

## SELF-HEALING POLYMER COMPOSITES

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### ABSTRACT

Thermosetting polymers, used in a wide variety of applications ranging from microelectronics to composite airplane wings, are susceptible to damage in the form of cracking. Often these cracks form deep within the structure where detection is difficult and repair is virtually impossible. In fiber reinforced polymer composites, cracking in the form of fiber-matrix interfacial debonding, ply delamination, and simple matrix cracking leads to degradation. In microelectronics, polymer encapsulates and polymer matrix composite printed circuit boards suffer from similar forms of damage, but in addition to mechanical failure, cracks cause electrical failure of the component. Microcracking induced by thermal and mechanical fatigue is a longstanding problem in polymer adhesives. Regardless of the application, once cracks have formed within polymeric materials, the integrity of the structure is significantly compromised. The concept of self-repair has been discussed previously, but the only successful crack healing methods that have been reported require some form of manual intervention. Inspired by biological systems in which damage triggers a healing response, here we demonstrate the development of a new structural polymeric material with the ability to *autonomically* heal cracks. Experiments on fracture specimens have yielded as much as 75% recovery of virgin toughness. This work will lead to safer and more reliable materials in a wide range of applications and represents the first step in developing materials systems that possess greatly extended lifetimes

### KEYWORDS

healing, repair, polymers, fracture, microcracking, failure, composites

### INTRODUCTION

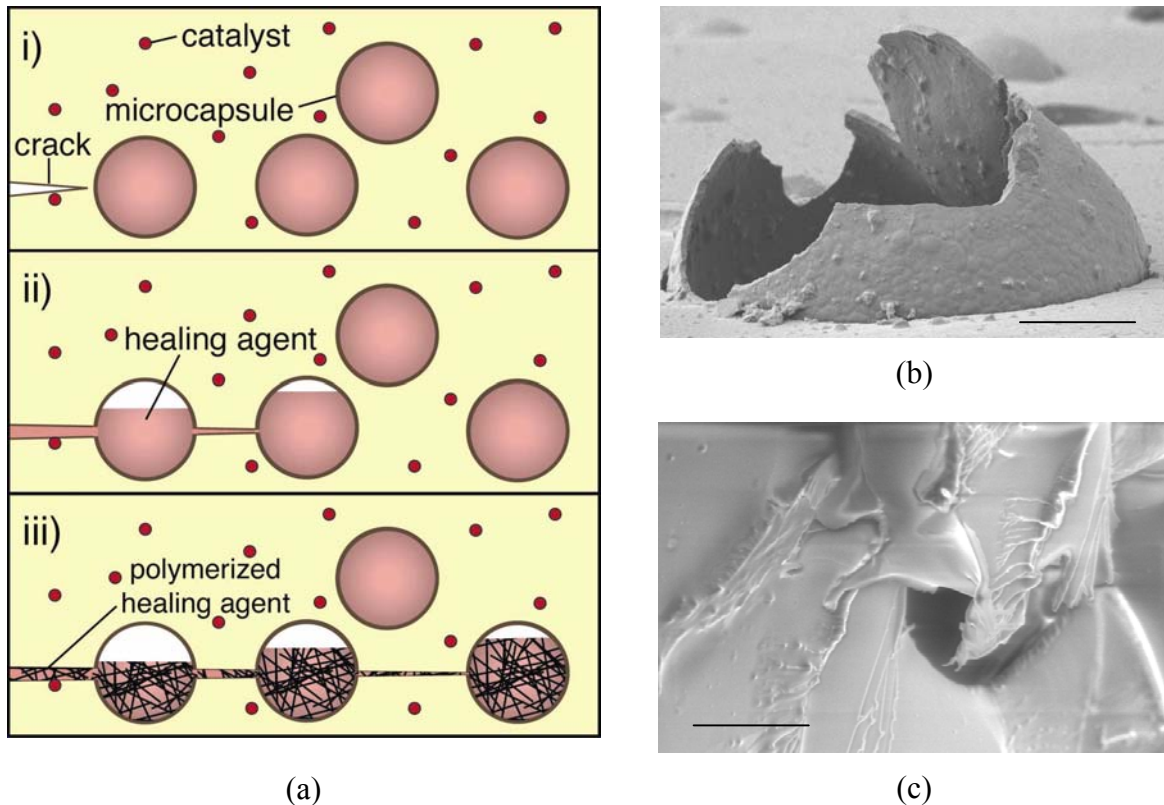
The natural process of fatigue in brittle polymers and composite leads to microcracking and other forms of micro-damage [1-5]. Eventually these microcracks coalesce to form large-scale cracks that propagate and lead to ultimate failure. The traditional approach to these problems has been to increase the inherent toughness of brittle polymers through addition of reinforcement phases or elastomers, or to repair the article once the cracks are large and of a critical size.

