel formation through DA and retro-DA reactions (Figures 1.11 and 1.12).

Recently they have used modified polyamides having various amounts of maleimide and furan pendant groups to obtain self-healing capability using DA and retro-DA reactions [59]. However, the prepared adduct does not show complete repairing of the cracks due to the low mobility of high molecular polyamide chains in bulk.

Recently Chung *et al.* [62] have reported for the first time light-induced crack healing. They have chosen 2 + 2 photochemical cycloaddition of cinnamoyl groups to obtain self-healing properties. Photo-cross-linkable cinnamate monomer, 1,1,1-tris-

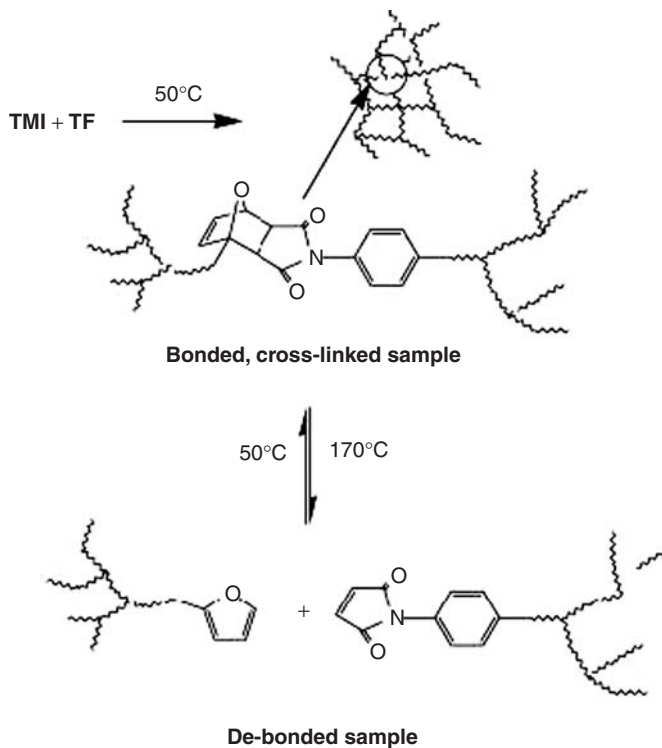


Fig. 1.9 Thermally reversible cross-linking reaction between TMI and TF through DA and retro-DA reactions [Adapted from Ref. 57].

(cinnamoyloxymethyl)ethane (TCE), was used for their study. The photocycloaddition and recycloaddition of cinnamoyl groups are schematically shown in Figure 1.13.

The authors demonstrated the self-healing capability of the complexes by measuring the flexural strength of cracked and healed samples and the reaction was confirmed by Fourier Transform Infrared (FTIR) spectroscopy. The photochemical healing is very fast and does not require catalysts, additives, or heat treatments.

1.3.2.2 Ionomers

Ionomers are a special class of polymeric materials that contain a hydrocarbon backbone and pendent acid groups, which are neutralized partially or fully to form salts [63–69]. The ion content of ionomeric polymers or ionomers varies over a wide range, but in general it is up to 15 mol%. The methods of synthesis of ionomers can be broadly divided into two main classes: (i) direct synthesis (copolymerization of a low-level functionalized monomer with an olefinic unsaturated monomer) and (ii) post-functionalization of a saturated preformed polymer. The ionic interactions present in ionomers usually involve electrostatic interactions between anions, such as carboxylates and sulfonates, and metal cations from Group 1A, Group 2A, or transitional metal cations. A wide variety of carboxylates, sulfonates or ionomers

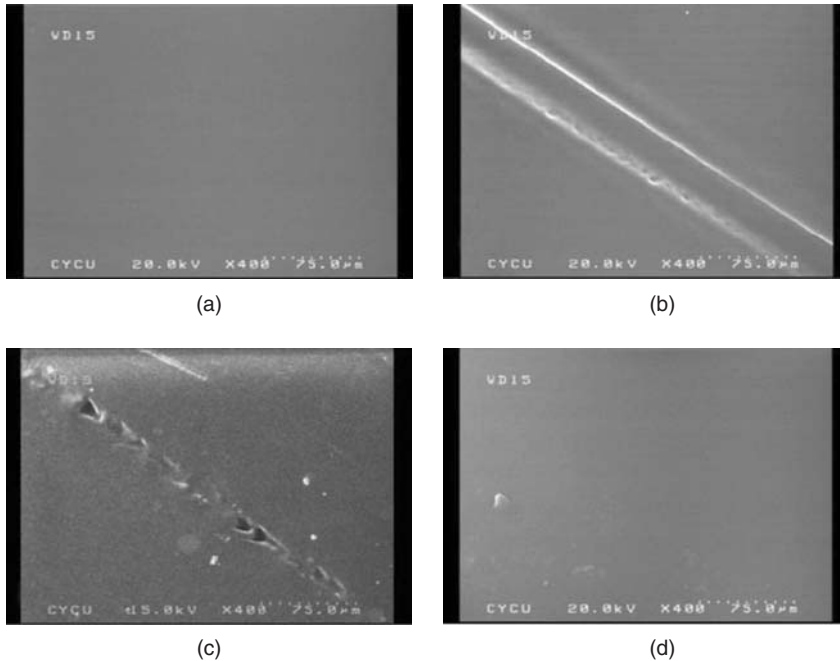


Fig. 1.10 SEM micrographs of (a) cross-linked adducts, (b) knife-cutting sample, and thermally self-repaired sample at 50 °C for (c) 12 h and (d) 24 h [Adapted from Ref. 57].

