

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);

2 | 1 Self-healing Materials: Fundamentals, Design Strategies, and Applications

- 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

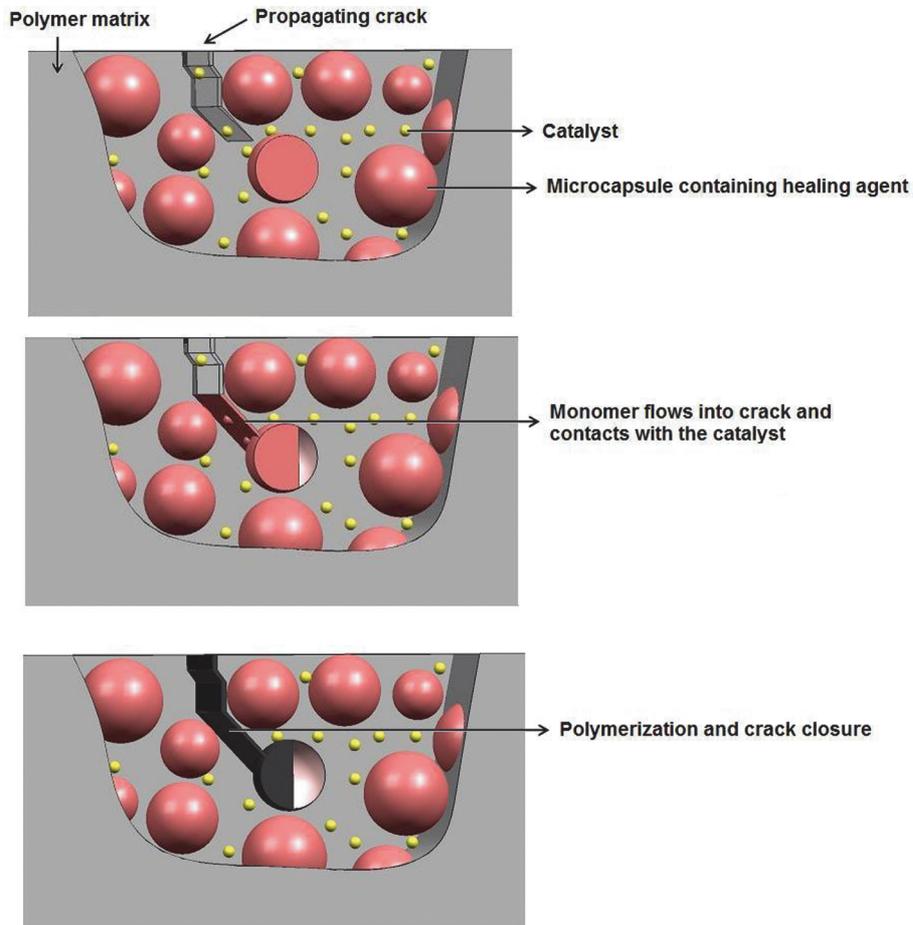


Fig. 1.1 Schematic representation of self-healing concept using embedded microcapsules.

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

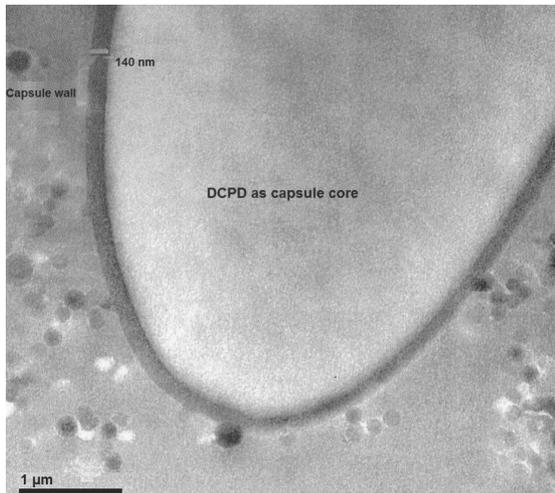
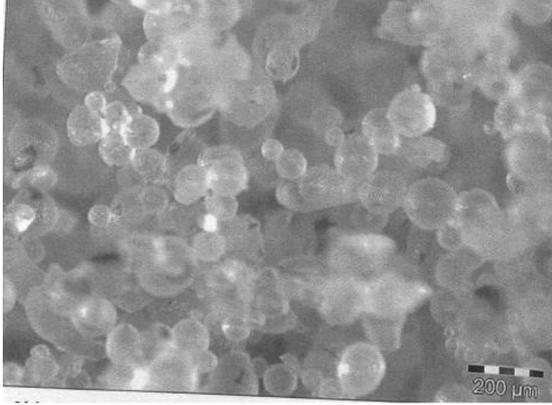


Fig. 1.2 Light microscopic picture of encapsulated DCPD and Grubb's catalyst. (Reprinted with permission from [18].)

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).

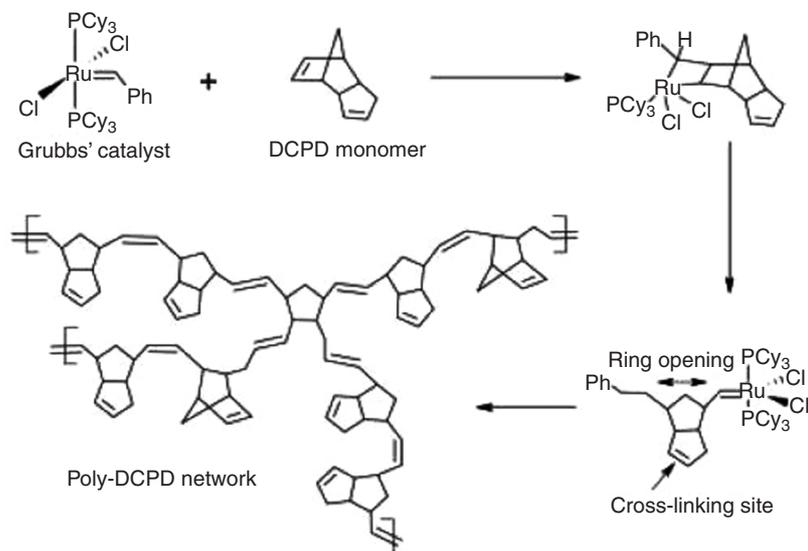


Fig. 1.3 Ring opening metathesis polymerization of DCPD. (Adapted from [19].)

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 physicochemical 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

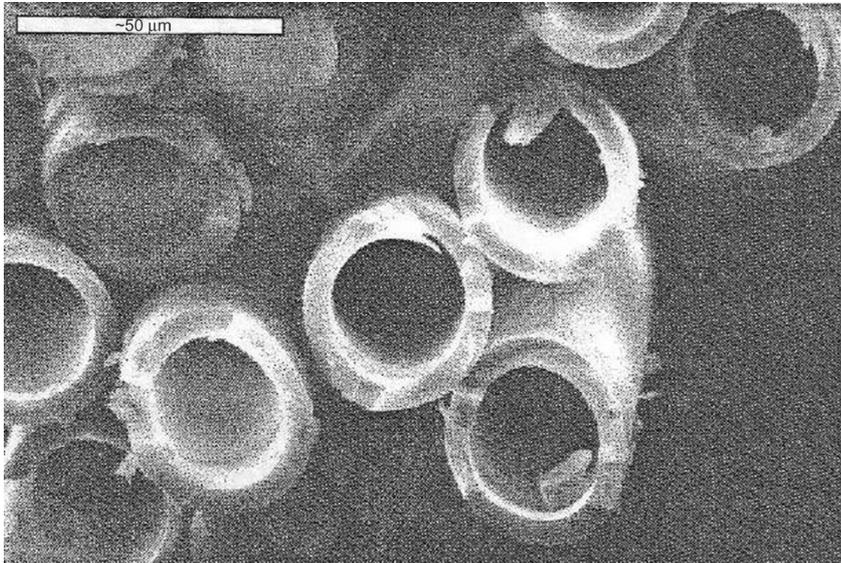


Fig. 1.4 Optical micrographs of hollow glass fibers.
(Reprinted with permission: Dr. J. P. Bond, University of Bristol, UK.)

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.