A new *self-healing* materials system was recently developed [6] and offers an alternative to these traditional approaches. Whenever damage occurs in a self-healing polymer, the repair process is triggered and after sufficient healing time, the inherent strength and toughness of the material is recovered. Self-healing polymers are designed to heal the microcracks that occur naturally during

fatigue, thereby preventing large-scale cracks from forming. As a result, the fatigue life and the useful mechanical function of these materials are expected to be significantly extended.

## SELF-HEALING CONCEPT

The self-healing concept is shown in Figure 1. A microencapsulated healing agent is embedded along with a catalyst into a polymer matrix. When damage occurs in the polymer a crack propagates through the matrix rupturing the microcapsules in the crack path. The ruptured microcapsules release the healing agent which is then drawn into the crack through capillary action. Once the healing agent within the crack plane comes into contact with the embedded catalyst, a chemical reaction is triggered and polymerization of the healing agent occurs. Afterwards, the crack faces are bonded and the strong singularity at the crack tip is relieved.

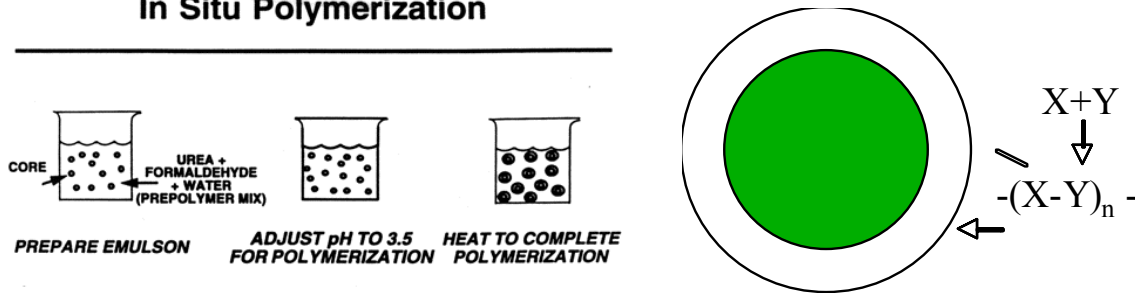


**Figure 1.** *The Self-Healing Concept.* (a) Schematic representation of self-healing material where i) a microencapsulated healing agent and catalyst is dispersed in a polymer matrix, ii) an advancing crack intersects the embedded microcapsules which rupture and release the healing agent into the crack through capillary action, iii) the healing agent contacts the catalyst and polymerization occurs. [scale bar = 10  $\mu\text{m}$ ] (b) SEM image of the fracture plane of a self-healing material showing a ruptured microcapsule. (c) SEM image of the healed fracture plane showing the polymerized healing agent covering the fracture plane. [scale bar = 100  $\mu\text{m}$ ].

