Fracture Testing of a Self-Healing Polymer Composite

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ABSTRACT

Inspired by biological systems in which damage triggers an autonomic healing response, we have developed a polymer composite material that can heal itself when cracked. This paper summarizes the self-healing concept for polymeric composite materials and investigates fracture mechanics issues consequential to the development and optimization of this new class of materials. The self-healing material under investigation is an epoxy matrix composite, which incorporates a microencapsulated healing agent that is released upon crack intrusion. Polymerization of the healing agent is triggered by contact with an embedded catalyst. The effects of concentration of catalyst and microcapsules on fracture toughness and healing efficiency are investigated. In all cases the addition of microcapsules significantly toughens the neat epoxy. Once healed, the self-healing polymer recovers as much as 90% of its virgin fracture toughness.

1 INTRODUCTION

In recent research, White *et al.* [1] have developed a self-healing polymer that mimics many of the features of a biological system. The self-healing system, shown schematically in Fig. 1, involves a three-stage healing process, accomplished by incorporating a microencapsulated healing agent and a catalytic chemical trigger in an epoxy matrix. Conclusive demonstration of self-healing was obtained with a healing agent based on the **r**ing-**o**pening **m**etathesis **p**olymerization (ROMP) reaction. Dicyclopentadiene (DCPD), a highly stable monomer with excellent shelf life, was encapsulated in microcapsules with a thin shell made of urea formaldehyde. A small volume fraction of microcapsules was dispersed in a common epoxy resin along with the Grubbs ROMP catalyst, a living catalyst that remains active after triggering the polymerization. The embedded microcapsules were shown to rupture in the presence of a crack and to release the DCPD monomer into the crack plane. Contact with the embedded Grubbs catalyst initiated polymerization of the DCPD and rebonded the crack plane. Crack healing efficiency was assessed by adopting a measurement of the ability to recover fracture [2],

$$\eta = \frac{K_{Ic_{healed}}}{K_{Ic_{virgin}}}, \qquad (1)$$

where $K_{Ic_{virgin}}$ is the fracture toughness of the virgin specimen and $K_{Ic_{healed}}$ is the fracture toughness of the healed specimen. Fracture test results using the ROMP-based healing system revealed that on average 60% of the fracture toughness was recovered in the healed samples [1].

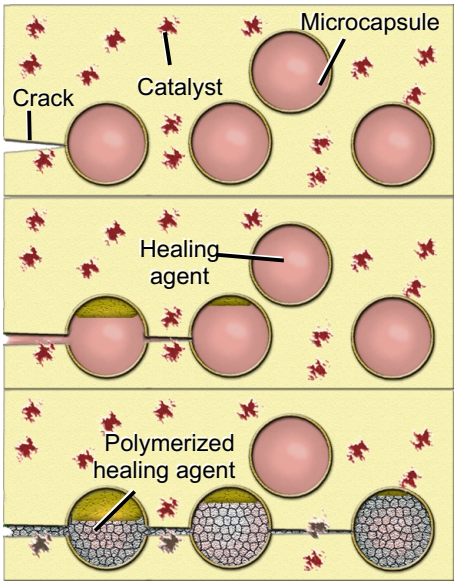

Fig. 1. Self-healing concept for a thermosetting polymer

Crack-healing phenomena have been discussed in the literature for a range of polymers [2-5]. While these previous works were successful in repairing or sealing cracks, the healing was not self-initiated and required some form of manual intervention (*e.g.* application of heat, solvents, or healing agents). Others have proposed a tube-delivery concept for self-repair of corrosion damage in concrete and cracks in polymers [6,7]. Albeit conceptually interesting, the introduction of large hollow tubes in a brittle matrix material cause stress concentrations that weaken the material and beneficial healing may be difficult to realize.

In contrast, the microcapsule concept developed by White *et al* [1]. is particularly elegant, practical, and promising for the healing of brittle thermosetting polymers. In this paper, we present a comprehensive experimental investigation of the

correlative fracture and healing mechanisms of this self-healing system. Effects of microcapsule concentration, catalyst concentration, and healing time are studied with a view towards improving healing efficiency.

