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 size and 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.

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Introduction

Fracture of the skeletal structure in biological systems provides an excellent model for developing a synthetic healing process for structural materials. For a bone to heal, nutrients and undifferentiated stem cells must be delivered to the fracture site and sufficient healing time must elapse.[1] The healing process consists of multiple stages of deposition and assembly of material,[2] as illustrated in Fig. 1. The network of blood vessels in the bone is ruptured by the fracture event, initiating autonomic healing by delivering the components needed to regenerate the bone.

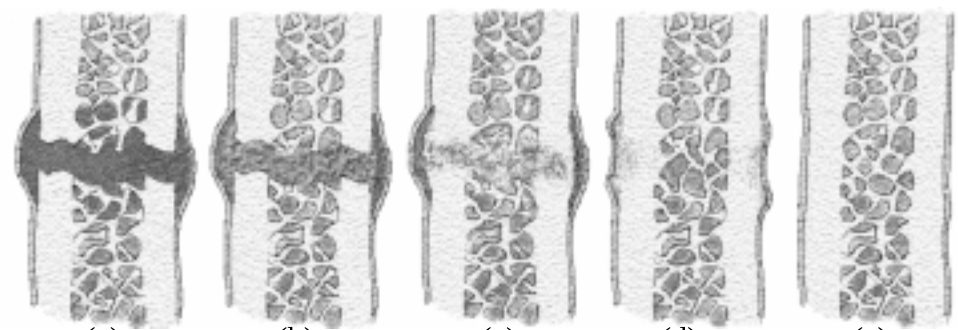

Fig. 1–Healing stages of bone; (a) internal bleeding, forming a fibrin clot, (b) development of unorganized fiber mesh, (c) calcification of the fibrocartilage, (d) calcification converted into fibrous bone, (e) transformation into lamellar bone

In recent research, White *et al.*[3] have developed a self-healing polymer that mimics many of the features of a biological system. The self-healing system, shown schematically in Fig. 2, 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,[4]

$$\eta = \frac{K_{Ic_{\text{healed}}}}{K_{Ic_{\text{virgin}}}}, \tag{1}$$

where $K_{Ic_{\text{virgin}}}$ is the fracture toughness of the virgin specimen and $K_{Ic_{\text{healed}}}$ 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.

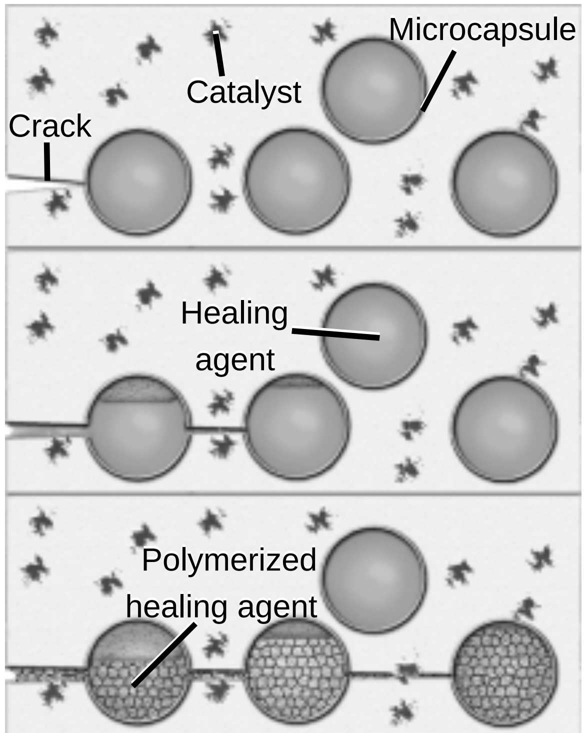

Fig. 2–Self-healing concept for a thermosetting polymer

Crack-healing phenomena have been discussed in the literature for several types of synthetic materials including glass, concrete, asphalt, and a range of polymers.[4-15] 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.[16,17] 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.*[3] 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.