## MANUFACTURING PROCEDURE

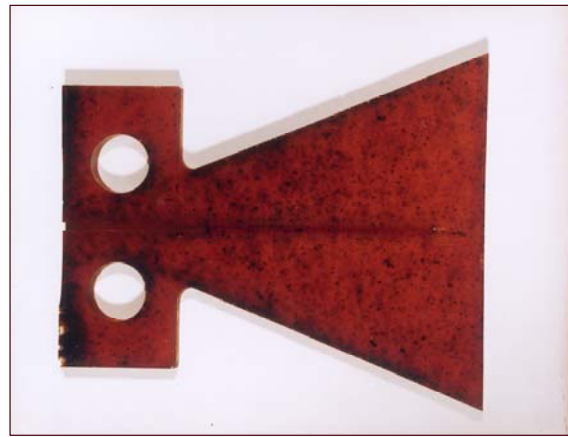
Self-healing polymers are created in a two-step process beginning with the microencapsulation of the healing agent. Figure 2 shows a schematic of the microencapsulation procedure. An emulsion of the healing agent (dicyclopentadiene, DCPD) is created with an aqueous solution of urea and formaldehyde. In situ polymerization occurs at the DCPD surface at controlled temperature and pH. The emulsion is agitated throughout the process and the size of the capsules can be controlled by the agitation rate. Typically, we obtain 100-200  $\mu\text{m}$  microcapsules at 450 rpm at 50°C and 3.5 pH.

## In Situ Polymerization



**Figure 2.** *Microencapsulation Procedure.* An emulsion of dicyclopentadiene (core) is created with urea and formaldehyde and water. In-situ polymerization of urea-formaldehyde occurs at the surface of the DCPD cores and continues under controlled temperature and pH.

Once the microcapsules are prepared they are mixed with the polymer matrix. For the examples which follow, a bisphenol-A based epoxide (EPON 828) was used along with a tetra-functional amine curing agent (DETA). The microcapsules are mixed with the epoxide prepolymer at 10 wt.% (total). The catalyst (Grubbs' catalyst)<sup>1</sup> [7] is then added at a typical concentration of 2.5 wt.% (total). The mixture is then degassed and the curing agent is then added. The resin mixture is next poured into a mold and cured at room temperature for 24 h followed by a postcure of 40°C for 24 h. Figure 3 shows an example self-healing fracture toughness specimen after manufacture.



**Figure 3.** *Self-Healing Polymer Specimen.* NOTE: The geometry of the fracture toughness sample is designed for controlled crack propagation along the centerline of the sample and constant compliance with increasing crack length.