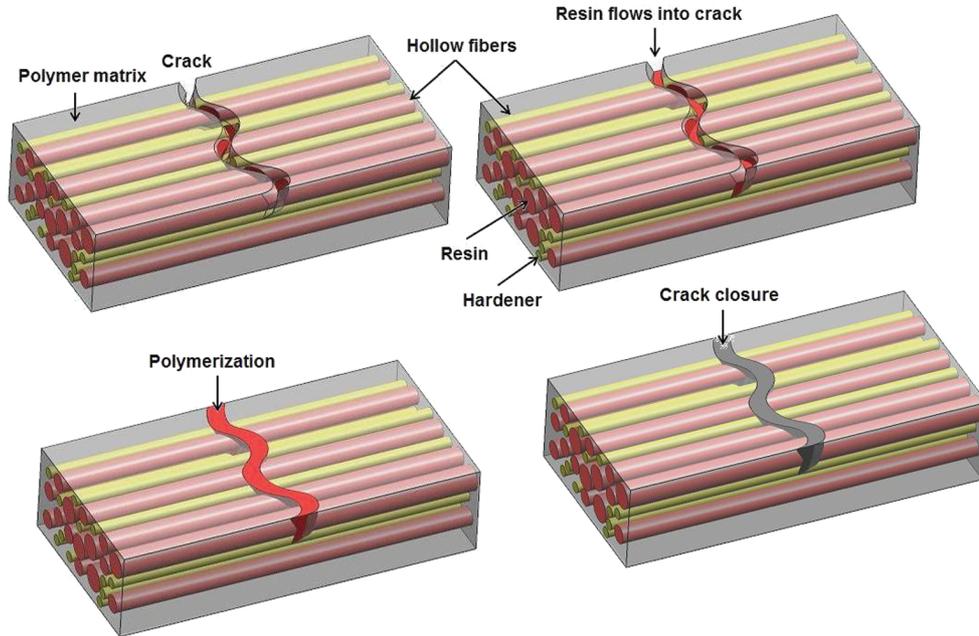


Fig. 1.5 Schematic representation of self-healing concept using hollow fibers.

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].

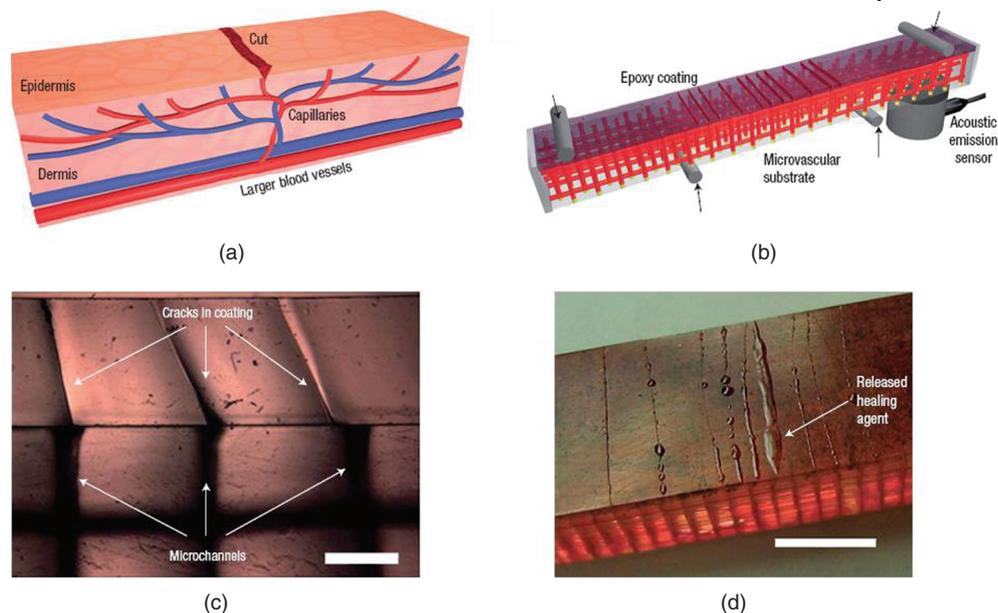


Fig. 1.6 Schematic showing self-healing materials with 3D microvascular networks. (a) Schematic diagram of a capillary network in the dermis layer of skin with a cut in the epidermis layer. (b) Schematic diagram of the self-healing structure composed of a microvascular substrate and a brittle epoxy coating 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 nonautonomic 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

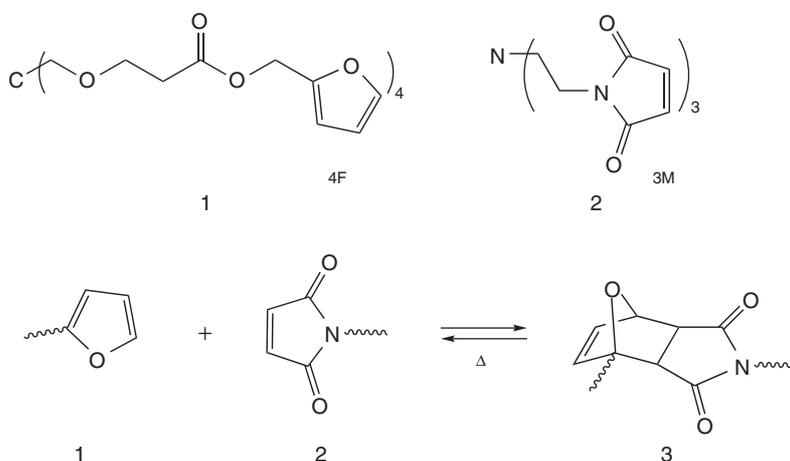


Fig. 1.7 Schematic showing formation of highly cross-linked polymer (3M4F) [polymer 3] using a multi-diene (four furan moieties, 4F) [monomer 1] and multi-dienophile (three maleimide moieties, 3M) [monomer 2] via DA reactions [adapted from Ref. 55].

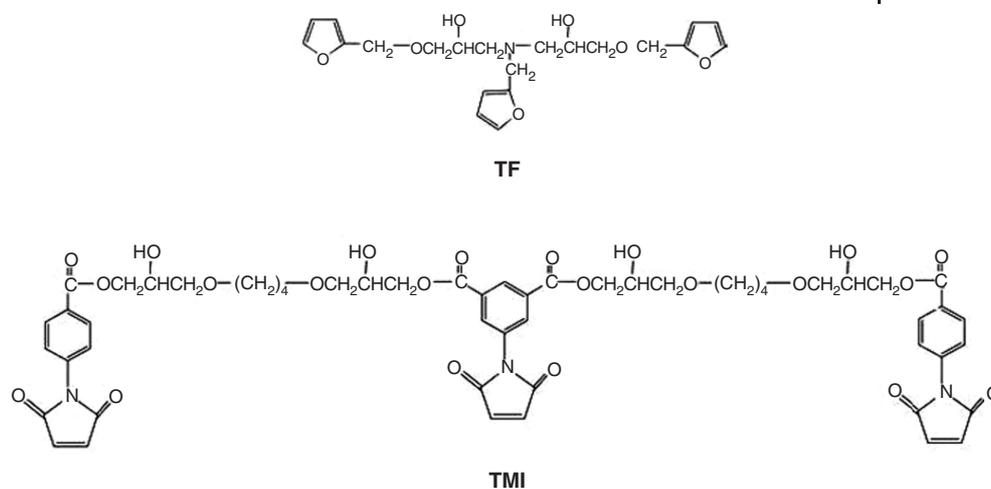


Fig. 1.8 Chemical structure of functionalized maleimide and furan monomers [adapted from Ref. 57].

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-

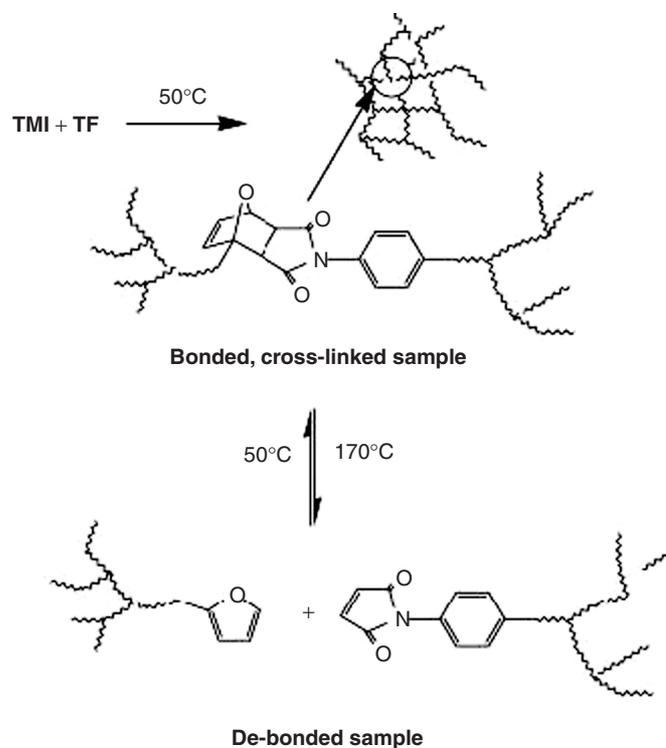


Fig. 1.9 Thermally reversible cross-linking reaction between TMI and TF through DA and retro-DA reactions [Adapted from Ref. 57].

