Performance of Embedded Microspheres for Self-Healing Polymer Composites

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ABSTRACT

Epoxy samples are successfully self healed using an *in situ* system of embedded Grubbs' ruthenium catalyst and DCPD encapsulated in microspheres. Fracture toughness of virgin and healed specimens is measured using a tapered double cantilever beam geometry. A degree of heal, defined as the ratio of critical strain energy release rates of the virgin and healed materials, is used to quantitatively measure crack healing. Values for degree of heal up to 52% are obtained.

1 INTRODUCTION

Self-healing materials are inspired by living organisms, in which minor damage triggers an autonomic healing response. One feature that distinguishes self-healing in living systems is that the fracture event itself is the triggering mechanism that initiates the healing process. Chemical signals released at the site of the fracture initiate a systemic response that transports repair agents to the site of injury and promotes healing.

The current work investigates a self-healing composite material which mimics many of the features of a biological system. Damage in the form of a crack serves as the triggering mechanism for self-healing as does the fracture event in biological systems. Dry and McMillan [1] proposed a methodology for self-repair of corrosion damage in concrete by storing an adhesive in long hollow tubes (several mm in diameter) within the material. In theory, the adhesive can be released by cracking, stretching or melting of the tubes. Dry [2] also proposed the tube delivery system for repair of polymeric structures. Both of these works were conceptual in nature and provided no quantitative evidence of self-healing. Furthermore, the introduction of hollow tubes in a brittle matrix material causes stress concentrations and would probably weaken the material to the extent that no beneficial healing could ever be realized.

In more recent work, Jung *et al.* [3] introduced the concept of self-healing composites using embedded microspheres to store a repair agent. Because of their small size and shape, the microspheres can be easily integrated into the composite matrix using existing manufacturing methods. In addition, established microencapsulation technology allows for tailoring of the encapsulant material, sphere wall material and sphere diameter. Figure 1 illustrates the self-healing mechanism. Once a crack propagates, the spheres rupture, the content fills the crack plane and a catalyst embedded in the matrix initiates polymerization. In the current study the performance of a candidate healing system comprised of dicyclopentadiene (DCPD) monomer and Grubbs' ruthenium based catalyst is evaluated for a common epoxy matrix. Polymerization of the crack filling agent, DCPD, is a two step process. When DCPD monomer is brought into contact with Grubbs' catalyst, the first ring of the 1,3-Cyclopentadiene dimmer is opened by ring opening metathesis polymerization forming branched poly-dicyclopentadiene. The double bond

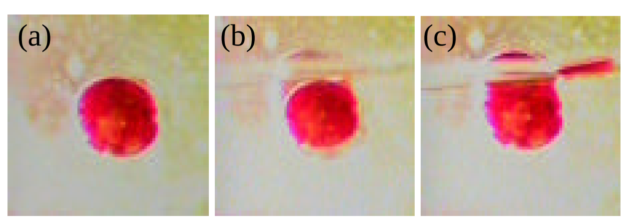

Fig. 1. The self-healing mechanism: (a) sphere in matrix, (b) crack propagation (from left to right), (c) content release.

in the second ring is then opened and the polymer is cross-linked by vinyl polymerization. Throughout the reaction, the "living" Grubbs' catalyst remains active.

2 EFFICIENCY OF HEALING

Quantitative measures of crack healing have been defined in the literature for several types of materials including glass, thermoplastic polymers and even asphalt. Jud and Kaush [4] defined healing in PMMA as the buildup of mechanical strength between two crack surfaces brought into contact above T_g. Wool and Conner [5] quantified the efficiency of crack healing in thermoplastic polymers by comparing the fracture toughness of the virgin material to the fracture toughness measured after crack closure and healing. For the current work, the measure used by Wool and Conner is adopted and a degree of heal is defined as the ratio of critical strain energy release rates of healed and virgin materials,

$$\eta = \frac{\tilde{G}_{Ic}}{G_{Ic}}, \tag{1}$$

where G_{Ic} is the fracture toughness of the virgin specimen and $\tilde{G}_{Ic}$ is the fracture toughness of the healed specimen.

3 EXPERIMENTAL PROCEDURE

Fracture experiments for this self-healing system were performed using a tapered double cantilever beam specimen developed by Mostovoy *et al.* [6]. Two sets of experiments were conducted; the first involved manual injection of DCPD into the crack plane of an epoxy matrix sample with embedded Grubbs' catalyst, the second focused on development of the fully self contained, or *in-situ*, system.

