Edited by Swapan Kumar Ghosh

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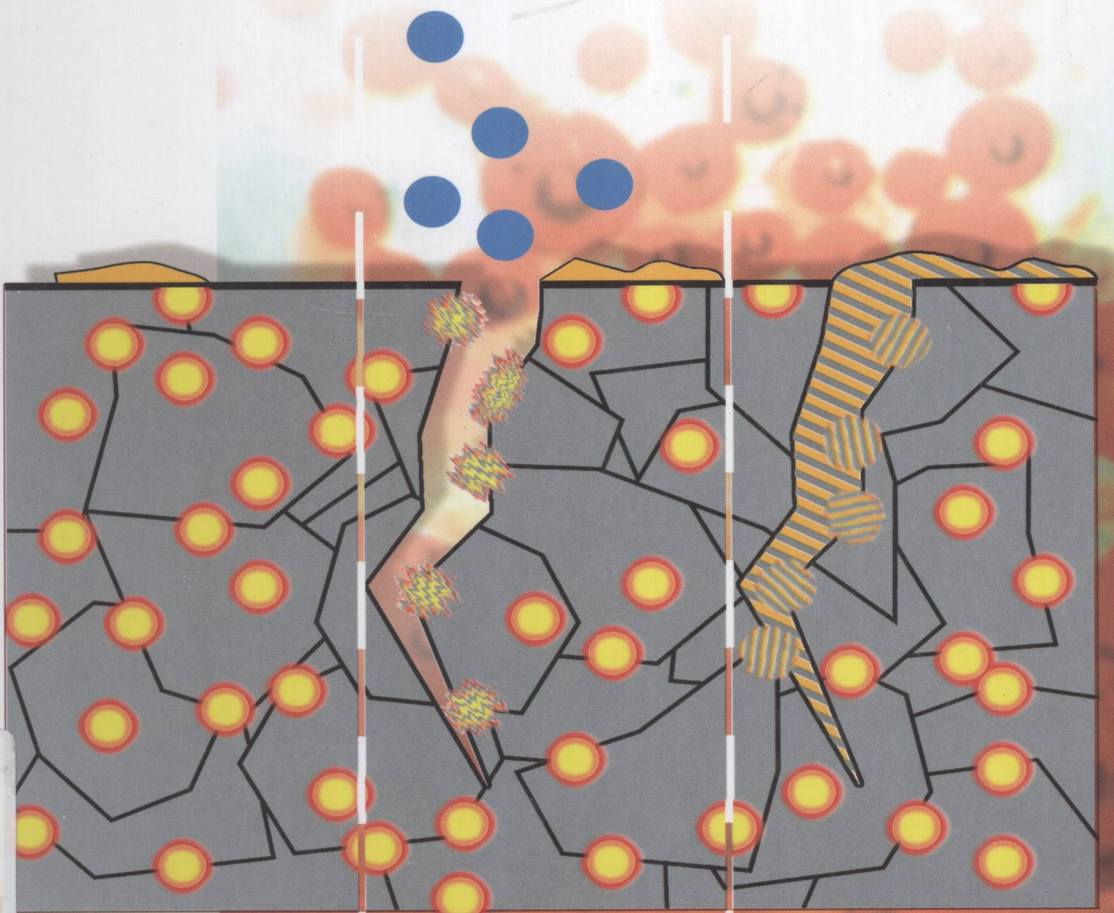
Fundamentals, Design Strategies, and Applications



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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 complied 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

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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.

Swapan Kumar Ghosh
September 2008

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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);

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- 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) benzylidine 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 Grubb's catalyst [15–18].

When DCPD comes into contact with the Grubbs' catalyst dispersed in the epoxy resin a *r*ing *o*pening *m*etathesis *p*olymerization (ROMP) [19, 20] starts and a highly cross-linked tough polycyclopendiene 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 polydiethyoxysilane (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 polycondensantaion 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, $CuBr_2(2\text{-MeIm})_4$, instead of