(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

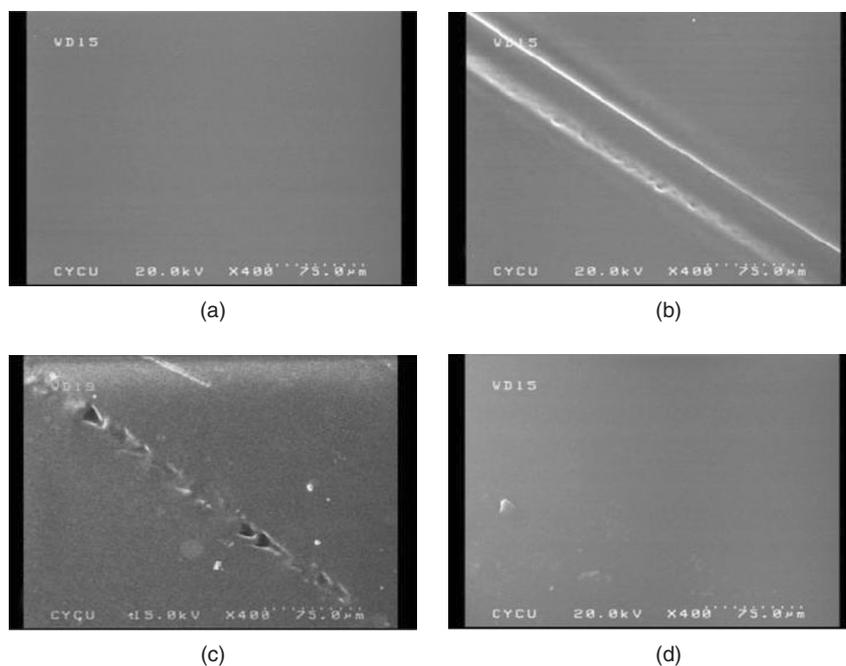


Fig. 1.10 SEM micrographs of (a) cross-linked adducts, (b) knife-cutting sample, and thermally self-repaired sample at 50 °C for (c) 12 h and (d) 24 h [Adapted from Ref. 57].

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

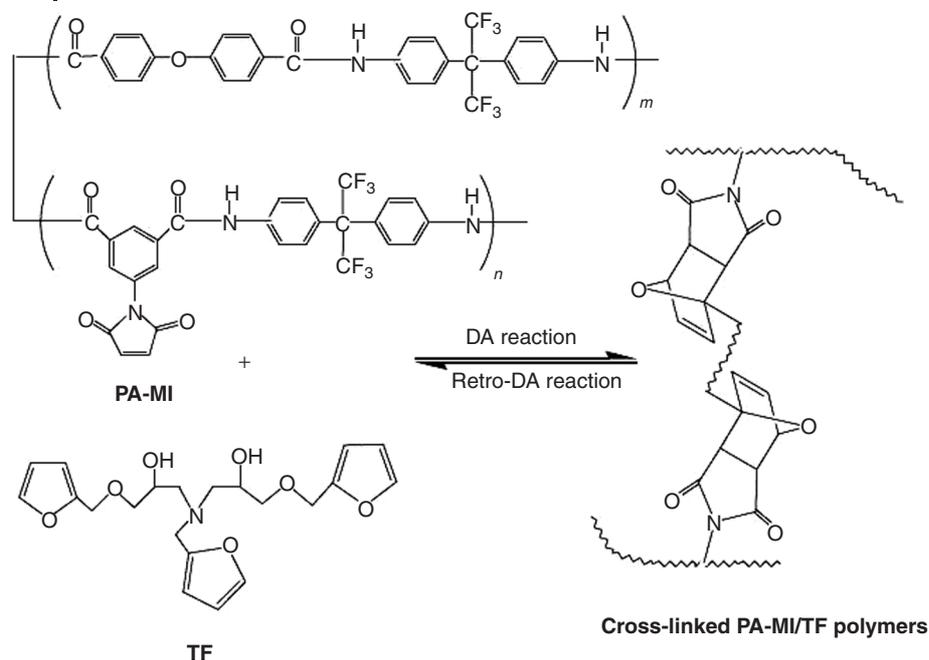


Fig. 1.11 Preparation of thermally reversible polyamides. (Reprinted with permission from [58].)

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 reversible interaction. 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 (Upy) monomers by using quadruple hydrogen bonding noncovalent interactions with

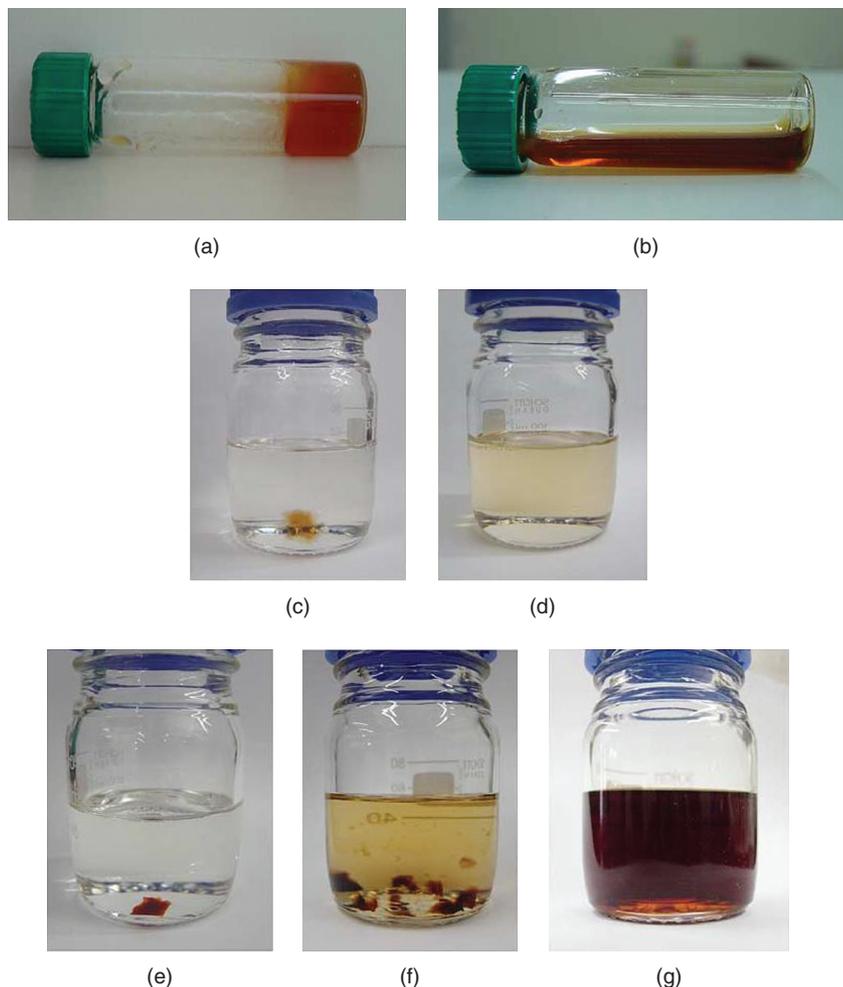


Fig. 1.12 Photographs showing thermally reversible cross-linking behavior of PA-MI/TF polymers (PA-MI-1/TF polymers have lowest cross-link density and PA-MI-10/TF polymers have highest cross-link density). Polymer gel of PA-MI-1/TF in N, N-dimethylacetamide (DMAc): (a) 30 °C, (b) 160 °C and cross-linked PA-MI-1/TF in DMAc: (c) 30 °C, 5 h, insoluble and (d) 120 °C, 2 h, soluble. Cross-linked PA-MI-10/TF polymer in DMAc: (e) 30 °C, 5 h insoluble, (f) 120 °C, 5 h partially soluble, and (g) 160 °C, 5 h, soluble. (Reprinted with permission from [58].)

high degree of polymerization [77, 78]. The resulting material display mechanical properties similar to traditional polymers. This discovery of using weak reversible hydrogen bonding interactions to produce supramolecular assemblies with high association constant and having polymeric properties makes this field an exciting area for materials research. The Upy compounds are cheap and can be incorporated into other polymeric systems to improve processability or other functionalities. This hydrogen bonded unit is further utilized in the chain extension of telechelic

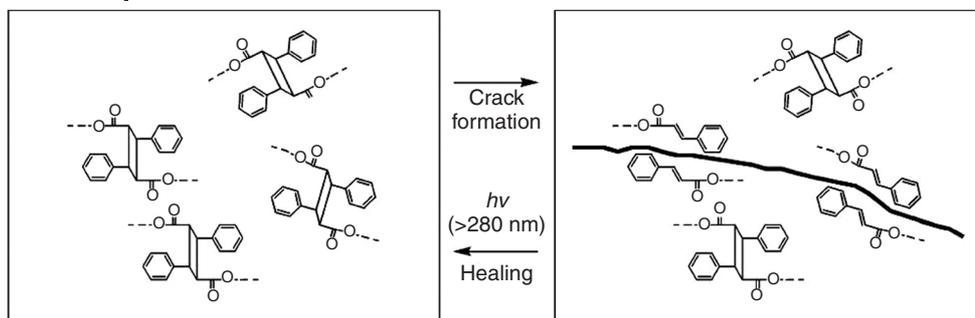


Fig. 1.13 Schematic illustration of photochemical self-healing concept [reprinted with permission from Ref. 62].