3.1 TDCB Specimen

The tapered double cantilever beam (TDCB) specimen, which exhibits a compliance that is related linearly with crack length, is a variation on the common double cantilever beam. The change in compliance with respect to crack length is constrained to be constant by appropriate choice of the TDCB geometry. According to simple beam theory and approximation of Poisson's ratio to be $\nu = \frac{1}{3}$, the derivative of compliance with respect to crack length is

$$\frac{dC}{da} = \frac{8}{Eb}\left[\frac{3a^2}{h^3} + \frac{1}{h}\right], \tag{2}$$

where the crack length is *a*, and *h* is the beam height at the crack tip. The implication of Eq (2) is that dC/da is only dependent on the height of the beam at the crack tip, and the equation holds independently of the specimen shape.

The TDCB geometry is designed so that the compliance changes linearly with crack length by requiring

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

where *m* is constant. The fracture toughness of the TDCB specimen is expressed as

$$G_{Ic} = \frac{P_c^2}{2b_n}\frac{8}{Eb}m. \tag{4}$$

Jung [7] solved Eq (3) for the best fit of the height profile *h(a)*

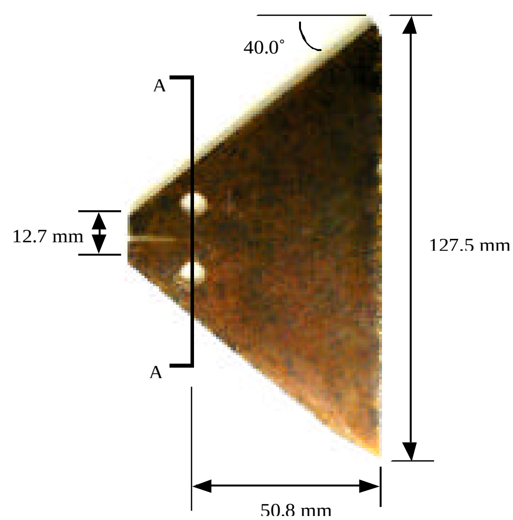

Fig.2. Dimensions of TDCB specimen.

to a 40° taper. Fig. 2 displays the dimensions for the TDCB sample used in the present work, where the crack length *a* is measured from the line A-A.

The value of *m* was also determined experimentally. The compliance was measured for 21 neat epoxy TDCB specimens with crack length varying from 2 to 20 mm. A constant value of dC/da was extracted from the data. Using a Young's modulus of E = 3.4 GPa, a value of m = 0.12 mm^{-1} was calculated.

3.2 Sample Preparation

Samples for the manual injection healing experiments were prepared by mixing EPON® 828 epoxy resin with 12 pph Anacmine® DETA curing agent and the Grubbs' catalyst. The amounts of Grubbs' catalyst was varied from 0.0 to 3.0 wt% to investigate the influence on the degree of heal. The epoxy mixture was then poured into a closed silicone rubber mold and cured for 24 hours at room temperature, followed by 24 hours at 40°C. After curing, specimens were removed from the mold. The average sample thickness was about 3.3 mm. A sharp pre-crack was created by gently tapping a razor blade into the molded started notch in the samples. Samples for the *in situ* healing experiments were prepared in the same fashion, except for the addition of DCPD encapsulated microspheres. Based on previous work by Jung [7], 10 wt% of spheres was chosen to optimize the toughness of the samples. Spheres were carefully mixed into the resin along with the curing agent and Grubbs' catalyst. For all of the in-situ samples, the amount of Grubbs' catalyst was fixed at 2.5 wt%.

3.3 Test Method

The TDCB specimens were tested on a displacement control tabletop load frame using a custom set of pin-loading grips. The bottom grip was rigidly fixed to a rail table, while the top grip was attached to a load cell via a ball joint rod end that allowed limited free rotation of the top grip. Rotation at the ball joint accommodated minor misalignment of the sample within the testing setup. Virgin samples were tested to failure. The virgin data was recorded and either the crack was injected with 0.05 cc DCPD or allowed to self-heal.

4 RESULTS OF DCPD INJECTION

4.1 DCPD Injection

After healing for 48 hours, all of the samples containing embedded Grubbs' catalyst healed sufficiently that the two sides remained connected when unclamped. The samples were retested to failure. Fig. 3 shows representative load displacement curves for a sample healed by injection of DCPD into a specimen containing 2.5 wt% of Grubbs' catalyst. A degree of heal of 0.83 was obtained. The average critical load for a neat sample with 0 wt% Grubbs' catalyst is represented by the dashed line in Fig. 3 (P_c = 134 N). Interestingly, the addition of Grubbs' catalyst alone toughens the specimen.