Experimental Procedure

Using the protocol established by White *et al.*[3], 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.*,[18] 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 defined by the theoretical relation

$$m = \frac{3a^2}{h(a)^3} + \frac{1}{h(a)}, \tag{3}$$

or is determined experimentally by the Irwin–Keys[19] method as

$$m = \frac{Eb}{8}\frac{\mathrm{d}C}{\mathrm{d}a}, \tag{4}$$

where E is the Young's modulus, C is the compliance, and $h(a)$ is the specimen height profile. For the TDCB sample geometry, the healing efficiency, Eq. 1, is rewritten as

$$\eta = \frac{P_{c_{\text{healed}}}}{P_{c_{\text{virgin}}}}. \tag{5}$$

TDCB Specimen

Valid profiles for a TDCB fracture specimen are determined by finding a height profile that when inserted into Eq. 3 yields a constant value of m over a desired range of crack lengths. Height profiles that provide exact solution are complex curves, but are approximated with linear tapers.[12,18,20,21] In the current work, the TDCB geometry developed and verified by Beres[20] is adopted. Relevant dimensions are shown in Fig. 3.

When the taper angle is small, a crack propagating in a brittle material exhibits a propensity to deflect significantly from the center line. Failure commonly occurs as arm break-off. To ensure that fracture follows the desired path, side grooves were incorporated into the TDCB geometry. Addition of side grooves is valid for the TDCB geometry, as there is no restriction that b and b_n have the same value. Stable crack propagation with maximum crack width b_n was obtained by selecting a groove with 45° internal angle.[22]

A series of 18 fracture toughness tests were performed on pure epoxy (EPON® 828/DETA) TDCB specimens with crack lengths ranging from 20 to 37 mm to determine m from Eq. 4. A plot of compliance *versus* crack length was constructed and a linear fit made, extrapolating a constant value of dC/da. The fracture toughness of the neat epoxy and the geometric constant m were measured to be 0.55 MPa $\mathrm{m}^{1/2}$ and 0.6 mm^{-1}, respectively. This experimental value of *m* is in excellent agreement with the value predicted by the finite-element method[20].

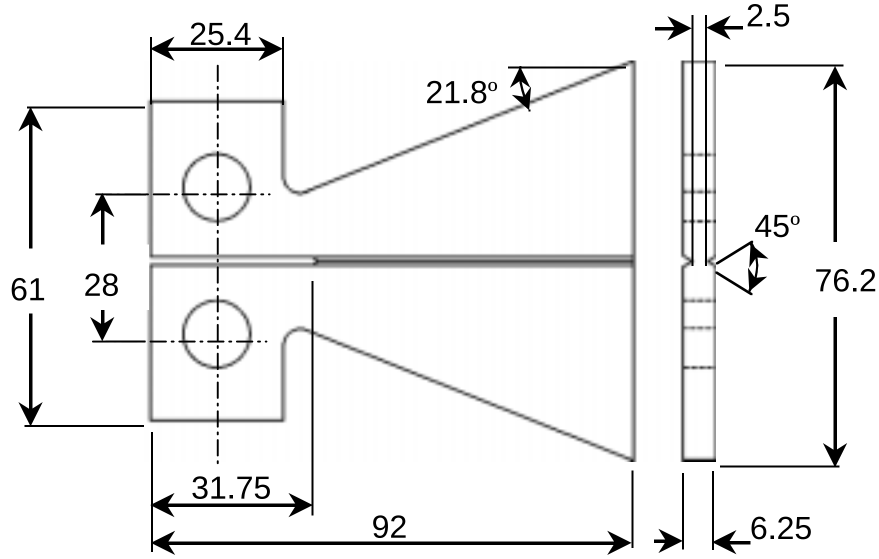

Fig. 3–Tapered double-cantilever beam (TDCB) geometry (dimensions in mm)

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. The emulsion microencapsulation method used is outlined in White *et al*.[3] Table 1 summarizes the different sample types.