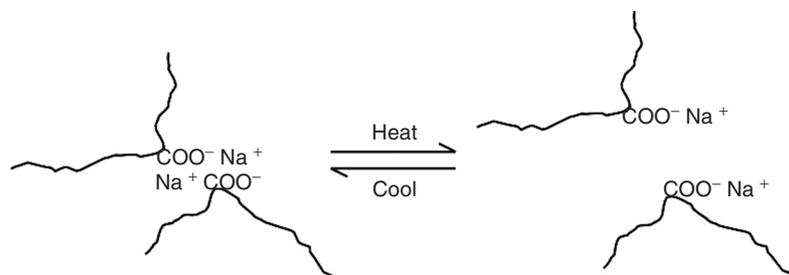


Fig. 1.14 Schematic showing reversible ionic interactions.

polysiloxanes, polyethers, polyesters, and so on. On the basis of the above discovery, a spin-off company from the Technical University of Eindhoven, SupraPolix BV, has already started exploring this field commercially [79]. Hybrid systems were also developed by using supramolecular monomers with traditional polymers. Cordier and colleagues have recently published a very interesting piece of research that brings together supramolecular chemistry and polymer physics to develop self-healing rubbers [80]. They have used fatty diacids and triacids from renewable resources and used two-step synthetic routes to produce self-healing rubbers. In the first step, acid groups were condensed with excess of diethylene triamine, and in the second step, the condensed acid groups were made to react with urea. The resulting material shows rubber-like characteristics and self-healing capability. The prepared material can be repaired by simply bringing the two cut ends together at room temperature without the need of external heat. However, if the broken parts are kept for a longer period (Figure 1.16), they need to be held together for longer period for self-mending.

Besides hydrogen bonding, metal–ligand supramolecular interactions are also being explored to design supramolecular polymers [81, 82, 83]. Metal complexes offered certain advantages due to its optical and photophysical properties. Moreover, its reversibility can be tuned by using different metal ions. Though bi-pyridine complexes are well known, it is the terpyridine-based metal–ligand complexes that are gaining increased attention as a new type of functional materials (Figure 1.17).

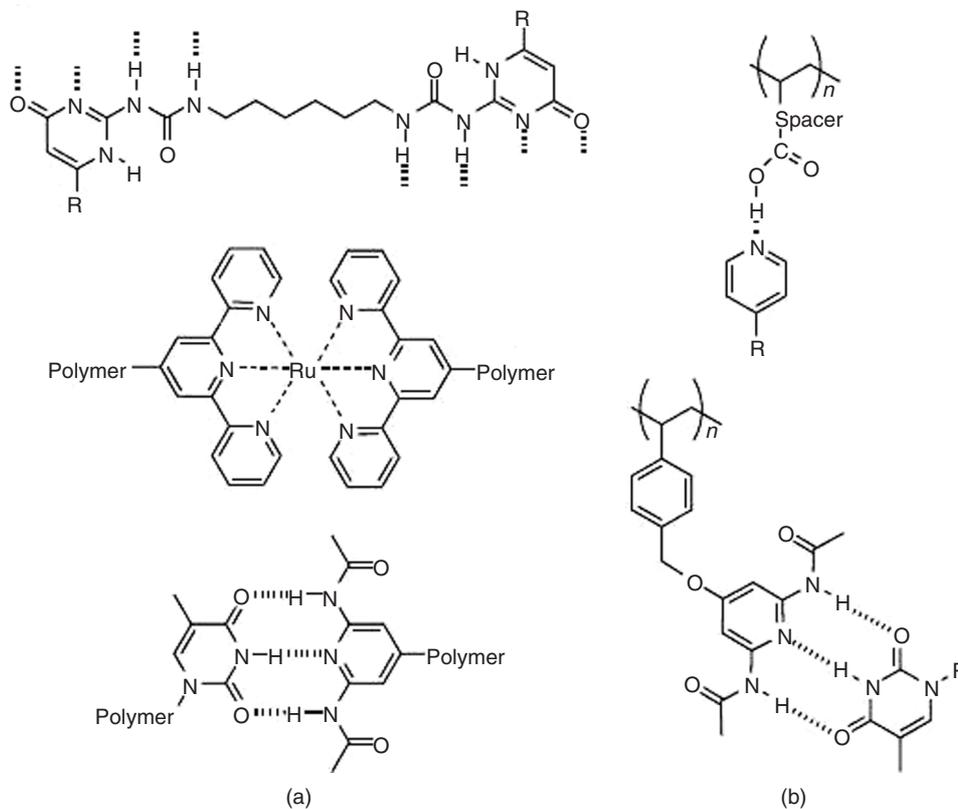


Fig. 1.15 Examples of supramolecular polymers from the literature: (a) main-chain supramolecular polymers and (b) side-chain supramolecular polymers.

These ligands can be introduced into polymeric systems by several ways, such as copolymerization of functionalized monomer, functionalization of end or side groups of preformed polymers, or by using functionalized initiators and/or end cappers in living or controlled polymerizations.

1.3.3

Miscellaneous Technologies

Technologies other than the most important self-healing approaches described above are available in the literature. These emerging technologies are discussed in the following sections of this review.

1.3.3.1 Electrohydrodynamics

In this approach, the blood clotting process was mimicked via colloidal particle aggregation at the defected site. Prof. Ilhan Aksay and his collaborators have used