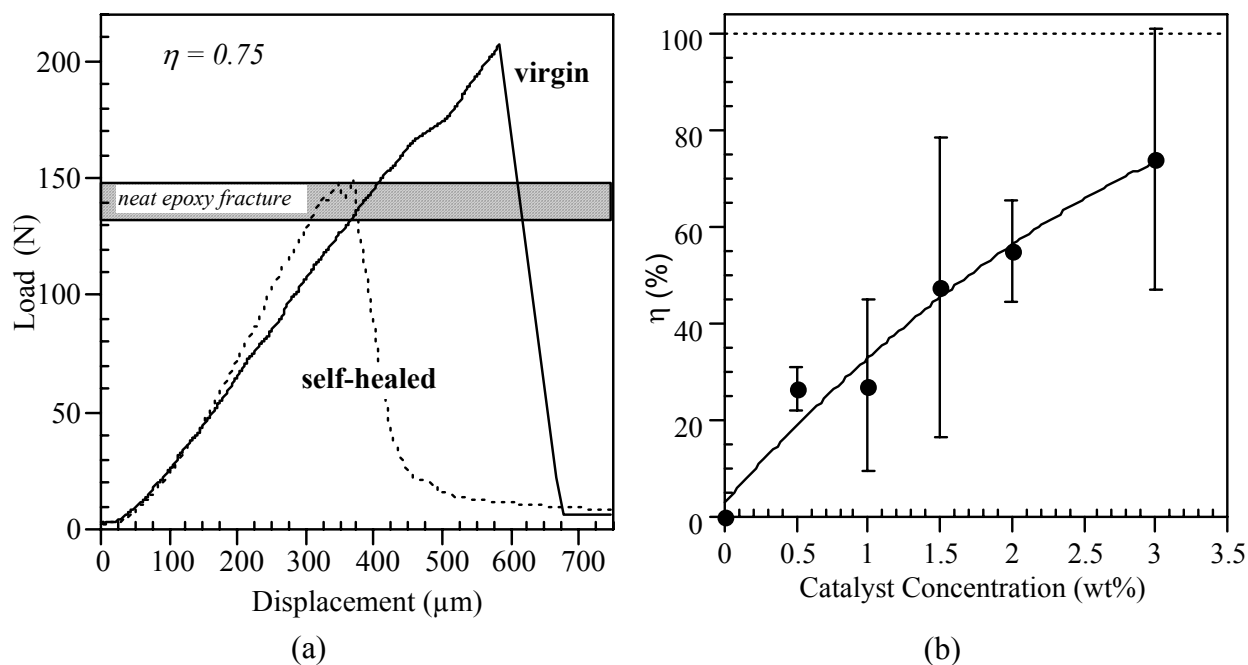
## HEALING EFFICIENCY

Based on the work of Jud and Kausch [8] and Wool and O'Connor [9] we define the *healing efficiency* as,

$$\eta = \frac{K_{IC}^{healed}}{K_{IC}^{virgin}} \quad (1)$$

where  $K_{IC}$  is the critical mode-I stress intensity factor. A ratio of unity indicates complete recovery after healing. The healing efficiency depends on a number of factors including the concentration of catalyst and healing agent, the healing kinetics, the diffusion rate of the healing agent in the polymer matrix, the capillary pressure in the crack plane, the adhesive bond strength between the healing agent and polymer matrix, etc. An example result from a fracture toughness test is included in Figure 4. A fracture toughness sample similar to the one shown in Figure 3 was loaded in mode-I and a starter crack was propagated along the centerline of the specimen. The curve labeled "virgin" corresponds to the load-deflection data obtained for this test. Subsequently, the specimen was unloaded and allowed to heal for a total of 48 hours. The specimen was then reloaded to failure and the load-deflection data labeled "self-healed" was obtained. Analysis of the fracture data reveals that the healing efficiency for this specimen is approximately 75%.

<sup>1</sup> Grubbs' catalyst is a Ruthenium transition metal catalyst that initiates a ring-opening metathesis polymerization of the DCPD healing agent.



**Figure 4.** *Self-Healing Fracture Toughness Results.* (a) A virgin specimen similar to that shown in Figure 3 is loaded to failure. The specimen is then unloaded and allowed to heal for 48 hours. The healed specimen is then loaded to failure again. The healing efficiency for this specimen is approximately 75%. (b) Effect of catalyst concentration on healing efficiency.

Optimization of the materials system for maximum healing efficiency is an on-going research goal. Healing efficiency is a complex material property that not only depends on the factors listed above, but on their interplay *in situ*. For example, the healing kinetics must be sufficient rapid so that the healing agent does not have time to diffuse into the surrounding polymer matrix. Yet, the rate of healing is controlled primarily by the concentration of the catalyst on the crack plane as well as the temperature at which healing occurs. Figure 4b shows the dependence of healing efficiency on catalyst concentration. With increasing concentration the healing efficiency increases monotonically. Yet, the concentration of catalyst on the crack plane itself can be quite different from that which is added to the resin mixture during manufacturing and this *in situ* concentration will depend on the uniformity of dispersion, the size of the catalyst particles, and any clustering of particles that occurs during manufacturing.

## FUTURE DIRECTIONS

Optimization of healing efficiency will require a more thorough understanding of the complex interplay between factors that influence healing kinetics. Research is on going to measure the *in situ* healing kinetics and the influence of catalyst concentration. Subsequent generations of self-healing polymers will incorporate more robust and active catalyst-healing agent materials systems with increased tolerance to thermal and environmental extremes. The future goals in this emerging field of research will include microcirculatory systems to replenish the supply of healing agents and catalysts to the host material.

## ACKNOWLEDGEMENTS

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