TABLE 1–SAMPLE TYPES

Sample type	Epoxy (EPON® 828:DETA)	Grubbs catalyst	Microencapsulated healing agent
Reference control	100:12	–	0-25 wt%
Self-activated control	100:12	0-5 wt%	–
In situ self-healing	100:12	2.5 wt%	5-10 wt%

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. 4 for the *in situ* healing case. Virgin fracture is brittle in nature, while the healed fracture exhibits prolonged stick-slip.

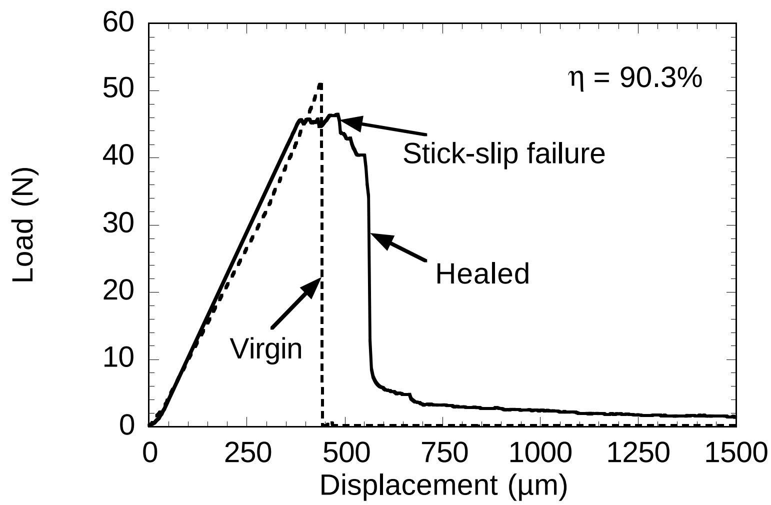

Fig. 4–Representative load–displacement curve for an *in situ* sample with 2.5 wt% Grubbs and 5 wt% capsules

Healing of the Reference System

Potential of the healing system is first investigated via fracture-toughness testing of reference samples. Following a virgin fracture test, approximately 0.03 ml of mixed DCPD monomer and catalyst was injected into the crack plane. An advantage of the Grubbs catalyst/DCPD monomer system is its catalytic reaction. Unlike two-part polymerization reactions, such as epoxy, which require a precise stoichiomerty ratio, the catalyst drives the reaction even with minimum concentration.

Catalyst Concentration

The effect of the ratio of Grubbs catalyst to DCPD monomer was investigated by measuring the healing efficiency in four sets of samples with catalyst to DCPD ratios of 2, 4.4, 10, and 40 g/l. Each set consisted of 18 samples. As shown in Table 2, the level of healing efficiency increased as the concentration of catalyst was increased, while the gel time decreased exponentially, taking approximately 600 s, 235 s, 90 s and 25 s, respectively.

TABLE 2–DEPENDENCE OF HEALING EFFICIENCY IN REFERENCE SAMPLES ON CATALYST CONCENTRATION

Concentration	Fracture toughness (MPa m$^{1/2}$)		
Grubbs:DCPD (g:l)	Virgin	Healed	Healing efficiency
40:1	0.55 ± 0.05	0.71± 0.08	Full heal
10:1	0.56 ± 0.04	0.61± 0.09	Full heal
4.4:1	0.55 ± 0.05	0.53± 0.10	97 ± 15%
2:1	0.54 ± 0.04	0.45± 0.08	84 ± 8%