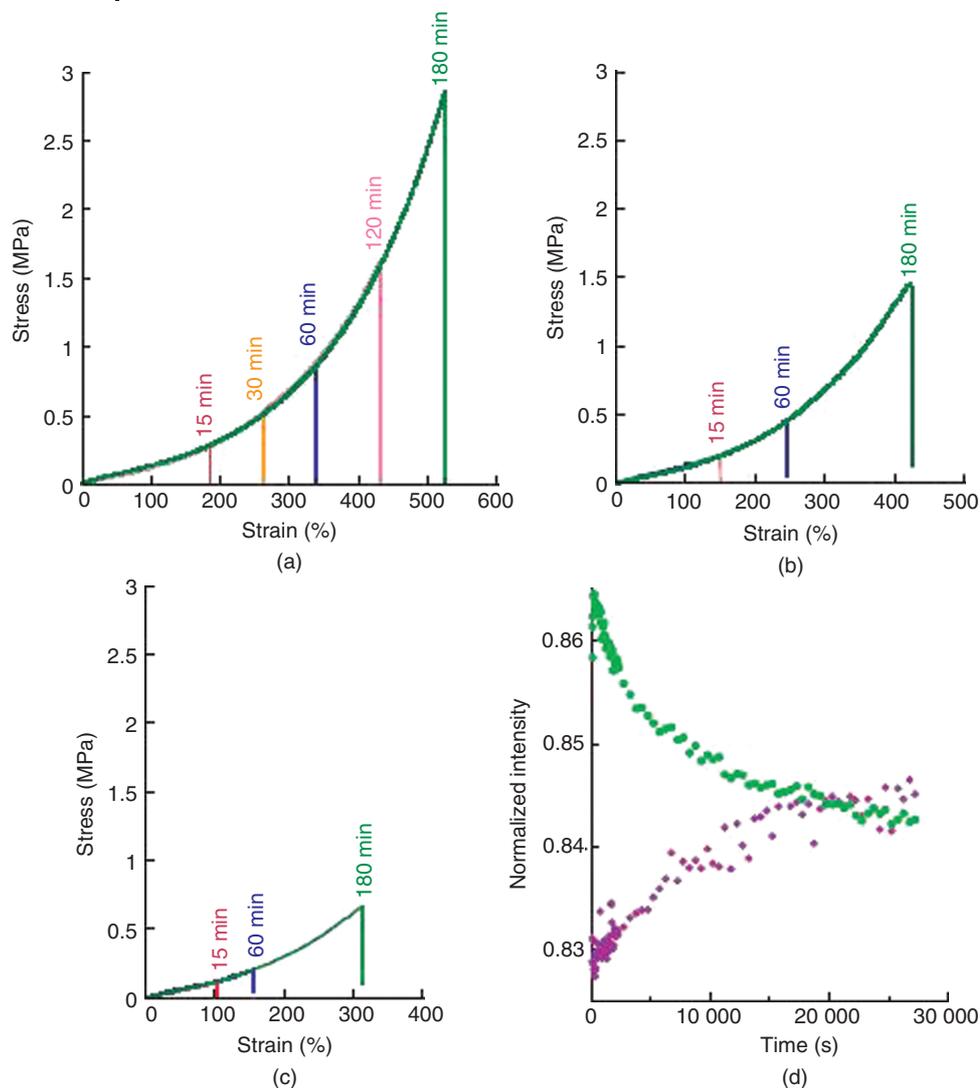


Fig. 1.16 Self-mending at room temperature. (a) Cut parts are brought into contact at 20°C immediately after being cut (waiting time <5 min). Curves represent stress–strain behavior measured for convenience at 40°C after different healing times. (b) Stress–strain behavior of mended samples at 40°C; mending was performed at 20°C after keeping broken samples apart for 6 h. (c) As in (b) but cut samples were kept apart for 18 h and then mended at 20°C. Colored vertical lines in (a–c) correspond to elongation at breaking for given healing times (for all healing times,

stress–strain curves superpose almost exactly and show elongation only at break changes). (d) Time-dependent infrared experiments. The sample was heated at 125°C for 10 min and then quenched to 25°C. Infrared absorption spectra evolutions were recorded. The intensity at 1524 cm⁻¹, characteristic of free N–H bending motions (green), decreases, whereas the intensity at 1561 cm⁻¹, characteristic of associated N–H bending motions (purple), increases. These data confirm the long lifetime of open hydrogen bonds when they are created in excess [reprinted with permission from Ref. 80].

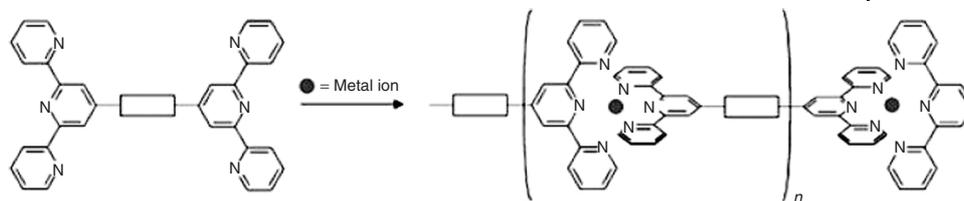


Fig. 1.17 Polymeric bis-terpyridine-metal complex (charge and anions omitted) [adapted from Ref. 81].

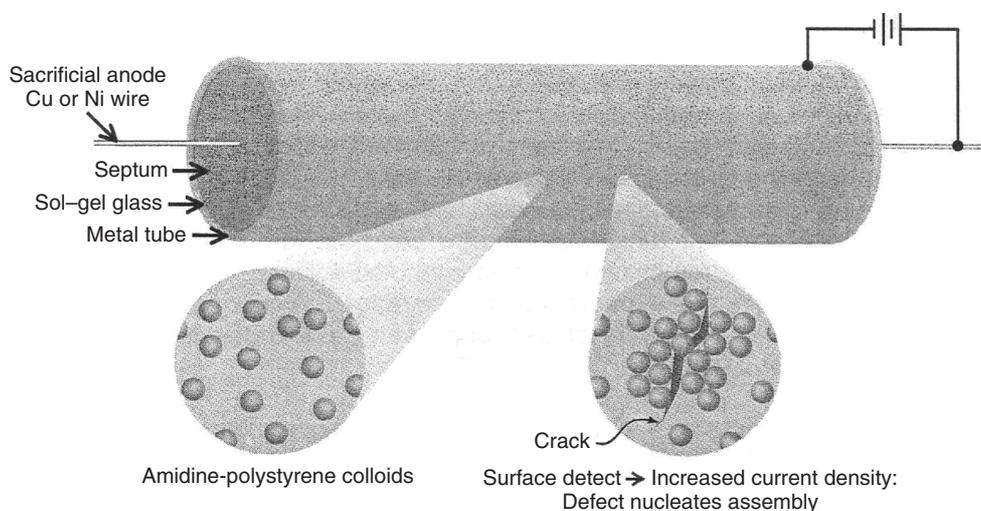


Fig. 1.18 Schematic showing electrohydrodynamic aggregation of particles [reprinted with permission from Ref. 83].

the principle of electrohydrodynamics (EHD) flow to design self-healing materials [84]. They have used suspension of colloidal particles, which is enclosed between the walls of a double-walled metallic cylinder (Figure 1.18). These walls are coated with a conductive layer followed by a ceramic insulating layer. A concentric metal wire is used to apply electric field to this system.

When damage occurs in the insulating layer, the current density at the damaged site is increased causing an agglomeration of the colloidal particles at the defected site through EHD flow. The aggregation of particles is not sufficient to heal the defects as the voids between colloidal particles prevent formation of a dense surface. The author suggests the use of polymeric colloidal particles or a sacrificial anode for simultaneous electrodeposition of metal at the defect site to achieve better healing efficiency. Thomas *et al.* have reported a concept of self-healing structural composites with electromagnetic functionality [85]. The self-healing is achieved through contributions of all components such as thermoreversible polymers, reinforcing fibers, and electromagnetic wires. The incorporated wires serve as both electrical and thermal conductor and distribute heat uniformly. The

added fibers also contribute to the healing mechanism. For example, when fibers having negative CTE is used to fill the core of the braid or fill in the weave of laminate, it will contract upon heating. This forces the matrix to compress and close the defect as the cracked polymer matrix (having positive CTE) expands upon contraction of the reinforcing fibers.

1.3.3.2 Conductivity

Polymeric materials are insulative in nature. By imparting conductivity into polymeric systems these materials can be made suitable for electronic applications. The tunable conductivities in polymeric materials can offer information on the structural integrity through electronic feedback that might give an insight to the most challenging task of detecting and quantifying microcracks. Thus, materials having conductivity as well as self-healing capability might be advantageous especially in deep sea or space applications. The conductivity, on the other hand, can also be used for inducing self-healing properties in polymeric systems. Williams *et al.* have exploited organometallic polymers based on *N*-heterocyclic carbenes and transition metals to design electrically conductive self-healing materials [86]. These polymers exhibit structurally dynamic characteristics in the solid state and have good processability characteristics. The electrical conductivity of the developed reversible systems is of 10^{-3} S cm^{-1} . Their approach of conductive self-healing material design is schematically shown in Figure 1.19. When a microcrack is formed in a system, it decreases the number of electron percolation pathways and thereby an increase in electrical resistance.

If an electrical source is connected, this drop in conductivity can be triggered to increase the applied electric field. Thus, if the rise in resistance is due to microcracking, then this voltage bias can generate localized heat at the microcrack, which can force the system back to its original state, that is, low resistance/high current situation. The organometallic polymeric systems based on *N*-heterocyclic carbenes and metals can be reversibly formed, which meet the conductivity

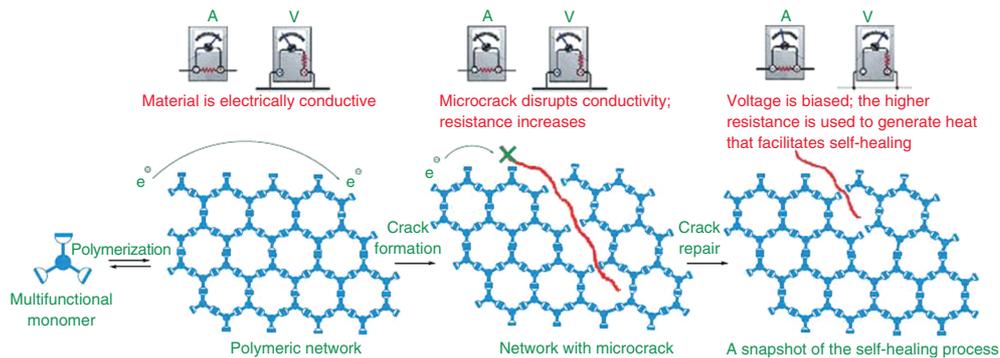


Fig. 1.19 Schematic showing conductive self-healing materials (A = amperes = volt) [reprinted with permission from Ref. 85].

requirements that make them suitable for self-healing applications. The author recommended that incorporation of bulky N-alkyl moieties into carbenes may reduce the viscosity upon depolymerization, which will enhance its flow into the cracks. Moreover, higher conductivities ($\sim 1 \text{ S cm}^{-1}$) should be achieved to have practical self-healing applications. Thostenson and his colleagues have successfully incorporated multiwalled nanotubes (MWNTs) in glass fiber–epoxy composites [87]. It was shown that a very low concentration of carbon nanotubes (0.1 wt%) is sufficient to achieve the percolation threshold in the prepared composites. The MWNT networks in the epoxy composite matrix can also accurately detect the onset, nature, and progression of damage. This property may be useful to have broad applications, including assessing self-healing strategies.