2 EXPERIMENTAL PROCEDURE

2.1 TDCB SPECIMEN

Using the protocol established by White *et al.* [1], we measured healing efficiency by carefully controlled fracture experiments for both the virgin and the healed material. These tests utilize a tapered double-cantilever beam (TDCB) geometry, which ensures controlled crack growth along the centerline of the brittle specimen. The TDCB fracture geometry, developed by Mostovoy *et al*. [8], provides a crack-length-independent measure of fracture toughness

$$K_{Ic} = 2P_c\sqrt{\frac{m}{b_n b}}, \tag{2}$$

which requires knowledge of only the critical fracture load P_c and geometric terms. The specimen and crack widths are given by b and b_n, respectively. The geometric term m is determined experimentally as

$$m = \frac{Eb}{8}\frac{\mathrm{d}C}{\mathrm{d}a}. \tag{3}$$

where E is the Young's modulus and C is the compliance. For the TDCB sample geometry, the healing efficiency, Eq. 1, is rewritten as

$$\eta = \frac{P_{c_{\text{healed}}}}{P_{c_{\text{virgin}}}}. \tag{4}$$

Valid profiles for a TDCB fracture specimen are determined by finding a height profile for which the compliance varies linearly with crack length. Linearly tapered height profiles provide a range of crack lengths for valid K_{Ic} measurement [4,8-10]. In the current work, the TDCB geometry developed and verified by Beres[9] is adopted (inset Fig. 2). The specimen geometry was experimentally calibrated as described in Brown *et al* [10]. The fracture toughness of the neat epoxy was measured to be 0.55 MPa $m^{1/2}$. For crack lengths ranging from 20 to 37 mm the geometric constant m was measured to be 0.6 mm^{-1} in excellent agreement with the value predicted by the finite-element method [9].

2.2 SAMPLE PREPARATION AND TEST METHOD

Samples were prepared by mixing EPON® 828 epoxy resin with 12 pph Anacmine® DETA curing agent. The epoxy mixture was degassed, poured into a closed silicone rubber mold, and cured for 24 hours at room temperature, followed by 24 hours at 30°C. After curing, a sharp pre-crack was created by gently tapping a razor blade into the molded starter notch in the samples. To facilitate investigation of the effects of the constituents of the self-healing system, varying weight percent of Grubbs catalyst and/or microcapsules were mixed into the resin prior to pouring.

Three types of experiment are conducted: the self-healing *in situ* tests and two types of control. The first type of control, referred to as reference samples, consists of neat epoxy without embedded catalyst. Reference samples are tested to failure and then manually healed by injection of DCPD monomer that is premixed with catalyst. Reference tests remove the variables associated with DCPD delivery and the embedding of Grubbs catalyst. The second control, referred to as self-activated samples, consists of epoxy with embedded catalyst but no microcapsules. Self-activated samples are tested to failure and then healed by manual injection of DCPD monomer into the crack plane. This intermediate-level control enables investigation of the embedded catalyst, without the variability of DCPD delivery through microencapsulation. The third type of sample is the fully self-contained, or *in situ*, system. *In situ* samples contain both the microencapsulated healing agent and Grubbs catalyst, enabling them to self-heal after fracture. Urea-formaldehyde microcapsules encapsulating DCPD monomer were manufactured using an emulsion method outlined in White *et al.* [1]

Fracture specimens were tested under displacement control, using pin loading and a 5μm/s displacement rate. Samples were tested to failure, measuring compliance and peak load. For the reference samples, 0.03 ml of premixed DCPD monomer and Grubbs catalyst was injected into the crack plane, prior to crack closing. For the case of self-activated samples, 0.03 ml of DCPD monomer was injected into the crack plane, which is subsequently allowed to close. *In situ* samples were unloaded, allowing the crack faces to come back into contact. After a sufficient time for healing efficiency to reach a steady value, the samples were retested. For the majority of experiments, retesting was performed after 48 hours. Values of fracture toughness and the subsequent healing efficiency were calculated. A representative load–displacement curve is shown in Fig. 2 for the *in situ* healing case. Virgin fracture is brittle in nature, while the healed fracture exhibits prolonged stick-slip.

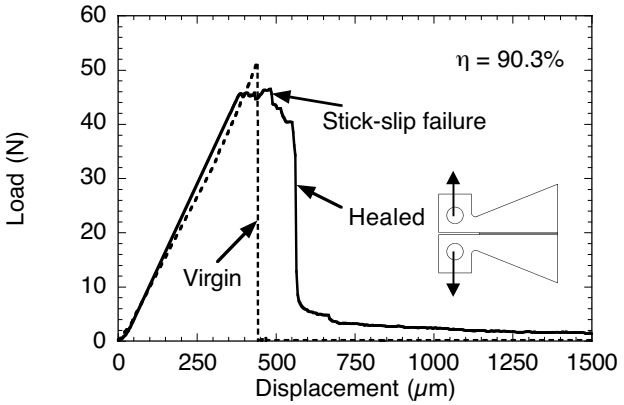

Fig. 2. Representative load–displacement curve for an *in situ* sample with 2.5 wt% Grubbs and 5 wt% capsules