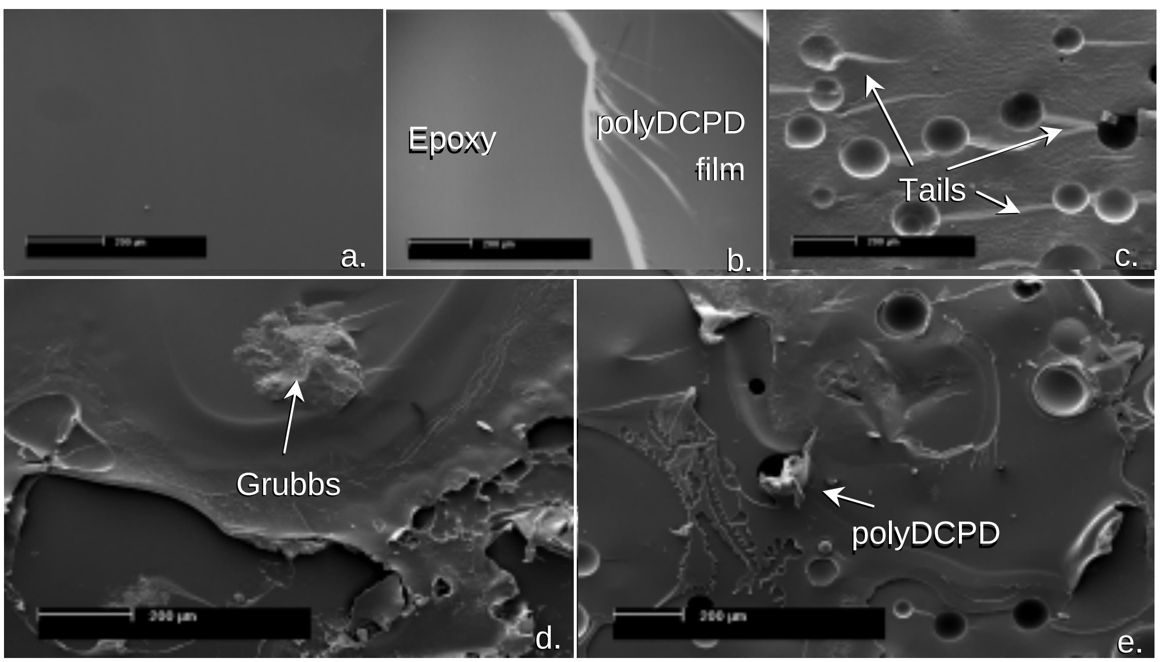

Fig. 5–Crack plane ESEM images: (a) neat epoxy, (b) polyDCPD separation from bulk epoxy, (c) reference sample (10 wt% capsules) showing tails related to the crack pinning toughening mechanism, (d) self-activated (2.5 wt% Grubbs catalyst) and (e) *in situ* samples sample (10 wt% capsules and 2.5 wt% catalyst)

Investigation of the fracture planes highlights two phenomena: fracture in pure epoxy results in locally smooth surfaces down to micron length scales (Fig. 5a), and fracture in the healed material occurs as separation between the bulk epoxy and polyDCPD film (Fig. 5b). It is believed that the increased healing efficiency is due to changes in the chemical kinetics and thermodynamics with increased catalyst concentration. Shorter cure times reduce the time required for healing efficiency to reach a steady value, and serve to prevent diffusion and evaporation of DCPD from the crack plane. The ability of the healed reference sample to obtain full healing (healing efficiency = 100%) indicates excellent adhesion between the polymerized DCPD and the epoxy.

Microcapsule Concentration

Reference samples were also 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 manually. As observed earlier in the literature for the addition of rigid particles,[23,24] the virgin fracture toughness of the material increased significantly with increasing concentration of microcapsules, as shown in Fig. 6. 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. 5c shows clear evidence of the characteristic tails that indicate crack pinning.