1.3.3.3 Shape Memory Effect

Certain strongly ordered intermetallic systems show the well-known shape memory effect, in which plastic deformation imparted to the low-temperature martensite phase can be reversed almost completely during transformation to the high-temperature austenite phase [88, 89]. These shape memory alloys (SMAs) can be used as self-healing materials. For example, SMAs such as Nitinol (nickel–titanium) exhibits the self-healing effect when heated [90]. If they are permanently deformed and heated above certain temperatures, they will return to their original shape (Figure 1.20). The transformation temperatures at which the alloys have their highest yield strength can be tuned between 100 and -100°C by

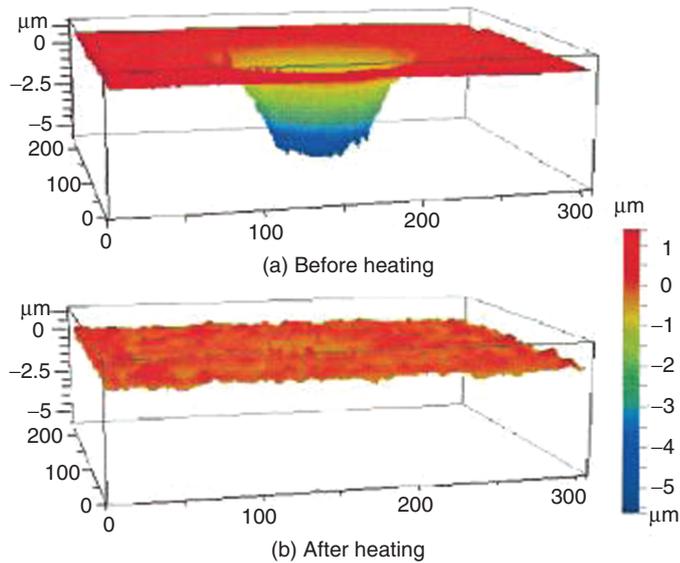


Fig. 1.20 Representative three-dimensional profiles of a spherical indent at load of 15 N: (a) fresh indent and (b) after heating above the austenite finish temperature [reprinted with permission from Ref. 90].

controlling the material properties. A detailed discussion on the use of SMAs as self-healing materials can be found in Chapter 8.

1.3.3.4 Nanoparticle Migrations

Balazs and coworkers have demonstrated that nanoparticles in a polymer fluid can segregate into cracks due to the polymer-induced depletion attraction between the particles and the surface [91–95]. The obtained morphology from the molecular dynamics simulations was used in a lattice spring model to determine the self-healing efficiency. The obtained model predicts restoration of mechanical properties up to 75–100%. Self-healing materials based on the above approach are yet to be demonstrated. Incorporation of nanoparticles into polymeric systems has twofold benefits: it increases the mechanical strength of the system and also segregates to the crack surface. Carbon nanotube is a potential candidate for developing self-healing materials based on this approach due to its superior mechanical properties compared to other particles.

1.3.3.5 Co-deposition

Electrolytic co-deposition can also be employed to design self-healing anticorrosive coatings (Figure 1.21). Microcapsules containing corrosion inhibitors can be added to composite plating coatings by this method [96–98]. Either liquid corrosion inhibitors or mesoporous nanoparticles containing absorbed corrosion inhibitors can be used as the core material to synthesize micro- or nanocapsules [99]. These capsules can be later deposited with metallic ions such as Zn^{+2} and Cu^{+2} to form composite metallic coatings. Upon crack formation in the composite layer, the capsule can release its contents to heal the crack.

Besides the above-mentioned self-healing strategies, many other approaches are expected to come in the near future for the development of self-healing materials. In this context, it is also important to note the different ways to evaluate quantitatively

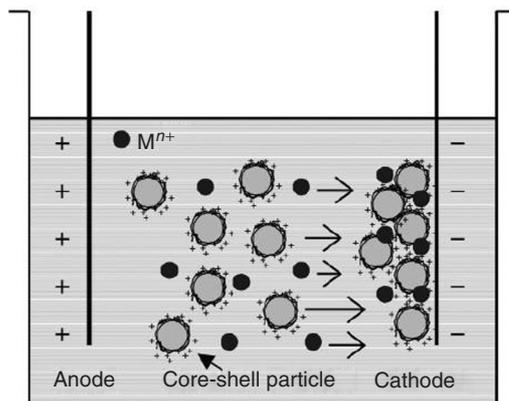


Fig. 1.21 Schematics showing electrolytic co-deposition of microcapsules (or mesoporous nanoparticles containing corrosion inhibitors) with metal ions.

the healing efficiency as different systems or authors use several methodologies to evaluate their systems. A summary of these quantitative routes can be found in the review of Kessler [5].

1.4 Applications

Product commercialization in industries is usually based on the following major milestones: idea generation (preliminary level) → laboratory implementation (product level) → pilot line up scaling (process level) → industrial applications (marketing level). Currently, self-healing materials development is either in the preliminary or product level, and so these materials are yet to be available for many applications. Applications of self-healing materials are expected almost entirely in all industries in future. The very few applications being developed to date are mainly in the automotive, aerospace, and building industries. For example, Nissan Motor Co. Ltd has commercialized world's first self-healing clear coat for car surfaces. The trade name of this product is "Scratch Guard Coat" [7]. According to the company, this hydrophobic paint repairs scratches (arising from car washings, off-road driving, or fingernails) on coated car surfaces and is effective for a period of three years. This newly developed paint contains high elastic resins that prevent scratches reaching the inner layers of a painted car surface. Depending on the depth of the scratch and the temperature in the surrounding environment, the entire recovery occurs between 1 and 7 days. Another example in this category is the two component polyurethane clear coats from Bayer MaterialScience [100]. The trade names of the raw materials used to formulate this coating are Desmodur and Desmophen. According to company sources (Figure 1.22), this coating heals small scratches under the influence of heat (sunlight) and the trick employed to design such coatings is based on the use of dense polymer networks with flexible linkages.

For both the above examples the scratch discussed is in the range of few micrometers, which is obviously visible to the naked eye, and therefore the products are suitable for keeping the aesthetics of the coating. Moreover, the above examples also follow similar self-healing mechanisms. Energy required to overcome the resistance of materials to create a scratch is higher in the case of thermosetting polymers (proportional to its plastic and/or elastic response) compared to thermoplastic polymers (viscoelastic response). Formation of a scratch in materials leads transport of materials from the affected zone to its side leaving the groove. In case of thermoplastic polymers, the energy is lost in the process of viscous flow in the absence of residual stress (due to viscoelastic or plastic deformation). Thus the most important driving force that helps the reflow of materials from the side to the groove is surface tension. However, for thermosetting polymers, the energy (below its yield's strength) incorporated to create a scratch is stored in the neighborhood of the conduit. When the mechanical stress is removed, the stored energy is relieved and the distorted polymer chains returns leveling the groove. This recovery process is highly dependent on the mobility of the polymer chains

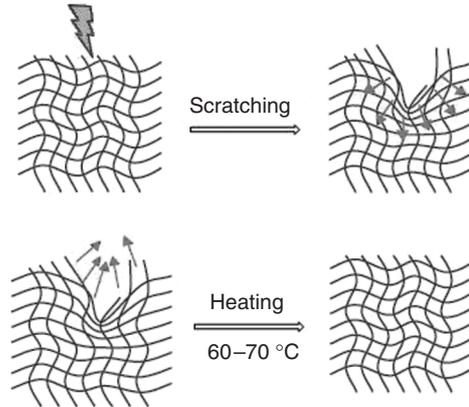


Fig. 1.22 Schematic showing the reflow effect of self-healing clear coats [adapted from a presentation [100] of Bayer Materials Science].

that is on their glass transition temperature (T_g). However, while scratching, if the mechanical stress also leads to cracking besides scratch formation, the stored energy will be released at the inappropriate time and a partial recovery (plastic residual strain allows some reflow) may be expected as surface tension-driven viscous process will not take place here due to the presence of opposing elastic force in the system. Thus, scratch with fractures is a permanent damage for thermosetting polymers, and therefore a compromise has to be considered between the above two processes for designing self-healing polymer coatings. External trigger can be useful in this case. Thus, polymers with high T_g (less material transport) in combination with high elastic response could be an option for the recovery of small scratches. In case of small fractures, triggering by temperature will enhance the mobility of the polymer chains and surface tension will play an important role for self-healing.