3 MICROCAPSULE CONCENTRATION (reference test)

Reference samples were used to study the influence of microcapsule concentration on the fracture of the virgin and healed epoxy. Reference samples containing 0% to 25% by weight of microcapsules (ca. 180 μm diameter) were tested

to failure and healed by injection of approximately 0.03 ml of mixed DCPD monomer and catalyst into the crack plane. As observed earlier in the literature for the addition of rigid particles [11], the virgin fracture toughness of the material increased significantly with increasing concentration of microcapsules, as shown in Fig. 3. A maximum is achieved at 15 wt% capsule concentration. This toughening is due to a classic crack pinning mechanism. Observation of the fracture surface in Fig. 4a shows clear evidence of the characteristic tails that indicate crack pinning.

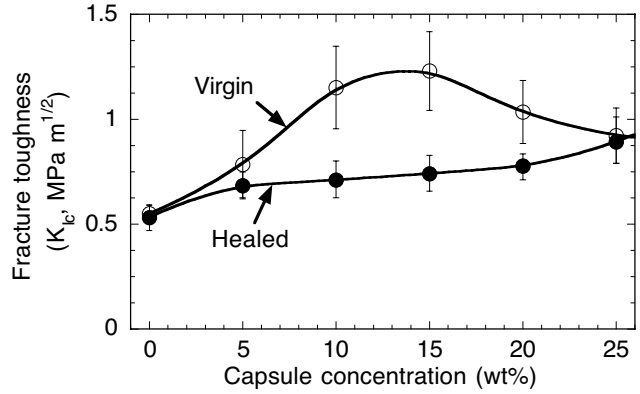

Fig. 3. Virgin and healed fracture toughness dependence on capsule concentration

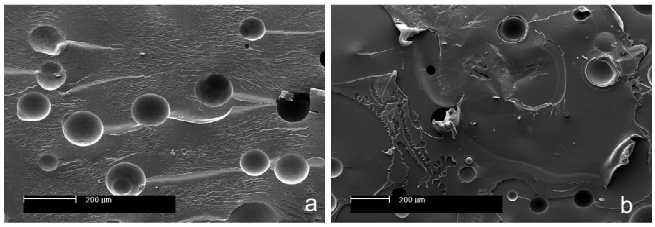

Fig. 4. Crack plane ESEM images: (a) reference sample (10 wt% capsules) showing tails related to the crack pinning toughening mechanism, (b) *in situ* samples sample (10 wt% capsules and 2.5 wt% catalyst)

Healing agent from the microcapsules was allowed to evaporate from the crack plane. Healed fracture toughness demonstrated minimal dependence on capsule concentration over a range of 5 to 20% by weight. For capsule concentrations close to the value that yields a maximum for the virgin fracture toughness (~ 15 wt%), a local minimum in healing efficiency occurs due to the minimal gains in healed fracture toughness. For capsule concentration of 25 wt% and greater near perfect healing is obtained. However, as the capsule concentration increases the manufacture of samples becomes more difficult due to increased viscosity of the uncured resin.

4 CATALYST CONCENTRATION (self-activated test)

To establish the catalyst concentration that provides for high healing efficiency without diminishing virgin fracture toughness, we manufactured six sets of self-activated TDCB samples with Grubbs catalyst concentration from 0 to 4 wt%. Each set consisted of six samples. Virgin and healed fracture toughness values and the corresponding healing efficiencies were measured (Fig. 5). The healed fracture toughness increases with the addition of catalyst. As more catalyst is added, however, the relative gain in healed fracture toughness for each additional increment decreases. For addition of catalyst beyond 3 wt%, the virgin fracture toughness begins to decreases. Although a high healing efficiency results at these high catalyst concentrations, gains are due to diminution of the virgin properties. At high catalyst concentration, scatter in the data is dramatically increased.