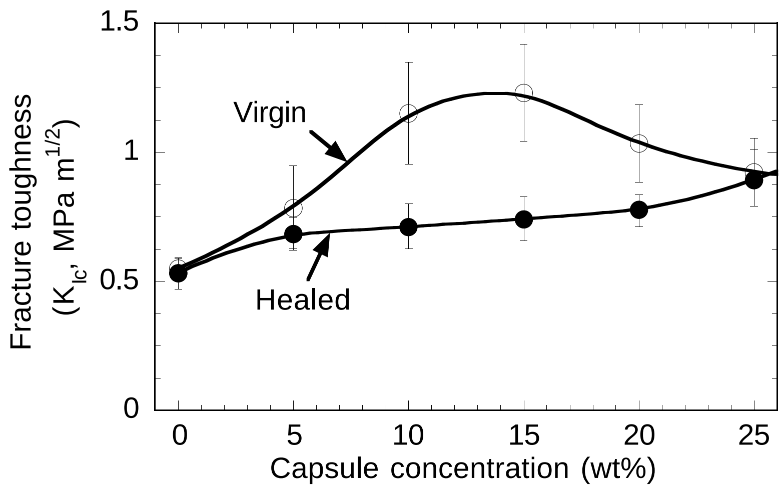

Fig. 6–Virgin and healed fracture toughness dependence on capsule concentration

Healing agent from the microcapsules was allowed to evaporate from the crack plane. The reference samples were then injected with a 4.4 g/l mixture of Grubbs catalyst and DCPD monomer. 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, illustrated in Fig 7. 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.

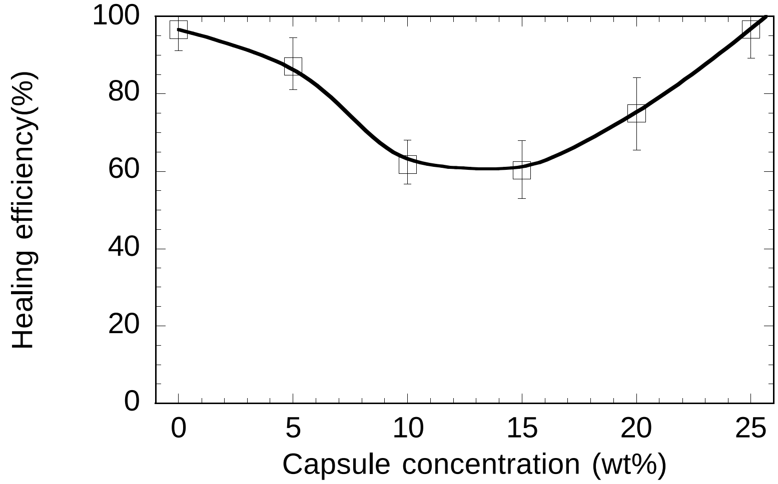

Fig. 7–Healing efficiency dependence on capsule concentration

Healing of the Self-Activated System

The Grubbs catalyst, which is the trigger mechanism for the polymerization of the healing agent, is a fine purple powder with a propensity to form small clumps. From chemical investigation of the interactions between the catalyst and the epoxy system it has been shown that contact of the catalyst during manufacture with the DETA curing agent can degrade the catalyst.[26] The availability of active catalyst is dependent on the order of mixing the catalyst, resin, and curing agent, the catalyst particle size, and the amount of catalyst added. These parameters are investigated with self-activated samples.

Mixing Order

Chemical investigation using proton NMR shows that Grubbs catalyst retains its activity in the presence of the EPON® 828/DETA system during curing. However, contact with only the DETA curing agent causes rapid deactivation of the catalyst. To ascertain the optimal mixing sequence of the three components (EPON® 828/12pph DETA/ 2.5 wt% Grubbs catalyst) to retain the activity of the catalyst and maximize healing efficiency, we manufactured six self-activated samples for each of the three possible sequences. In each case, the first two components were mixed and degassed for 5 minutes. The third component was then integrated and degassed for an additional 5 minutes. Results are summarized in Table 3. Virgin fracture toughness values were statistically unchanged for the three mixing sequences. The healed fracture toughness values and, in turn, the efficiency of healing indicated the importance of mixing order. Mixing the catalyst and DETA curing agent first results in no measurable healing. Failure to recover fracture toughness was interpreted as an indication that the catalyst was extensively deactivated. As shown in Table 3, the other two mixing orders had little effect on the healing efficiency.