The next industrial segment where applications of self-healing materials are foreseen is the aviation industry. Use of composites in aircrafts has grown significantly in the past years. Hollow fibers reinforced composites are a possible solution to recover cracking or damages. Self-healing polymers have paved its way in space applications.

The construction industry will also find many applications of self-healing materials. For example, self-healing concretes may become a reality soon. Self-healing corrosion resistant coatings could be beneficial for structural metallic components such as steel for achieving long-term service life with reduced maintenance cost. Other areas of applications of self-healing materials are in medical segments. Biocompatible self-healing composite may extend the service life of artificial bone, artificial teeth, and so on. The very recent discovery of self-healing rubber may find applications in the toy industry.

Finally, it could be said that the available technologies to design self-healing materials are not cost effective. This limits the wide use of these materials for

different commercial applications. In future, one can expect to see new technologies that will enable the possibility of using self-healing materials in our day-to-day life.

1.5

Concluding Remarks

Microcracking and hidden damages are the initiators for structural failures. On the other hand, high maintenance and repairing costs limit the acceptance of different materials in engineering disciplines. Repairing at remote locations is very difficult. In this context, self-healing materials possess tremendous potential in increasing the longevity of structural materials. Consequently, a large number of academic and industrial research organizations have come forward to explore new concepts in this promising field. A growing trend of investments is also being seen from both the government and industrial funding agencies. Though this field of innovative product research shows high promises, it has some practical limitations in understanding crack healing kinetics and stability of healing functionality. Thus the main challenge of self-healing material development is autonomic detection of cracks and its subsequent healing.

To be able to develop new innovative solutions based on biomimetic approaches, it is an ultimate need to overcome the difficulties of damage detection and achieving an autonomic-healing phenomenon. Besides autonomic-healing, nonautonomic processes will also find industrial applications. It is sure that this wonderful field of self-healing materials will continue to grow beyond the technologies reviewed here and it will become available for our daily uses.

References

- 1 Weiner, S. and Wagner, H.D. (1998) *Annual Review of Materials Science*, **28**, 271–98.
- 2 Zhou, B.L. (1996) *Materials Chemistry and Physics*, **45** (2), 114–19.
- 3 Fratzl, P. and Weinkamer, R. (2007) in *Self Healing Materials. An Alternative Approach to 20 Centuries of Materials Science* (ed S. vanderZwaag), Springer, pp. 323–35.
- 4 Vermolen, F.J., van Rossum, W.G., Javierre, E. and Adam, J.A. (2007) *Self Healing Materials. An Alternative Approach to 20 Centuries of Materials Science* (ed S. vanderZwaag), Springer, pp. 337–63.
- 5 Kessler, M.R. (2007) *Proceedings of the Institution of Mechanical Engineers Part G-Journal of Aerospace Engineering*, **221**, 479–95.
- 6 Wool, R.P. (2008) *Soft Matter*, **4**, 400–18.
- 7 <http://www.nissan-global.com/EN/TECHNOLOGY/INTRODUCTION/DETAILS/SGC/index.html>. (Access year 2008).
- 8 Thies, C. (1987) Microencapsulation, in *Encyclopedia of Polymer Science and Engineering*, Vol. **9**, John Wiley & Sons, Inc, New York, pp. 724–45.
- 9 Benita, S. (1996) *Microencapsulation: Methods and Industrial Applications*, Marcel Dekker, New York.
- 10 Arshady, R. (1999) *Microspheres, Microcapsules and Liposomes*, Citrus Books, London.

- 11 Ghosh, S.K. (2006) *Functional Coatings by Polymer Microencapsulation*, Wiley-VCH Verlag GmbH, Germany.
- 12 Dry, C. (1996) *Composite Structures*, **35**, 263–69.
- 13 Jung, D., Hegeman, A., Sottos, N.R., Geubelle, P.H. and White, S.R. (1997) *The American Society for Mechanical Engineers Materials Division*, **80**, 265–75.
- 14 White, S.R., Sottos, N.R., Geubelle, P.H., Moore, J.S., Kessler, M.R., Sriram, S.R., Brown, E.N. and Viswanathan, S. (2001) *Nature*, **409**, 794–97.
- 15 Jones, A.S., Rule, J.D., Moore, J.S., White, S.R. and Sottos, N.R. (2006) *Chemistry of Materials*, **18**, 1312–17.
- 16 Brown, E.N., Kessler, M.R., Sottos, N.R. and White, S.R. (2003) *Journal of Microencapsulation*, **20** (6), 719–30.
- 17 Shansky, E. (2006) *Synthesis and Characterization of Microcapsules for Self-healing Materials*, Department of Chemistry, Indiana University, Bloomington.
- 18 Tillner, S. and Mock, U. (2007) *Farbe Und Lack*, **10**, 35–42.
- 19 Larin, G.E., Bernklau, N., Kessler, M.R. and DiCesare, J.C. (2006) *Polymer Engineering and Science*, **46**, 1804–11.
- 20 Rule, J.D. and Moore, J.S. (2002) *Macromolecules*, **35**, 7878–82.
- 21 Cho, S.H., Andersson, H.M., White, S.R., Sottos, N.R. and Braun, P.V. (2006) *Advanced Materials*, **18**, 997–1000.
- 22 Keller, M.W., White, S.R. and Sottos, N.R. (2006) An elastomeric self-healing material, in *Proceedings of the 2006 SEM Annual Conference and Exposition on Experimental and Applied Mechanics*, Society for Experimental Mechanics Vol. 1, pp. 379–82.
- 23 Rule, J.D., Sottos, N.R. and White, S.R. (2007) *Polymer*, **48**, 3520–29.
- 24 <http://www.sciencedaily.com/releases/2007/11/071127105523.htm>. (Access year 2008).
- 25 Kessler, M.R. and White, S.R. (2001) *Composites Part A*, **32**, 683–99.
- 26 Kessler, M.R., Sottos, N.R. and White, S.R. (2003) *Composites Part A*, **34**, 743–53.
- 27 Brown, E.N. (2003) Fracture and fatigue of a self healing polymer composite materials, Ph.D Thesis, University of Illinois at Urbana-Champaign, Urbana-Champaign.
- 28 Brown, E.N., White, S.R. and Sottos, N.R. (2004) *Journal of Materials Science*, **39**, 1703–10.
- 29 Brown, E.N., White, S.R. and Sottos, N.R. (2005) *Composite Science and Technology*, **65**, 2466–80.
- 30 Rule, J.D., Brown, E.N., Sottos, N.R., White, S.R. and Moore, J.S. (2005) *Advanced Materials*, **17** (2), 205–8.
- 31 Yin, T., Rong, M.Z., Zhang, M.Q. and Yang, G.C. (2007) *Composites Science and Technology*, **67**, 201–12.
- 32 Dry, C.M. (1995) *Proceedings of SPIE - International Society for Optical Engineering*, **2444**, 410–13.
- 33 Dry, C.M. and McMillan, W. (1996) *Proceedings of SPIE - International Society for Optical Engineering*, **2718**, 448–51.
- 34 Motuku, M., Vaidya, U.K. and Janowski, G.M. (1999) *Smart Materials and Structures*, **8**, 623–38.
- 35 Bleay, S.M., Loader, C.B., Hawyes, V.J., Humberstone, L. and Curtis, V. (2001) *Composites A, Applied Science Manufacturing*, **32**, 1767–76.
- 36 Hucker, M., Bond, I., Foreman, A. and Hudd, J. (1999) *Advanced Composites Letters*, **8** (4), 181–89.
- 37 Trask, R.S. and Bond, I.P. (2006) *Smart Materials and Structures*, **15**, 704–10.
- 38 Pang, J.W.C. and Bond, I.P. (2005) *Composites Part A-Applied Science and Manufacturing*, **36**, 183–88.
- 39 Pang, J.W.C. and Bond, I.P. (2005) *Composites Science and Technology*, **65**, 1791–99.
- 40 Williams, H.R., Trask, R.S. and Bond, I.P. (2006) “Vascular Self-Healing Composite Sandwich Structures”, 15th US National Congress of Theoretical and Applied Mechanics. Boulder, CO, 25–31 June.

