Chapter 7

Self-healing in polymers and structural composites

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Abstract

By mimicking biological healing processes in which the onset of damage triggers a repairing mechanism, the main failure modes of composites such as micro-cracking may be prevented before macroscopic damage occurs. An introduction to self-healing polymers and their inclusion in structural composites is provided in this chapter in four main sections: (1) An introduction to the design and chemistry of self-healing materials, (2) a review of self-healing structural polymer composites, (3) a description of the approaches used to evaluate and characterize self-healing polymers and composites, and (4) a discussion of the challenges and future directions in this field.

7.1 Introduction to self-healing polymers

Biomimetic materials are inspired by biological systems, which make use of nature's advanced mechanisms for function or healing. For example, the human epidermis, a biomaterial of sorts, is not completely resistant to damage but it is able to repair itself once damage has occurred. A cut or scratch of the human epidermis triggers a three-step healing process and creates scar tissue, which is 80% as strong as the original tissue [1]. By analogy with the biological wound healing process, we can describe the two main approaches to self-healing synthetic polymers: transport assisted self-healing and homogeneous self-healing.

The stages of skin regeneration in secondary wound healing (relating to some tissue loss) [2], shown in Figure 7.1.A , include i) inflammation, in which an increase in viscosity causes blood clotting. This is followed by ii) the proliferative phase where new tissue is generated by fibroblasts and endothelial cells and iii) the remodeling

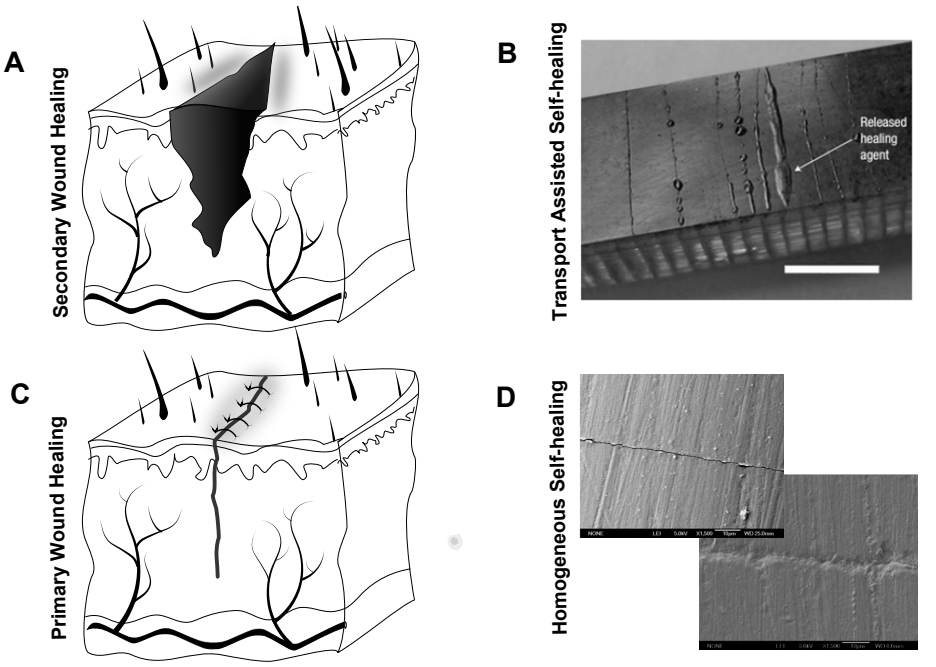

Figure 7.1: A) Secondary healing includes the inflammation, proliferative phase, and remodeling stages common for tissue regeneration. Similarly, B) depicts transport assisted self-healing in which vascular channels deliver liquid healing agent to polymerize at scratched surface. Reproduced from [3], copyright (2007), with permission from Macmillan Pub. Ltd. C) Primary wound healing relies on close contact of the skin (no tissue loss) for repair much like D) homogeneous self-healing which relies on molecular interactions between polymer surfaces to heal. Reprinted from [4], copyright (2008) ACS, with permission from American Chemical Society.

stage where granulation tissue is thickened and the reformation of tissue finalizes to form scar tissue.

Similarly, as the example shown in Figure 7.1.B , self-healing polymers based on transport assisted self-healing are capable of using a damage event such as a crack, puncture, or scratch as the trigger mechanism to i) transport a healing agent to a damaged area and fill the site, ii) activate the healing agent with a catalyst, initiator, or secondary healing agent, inducing an increase in viscosity, and iii) cure the healing agent in the damage zone to restore the mechanical properties of the material. Healing agent transport normally relies on an epoxy polymer matrix with embedded vessels for encapsulation such as microcapsules, hollow fibers, or an interconnected system of conduits.

Another form of healing relies on a model called primary wound healing, for the analogy with skin this is shown in Figure 7.1.C, in which the severed areas are brought into close contact by suturing. In this case no tissue is lost and skin is in intimate contact. In theory the epidermis fuses together without the need for new tissue formation [2]. In this chapter we refer to homogeneous self-healing, example in

Figure 7.1.D , as the type of self-healing in which no liquid healing agent is required but rather the close contact of the crack faces allows for processes such as diffusion, reversible bonds, and ionic interactions in the polymers, to rejoin the materials. This system has commonly been categorized as intrinsic healing in the literature because the healing properties come from interactions within the material itself, without introducing external healing agents [5, 6]. However, the inherent healing properties often come with a price, as the 'intrinsic' healing nature is normally triggered by external stimuli, such as heat or UV radiation, in which case these can no longer be defined as autonomous. In addition, these materials are not commonly used in structural or composites applications and will only briefly be discussed.

When evaluating either homogeneous or transport assisted healing it is important for us to define the restoration of properties after the healing event. This is referred to as the healing efficiency η defined as the ratio of a specific property after healing to the original virgin material property

$$\eta = \frac{P_{healed}}{P_{inital}} \tag{7.1}$$

where P is the property being evaluated: toughness, strength, stiffness, etc.

This chapter examines self-healing polymeric materials, paying particular attention to autonomous self-healing in structural composites. Here, we define an autonomous system as a self-healing system in which the only trigger for healing is the onset of damage and no external stimuli, such as electrical current, electromagnetic radiation, mechanical force or heat, are necessary. Self-healing systems triggered by external stimuli have been covered elsewhere [4, 7–9].

7.2 Self-healing systems: background and design

7.2.1 Transport assisted self-healing

Transport assisted self-healing systems require the transport of liquid healing agents to fill cracks, polymerize, and restore the material properties. These systems often follow repair mechanisms generally observed in biological systems, e.g., skin regeneration. The most widely studied self-healing systems are based on encapsulated systems, such as the one shown in Figure 7.1.B , where vascular channels embedded within a matrix deliver a liquid healing agent. Studies range from encapsulation of healing agents in i) micro- and nanocapsules, ii) hollow fibers, to iii) vascular networks, some in which pressure differentials drive the healing agent. Within these vessels, the three major types of encapsulations are:

i. An encapsulated liquid healing agent distributed among catalyst (or initiator) particles [10–12]

ii. An encapsulated resin and a secondary encapsulated hardener [13, 14]

iii. An encapsulated solvent-resin mixture [15–17]