TABLE 3–DEPENDENCE OF HEALING EFFICIENCY IN REFERENCE SAMPLES ON MIXING ORDER

	Fracture toughness (MPa m$^{1/2}$)		
Mixing order	Virgin	Healed	Healing efficiency
(EPON® 828 + DETA) + Grubbs	0.73 ± 0.06	0.45 ± 0.8	63 ± 6%
(EPON® 828 + Grubbs) + DETA	0.75 ± 0.05	0.45± 0.09	60 ± 6%
(DETA + Grubbs) + EPON® 828	0.76 ± 0.07	0	0%

Catalyst Particle Size

The size of the Grubbs catalyst particles also influences the behavior of the virgin and healed composite. To determine the size distribution of catalyst that provides the maximum healing efficiency, we ground a sample of catalyst to provide a powder with particle diameters of less than 1mm; the distribution of particle sizes is shown in Fig. 8. Sets of six self-activated samples were manufactured with 2.5 wt% of catalyst with particle sizes of less than 75 μm, 75–180 μm, 180–355 μm, and 355–1000 μm. As illustrated in Fig. 9, both the virgin and healed fracture toughness values increase as the catalyst particle size increases. In the virgin material, the catalyst particles serve as a toughening mechanism through crack pinning,[27] as shown in Fig. 5d. In the healed material, the competing effects of smaller particles provide improved dispersion—and thus availability of catalyst in the crack plane for polymerization of DCPD—and of larger particles providing a reduced surface-area-to-volume ratio for the catalyst. The smaller surface-area-to-volume ratio is believed to reduce the opportunity for DETA curing agent to react with the Grubbs catalyst. Poor healing efficiency was obtained for small particles due to low healed fracture toughness. Large particles do not yield high healed fracture toughness coterminous with their high virgin fracture toughness, also obtaining poor healing efficiency. The highest healing efficiency corresponds to catalyst particle size of 180–355 μm.

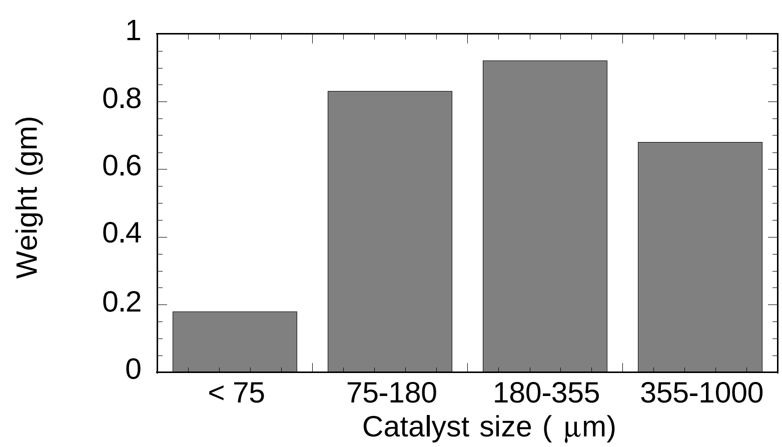

Fig. 8–Particle size distribution of Grubbs catalyst following grinding

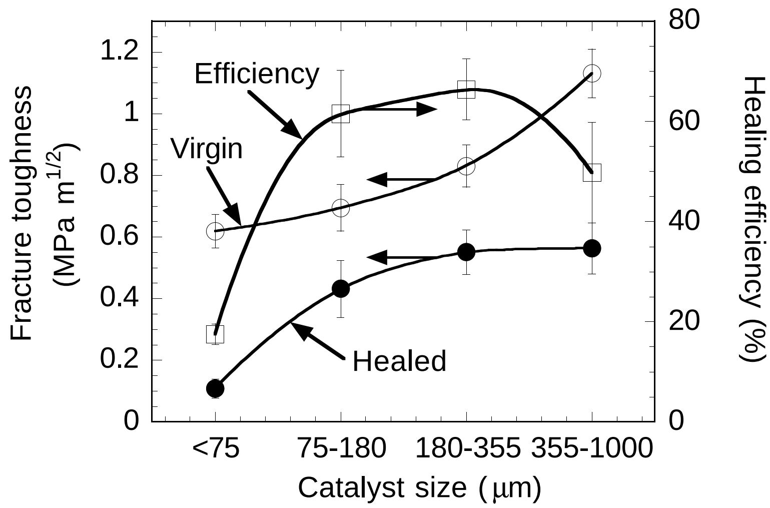

Fig. 9–Dependence of fracture toughness and healing efficiency on catalyst particle size

Catalyst Concentration

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. 10). 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.