- 41 Williams, G.J., Trask, R.S. and Bond, I.P. (2007) *Composites A*, **38** (6), 1525–32.
- 42 Sanada, K., Yasuda, I. and Shindo, Y. (2006) *Plastics, Rubber and Composites*, **35** (2), 67–71.
- 43 Therriault, D., White, S.R. and Lewis, J.A. (2003) *Nature Materials*, **2**, 265–271.
- 44 Toohey, K.S., Sottos, N.R., Lewis, J.A., Moore, J.S. and White, S.R. (2007) *Nature Materials*, **6**, 581–85.
- 45 Therriault, D., Shepherd, R.F., White, S.R. and Lewis, J.A. (2005) *Adv. Mater.*, **17**, 395–399.
- 46 Kim, S., Lorente, S. and Bejan, A. (2006) *J. Appl. Phys.*, **100**, (6), 063525(1–8).
- 47 Toohey, K.S., White, S.R. and Sottos, N.R. (2005) in *Proceedings of the Society for Experimental Mechanics (SEM) Annual Conference and Exposition on Experimental and Applied Mechanics*, 241–244.
- 48 Lewis, J.A. and Gratson, G.M. (2004) *Mater. Today*, **7**, 32–39.
- 49 Adhikari, B., De, D. and Maiti, S. (2000) *Progress in Polymer Science*, **25** (7), 909–48.
- 50 Bergman, S.D. and Wudl, F. (2008) *Journal of Materials Chemistry*, **18**, 41–62.
- 51 Bergman, S.D. and Wudl, F. (2007) van der Zwaag, S. (ed.) *Self-healing materials. An Alternative Approach to 20 Centuries of Materials Science*, Springer, pp. 45–68.
- 52 Chen, X., Dam, A., Ono, K., Mal, A., Shen, H., Nutt, S.R., Sheran, K. and Wudl, F. (2002) *Science*, **295** (5560), 1698–701.
- 53 Chen, X., Wudl, F., Mal, A.K., Shen, H. and Nutt, S.R. (2003) *Macromolecules*, **36**, 1802–7.
- 54 Chen, X. (2003) Novel polymers with thermally controlled covalent cross-linking, Ph. D Thesis, University of California, Los Angeles.
- 55 Chen, X., Dam, M.A., Ono, K., Mal, A., Shen, H., Nutt, S.R., Sheran, K. and Wudl, F. (2002) *Science*, **295** (5560), 1698–702.
- 56 Liu, Y.-L. and Wang, Y.-H. (2004) *Journal of Polymer Science. Part A-1, Polymer Chemistry*, **42**, 3178–88.
- 57 Liu, Y.-L. and Hsieh, C.-Y. (2006) *Journal of Polymer Science. Part A-1, Polymer Chemistry*, **44**, 905–13.
- 58 Liu, Y.-L., Hsieh, C.-Y. and Chen, Y.-W. (2006) *Polymer*, **47**, 2581–86.
- 59 Liu, Y.-L. and Chen, Yi.-W. (2007) *Macromolecular Chemistry and Physics*, **208**, 224–32.
- 60 Chang, J.Y., Do, S.K. and Han, M.H. (2001) *Polymer*, **42**, 7589–94.
- 61 Scott, T.F., Schneider, A.D., Cook, W.D. and Bowman, C.N. (2005) *Science*, **308** (5728), 1615–18.
- 62 Chung, C.-M., Roh, Y.-S., Cho, S.-Y. and Kim, J.-G. (2004) *Chemistry of Materials*, **16**, 3982–84.
- 63 Eisenberg, A. and Kim, J.S. (eds) (1998) *Introduction to Ionomers*, John Wiley & Sons, New York.
- 64 Eisenberg, A. and King, M. (1977) *Ion Containing Polymers*, Academic Press, New York.
- 65 Holliday, L. (ed) (1975) *Ionic Polymers*, Applied Science Publishers, London.
- 66 Eisenberg, A. (ed) (1980) *Ions in Polymers*, American Chemical Society, Washington, DC.
- 67 Schlick, S. (ed) (1996) *'Ionomers', Characterizations, Theory and Applications*, CRC Press, Boca Raton.
- 68 Tant, M.R., Mauritz, K.A. and Wilkes, G.L. (eds) (1997) *Ionomers: Synthesis, Structure, Properties and Applications*, Chapman & Hall, London.
- 69 Ghosh, S.K. (1999) Studies on elastomeric ionomers based on EPDM terpolymer and SEBS block copolymer, Ph. D Thesis, December I.I.T, Kharagpur, India.
- 70 Fall, R. (2001) Puncture reversal of ethylene ionomers—mechanistic studies, Master Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.
- 71 Kalista, S.J. Jr. (2003) Self-healing of thermoplastic poly(Ethylene-co-Methacrylic Acid) copolymers following projectile puncture,

- Master Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.
- 72 Sun, C.X., van der Mee, M.A.J., Goossens, J.G.P. and van Duin, M. (2006) *Macromolecules*, **39**, 3441–49.
- 73 Bouteiller, L. (2007) *Advances In Polymer Science*, **207**, 79–112.
- 74 Lehn, J.M. (2002) *Polymer International*, **51**, 825–39.
- 75 Weck, M. (2007) *Polymer International*, **56**, 453–60.
- 76 Shimizu, L.S. (2007) *Polymer International*, **56**, 444–52.
- 77 Beijer, F.H., Sijbesma, R.P., Kooijman, H., Spek, A.L. and Meijer, E.W. (1998) *Journal of the American Chemical Society*, **120**, 6761.
- 78 Söntjens, S.H.M., Sijbesma, R.P., van Genderen, M.H.P. and Meijer, E.W. (2001) *Macromolecules*, **34**, 3815.
- 79 <http://www.suprapolix.com/>. (Access year 2008).
- 80 Cordier, P., Tournilhac, F., Soulie'-Ziakovic, C. and Leibler, L. (2008) *Nature*, **451**, 977–80.
- 81 Andres, P.R. and Schubert, U.S. (2004) *Advanced Materials*, **16** (13), 1043–68.
- 82 Hoogenboom, R., Winter, A., Marin, V., Hofmeier, H. and Schubert, U.S. (2007) *American Chemical Society Proceedings*.
- 83 Ristenpart, W.D., Alesay, I.A. and Saville, D.A. (2007) *Langmuir*, **23** (7), 4071–4080.
- 84 Aksay, I. (2000) Princeton University.
- 85 Plaisted, T.A., Amirkhizi, A.V., Arbelaez, D., Nemat-Nasser, S.C. and Nemat-Nasser, S. (2003) *Proceedings of SPIE*, **5054**, 372–81.
- 86 Williams, K.A., Boydston, A.J. and Bielawski, C.W. (2007) *Journal of the Royal Society of Interface*, **4**, 359–62.
- 87 Thostenson, E.T. and Chou, T.-W. (2006) *Advanced Materials*, **18**, 2837–41.
- 88 Otsuka, K. and Wayman, C.M. (1998) *Shape Memory Materials*, Cambridge University Press, Cambridge, p. 49.
- 89 Liu, Y., Xie, Z., Humbeeck, J.V. and Delaey, L. (1999) *Materials Science and Engineering*, **679**, A273–75.
- 90 Nia, W., Cheng, Y.-T. and Grummon, D.S. (2002) *Applied Physics Letters*, **80** (18), 3310–12.
- 91 Lee, J.Y., Boxton, G.A. and Balazs, A.C. (2004) *Journal of Chemical Physics*, **121**, 5531–40.
- 92 Tyagi, S., Lee, J.Y., Boxton, G.A. and Balazs, A.C. (2004) *Macromolecules*, **37**, 9160–68.
- 93 Smith, K.A., Tyagi, S. and Balazs, A.C. (2005) *Macromolecules*, **38**, 10138–47.
- 94 Gupta, S., Zhang, Q., Emrick, T., Balazs, A.C. and Russell, T. (2006) *Nature Materials*, **5**, 229–33.
- 95 Balazs, A.C., Emrick, T. and Russell, T.P. (2006) *Science*, **314**, 1107–10.
- 96 Stempniewicz, M., Rohwerder, M. and Marlow, F. (2007) *Chem Phys Chem*, **8**, 188–94.
- 97 <http://www.imprs-surmat.mpg.de/IMPSSurMat/impssurmat.html>.
- 98 Liqun, Z. (2006) in *Functional Coatings by Polymer Microencapsulation*, (ed S.K., Ghosh), Wiley-VCH Verlag GmbH, Weinheim, Germany, pp. 297–342.
- 99 Schukin, D.G. and Möhwalld, H. (2007) *Small*, **3** (6), 926–43.
- 100 http://www.research.bayer.com/edition_16/Self_healing_automotive_coating.aspx. (Access year 2008).