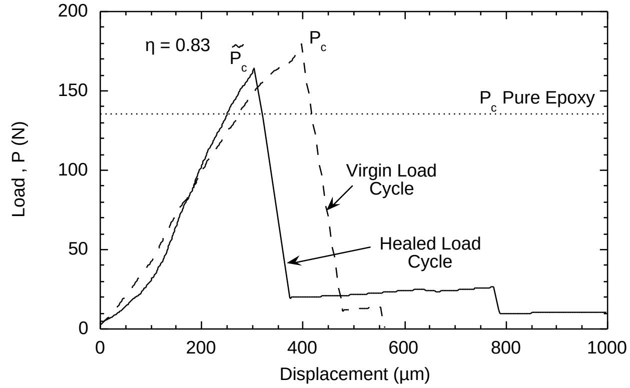

Fig 3. Load-displacement of virgin and healed sample.

Figure 4 shows the average degree of heal obtained for injected specimens as a function of the wt% of Grubbs' catalyst. As the amount of catalyst increases, the degree of heal also increases. Large scatter was observed in the data due to problems with mixing and stability of the Grubbs' catalyst.

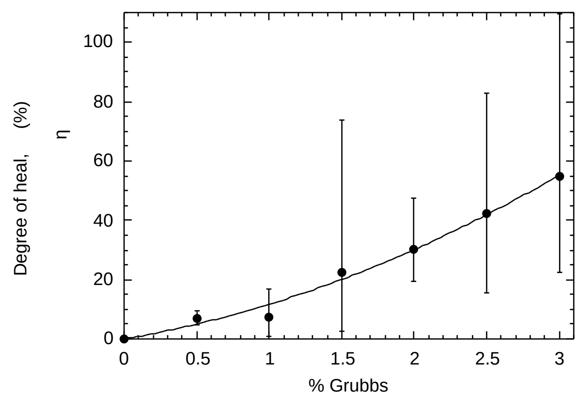

Fig 4. Degree of Heal vs weight % of embedded Grubbs'.

4.2 *In Situ* Healing

A total of four *in situ* samples with 10 wt% of DCPD encapsulated microspheres were tested to failure. When fracture occurred, DCPD was observed to filled the crack plane of the TDCB specimen. When the crack was closed, excess DCPD was forced out of the crack plane. Representative virgin and healed load displacement curves are shown in Fig. 5. The average degree of heal measured was 0.35 for the four samples, with a maximum of 0.52. Again, the average critical load for a neat epoxy sample (no microspheres or Grubbs' catalyst) is represented by the dotted line in Fig. 5. Both the Grubbs' catalyst and microspheres embedded in the matrix material act as reinforcing particles to toughen the specimens. Hence, the self-healed specimens, which recovered on average 59% of their virgin load, can carry more than 100% of the critical load for virgin epoxy.

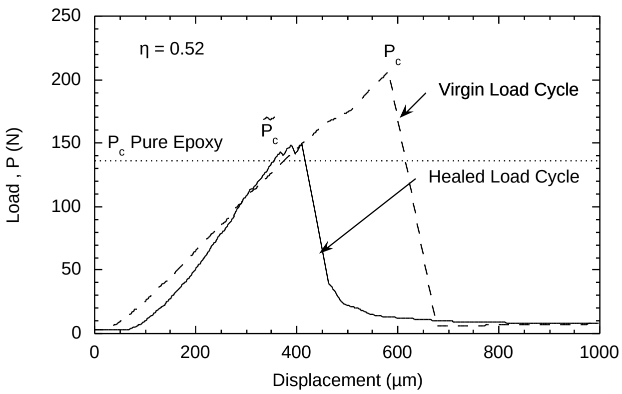

Fig 5. Load-displacement of virgin and healed sample.

5 CONCLUSIONS

Epoxy samples were successfully healed using an embedded Grubbs' ruthenium catalyst and DCPD encapsulated in microspheres. Unlike earlier attempts at polymer healing, this system allows for *in situ* healing triggered by crack growth. Use of the TDCB allowed for investigation of the fracture behavior independent of initial crack length and for direct comparison of results between specimens. The degree of heal obtained was dependent on the amount of Grubbs' catalyst embedded in the matrix. *In situ* healed specimens had toughness values up to 52% of the virgin values.

The addition of Grubbs' catalyst and microspheres both increased the critical load of the fracture specimens. Healed specimens containing Grubbs' catalyst and microspheres were able to carry loads greater than the virgin failure load of neat epoxy (no microspheres or Grubbs' catalyst).

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