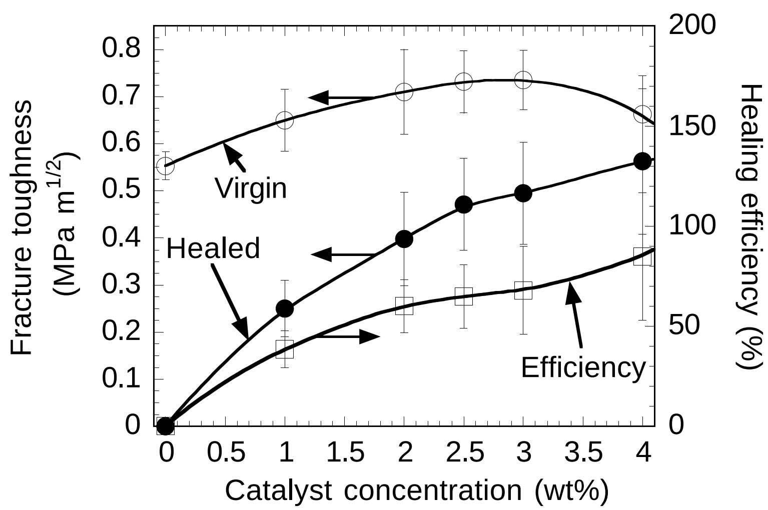

Fig. 10–Healing efficiency as a function of catalyst concentration

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. The effect of microcapsule size on healing efficiency and the evolution of healed fracture toughness over time were 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.

Microcapsule Size

Three sets of samples were manufactured with 180 ± 40 μm, 250 ± 80 μm and 460 ± 80 μm diameter capsules. When fracture occurred, DCPD monomer was observed to fill the crack plane of the TDCB specimen. Variation in the healed fracture toughness was small, with a trend for increased toughness with decreased capsule diameter, as shown in Fig. 11. Divergence of healing efficiency was governed by the virgin fracture toughness, which increased significantly with decreased capsule diameter. The self-healed specimens with 460 μm diameter capsules exhibited the greatest healing efficiency, recovering 63% of virgin load on average. Investigation of the crack planes revealed that all the microcapsules fractured, releasing the encapsulated healing agent. In Fig. 5e, all the capsules on the fracture plane are fractured with no mounds or protruding shell material representative of debonding.

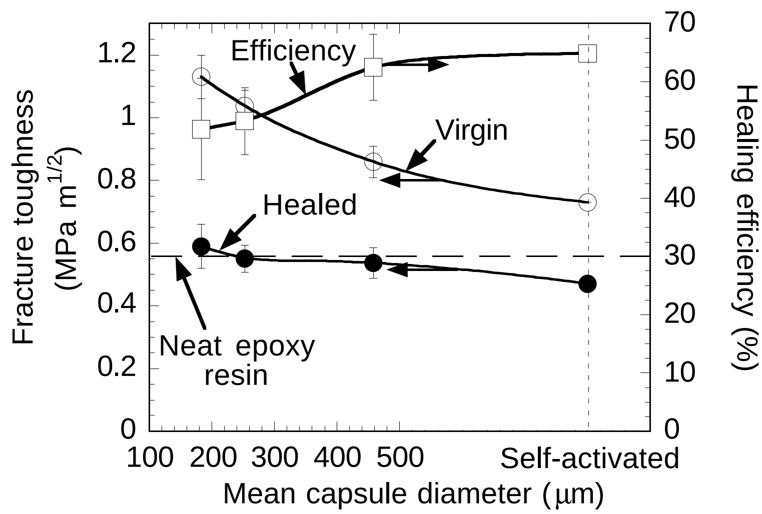

Fig. 11–Influence of microcapsule size on fracture toughness and healing efficiency

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[4,10,11] 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. 12. 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.