having both carboxylated and sulfonated groups in the same chain can be found in the literature. The polar ionic groups tend to aggregate as a result of electrostatic interactions despite the opposing tendency of the chain elastic forces. The presence of ionic groups and their interactions produce physical cross-links that are reversible in nature (Figure 1.14).

Introduction of a small amount of ionic group causes dramatic improvement in polymer properties, such as tensile strength, tear resistance, impact strength, and abrasion resistance. As ionomers are not thermosetting materials, they can be processed like thermoplastics. This unique combination of physical properties and processing ease has led this class of polymers to be used in food packaging, membrane separation, roofing materials, automobile parts, golf ball covers, coatings, and so on. Besides the above-mentioned applications, the reversible nature of ionic bonds makes them suitable for designing self-healing polymeric systems [70–72]. A detailed discussion on ionomer morphology and its potential as a self-healing material can be found in Chapter 3.

1.3.2.3 Supramolecular Polymers

Polymeric properties in traditional polymers are achieved due to the length and entanglement of long chains of monomers, which are held together by covalent bonds. Recently, low molar mass monomers are assembled together by reversible noncovalent interactions to obtain polymer-like rheological or mechanical

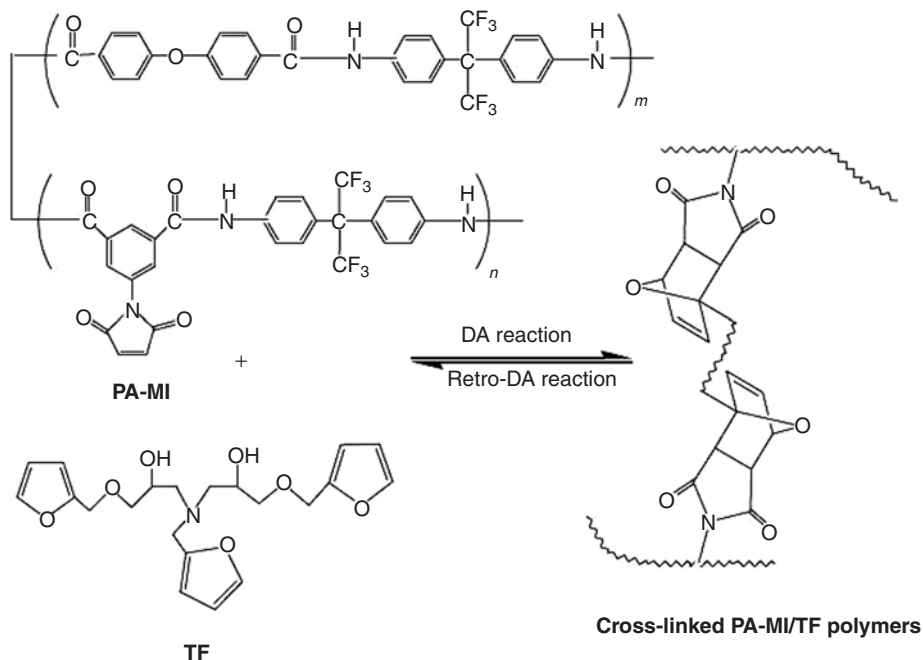


Fig. 1.11 Preparation of thermally reversible polyamides. (Reprinted with permission from [58].)

properties [73–76]. As noncovalent interactions can be reversibly broken and can be under thermodynamic equilibrium, this special class of macromolecular materials, that is, the so-called supramolecular polymers show additional features compared to usual polymers. These features include switchable environment-dependent properties, improved processing, and self-healing behavior. In general, supramolecular polymers can be divided broadly into two categories, which are main- and side-chain types. Although noncovalent interactions hold the backbone of the main-chain supramolecular polymers, it is used to either change or functionalize conventional covalent polymers in case of side-chain supramolecular polymers. Some examples of both classes of supramolecular polymers are shown in Figure 1.15.

Different types of assembly forces, such as metal–ligand interactions, π – π interactions, hydrophobic, electrostatic interactions, and hydrogen bonding are used to design supramolecular polymers. Hydrogen bonding is the most popular route of achieving supramolecular polymers. The main challenge in this approach is to find the right balance between the association constant and a reversible system. The higher the association constant, the lesser is the reversibility. In contrast, the lower the association constant, the better the reversibility, that is, smaller assemblies and poor mechanical properties.

Meijer and coworkers were the first to assemble ureidopyrimidone (U_{py}) monomers by using quadruple hydrogen bonding noncovalent interactions with