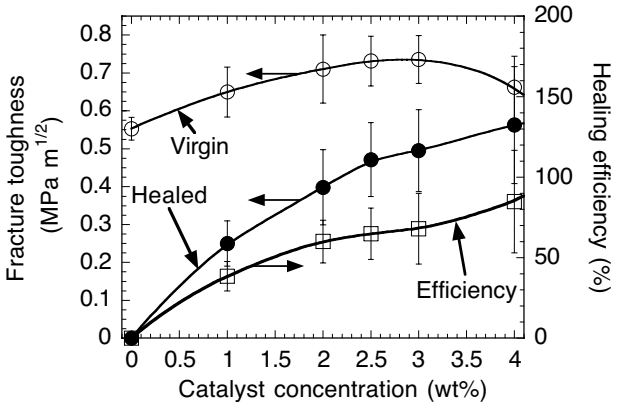

Fig. 5. Healing efficiency as a function of catalyst concentration

5 SELF-HEALING OF THE *IN SITU* SYSTEM

The ultimate goal of this research is the development of a self-healing polymer composite. To achieve this goal, microencapsulated DCPD monomer and Grubbs catalyst were incorporated into an *in situ* sample. Evolution of healed fracture toughness over time was investigated using *in situ* samples with 2.5 wt% Grubbs catalyst and 10 wt% of DCPD monomer encapsulated microcapsules. The findings of these studies and the results presented above were used to optimize the healing system through choice of catalyst and microcapsule concentration. PolyDCPD film is detected on the healed fracture plane, shown in Fig. 4b.

5.1 DEVELOPMENT OF HEALING EFFICIENCY

The healing efficiencies presented thus far have been measured after waiting 48 hr from the virgin test. This time was chosen to ensure sufficient time for healing. Previous research on healing of thermoplastics [2,3] showed that healing efficiency is strongly tied to time. A series of 28 *in situ* samples was manufactured with 10 wt% of 180 μm diameter capsules and 2.5 wt% of catalyst. The virgin fracture tests were performed in rapid succession with the exact time of the fracture event noted for each specimen. Healed fracture tests were performed at time intervals ranging from 10 min to 72 hr. The resulting healing efficiencies are plotted *versus* time in Fig. 6. A significant healing efficiency developed within 25 minutes, which closely corresponds to the gelation time of the polyDCPD. Steady-state values were reached within 10 hr.

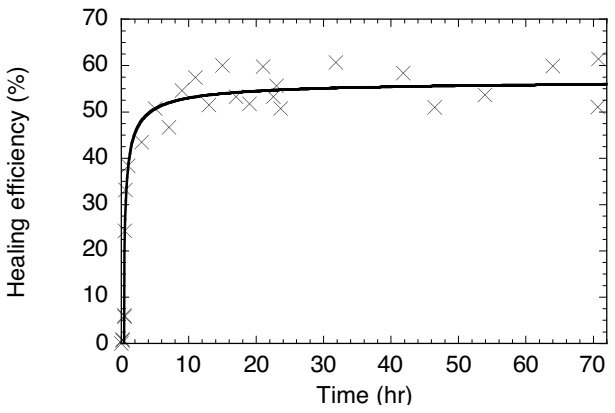

Fig. 6. Development of healing efficiency

5.2 MICROCAPSULE CONCENTRATION

In earlier work on this self-healing system, [1,12] it was perceived that the ability to deliver sufficient healing agent could be a limiting factor to healing efficiency. Microcapsule concentration was chosen to be 10 wt% to maximize DCPD delivery, while retaining near-maximum virgin fracture toughness. However, excess DCPD was observed flowing out of the inferace. The reference sample data in Fig. 3 indicates that a reduction in concentration from 10 to 5 wt% has minimal impact on the observed healed fracture toughness. By reducing the capsule concentration, the virgin fracture toughness can be optimized to yield near perfect healing. A set of six *in situ* samples was manufactured with 5 wt% of 180 μm diameter capsules and 2.5 wt% of catalyst. With a decrease from 10 wt% to 5 wt% of microcapsules, the healing efficiency of the *in situ* system increased from 52±8% to 85±5%, illustrating the successful development of an optimized self-healing system.

6 CONCLUSIONS

Use of a tapered double-cantilever beam fracture geometry provided an accurate method to measure the fracture behavior and healing efficiency of self-healing polymer composites and to compare with appropriate controls. Virgin fracture properties of the polymer composite are improved due to crack pinning by microcapsules and catalyst particles. The concentration of catalyst was shown to have a significant impact on the virgin properties of the composite and the ability to catalyze the healing agent. Catalyst concentrations greater than 2.5 wt% provided diminishing gains in healed fracture toughness. Significant loss of virgin fracture toughness was observed for catalyst concentration above 3%. Addition of microcapsules, up to 15 wt%, served to increase the virgin toughness. Maximum healing efficiency was obtained within 10 hours of the fracture event. By optimizing the concentrations of catalyst and microcapsules, we increased the healing efficiency of the system to over 90%.

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