Microcapsule Concentration

In earlier work on this self-healing system,[3,28] 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. For the range of microcapsule sizes investigated in Fig. 11, reducing the available healing agent by a factor of seven does not significantly reduce healed fracture toughness, while excess DCPD was observed for all capsule sizes. The data in Fig. 6 for reference samples 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. An average healing efficiency of 85 ± 5% was measured. The relative healing efficiencies of neat epoxy and the *in situ* system with 10 wt% and 5 wt% microcapsules are shown in Fig. 13, illustrating the successful development of an optimized self-healing system.

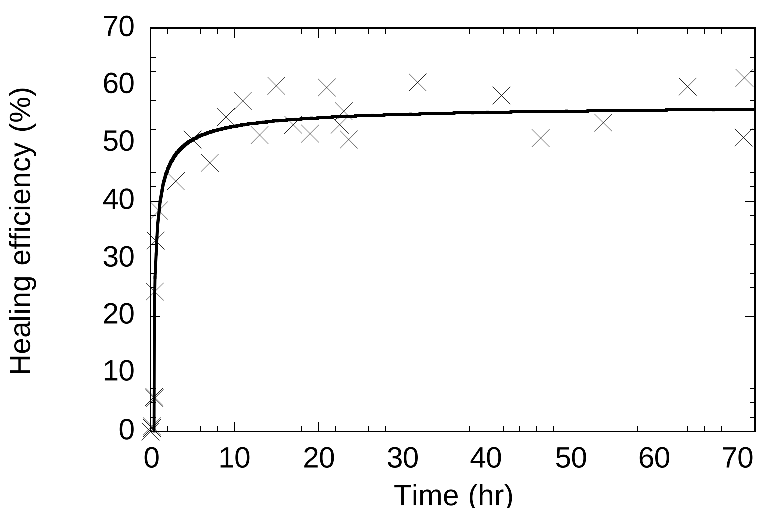

Fig. 12–Development of healing efficiency

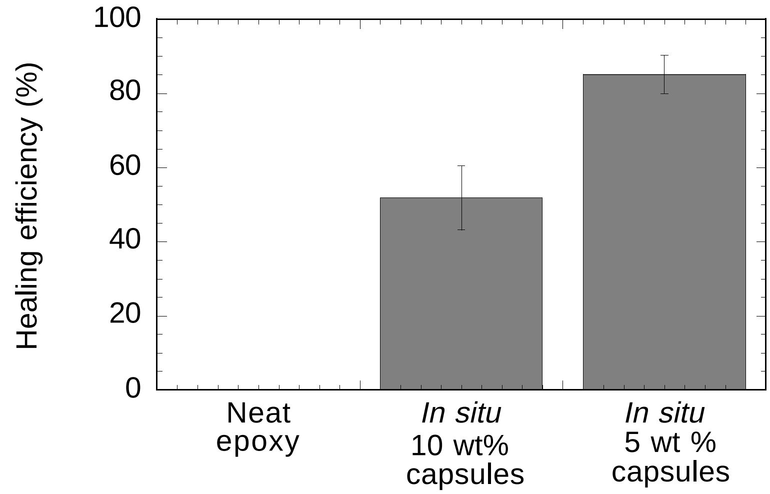

Fig. 13–Comparison of *in situ* healing efficiency for different capsule concentrations (2.5 wt% catalyst)

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 size and concentration of catalyst were shown to have a significant impact on the virgin properties of the composite and the ability to catalyze the healing agent. The highest healing efficiency was obtained with 180–355 μm catalyst particles. 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%. The catalyst was found to remain active following the curing process, given that it was not first mixed with the DETA curing agent. Addition of microcapsules, up to 15 wt%, served to increase the virgin toughness. Capsule size had a direct influence on the volume of DCPD monomer released into the crack plane, but over the range of capsule sizes investigated, healing efficiency was not restricted by lack of healing agent. 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%.

Acknowledgments

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