

## FRACTURE AND FATIGUE BEHAVIOR OF A SELF-HEALING POLYMER COMPOSITE

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### ABSTRACT

Inspired by biological systems, in which damage triggers an autonomous healing response, a polymer composite material that can heal itself when cracked has been developed. The material consists of an epoxy matrix composite, which utilizes embedded microcapsules to store a healing agent and an embedded catalyst. This paper investigates issues of fracture and fatigue consequential to the development and optimization of this new class of materials. When damage occurs, the propagating crack ruptures the microcapsules, which releases healing agent into the crack plane. Polymerization of the healing agent is triggered by contact with exposed catalyst, which bonds the crack faces closed. The efficiency of crack healing is defined as the ability of a healed sample to recover fracture toughness. Healing efficiencies of over 90% have been achieved. Embedded microcapsules significantly increase the fracture toughness and reduce the fatigue crack propagation rate of epoxy. Fracture mechanisms for neat epoxy and epoxy with embedded microcapsules are presented.

### INTRODUCTION

Thermosetting polymers are used in a wide variety of applications ranging from structural composites to microelectronics. Due to the low strain-to-failure exhibited by these polymers they are highly susceptible to damage in the form of cracks. These cracks frequently initiate deep within a structure where detection is difficult and repair often impossible, ultimately leading to catastrophic failure. White *et al.* [1] have introduced a novel approach to recover the fracture properties of thermosetting polymers following crack propagation through the addition of self-healing functionality. Healing is achieved through the inclusion of urea-formaldehyde microcapsules that contain dicyclopentadiene (DCPD) healing agent. A propagating crack ruptures the microcapsules and exposes Grubbs' catalyst particles embedded in the matrix. Opening of the crack draws the healing agent into the crack plane where contact with the catalyst phase initiates polymerization. Crack healing efficiency is defined as the ability to recover fracture [3],

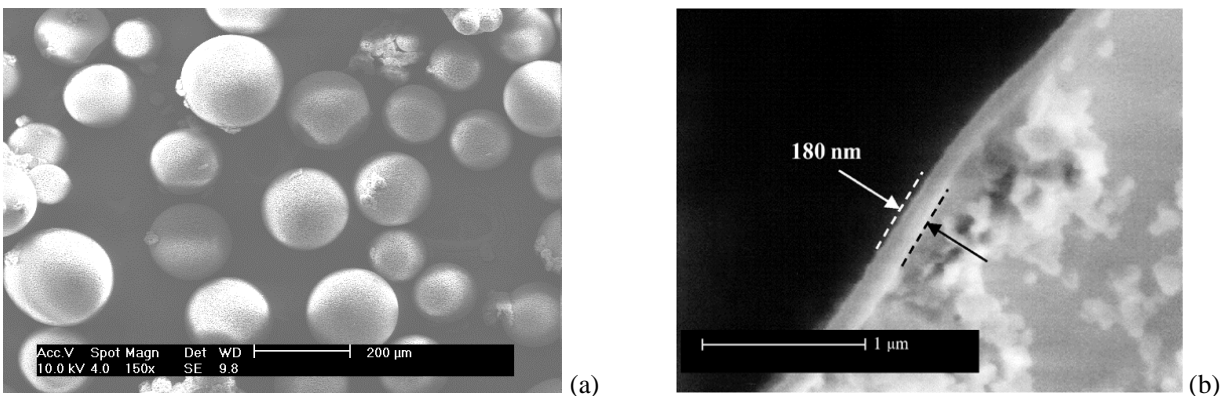
$$\eta = \frac{K_{IC_{healed}}}{K_{IC_{virgin}}}, \quad (1)$$

where  $K_{IC_{virgin}}$  is the fracture toughness of the virgin specimen and  $K_{IC_{healed}}$  is the fracture toughness of the healed specimen. This self-healing material has been reported to recover up to 90% of its virgin fracture toughness [2]. Moreover, the inclusion of microcapsules increases the fracture toughness of the matrix material by up to 127%. The current work investigates the issue

of microcapsule toughening in greater depth and the corresponding effect on healing efficiency and fatigue loading.

## EXPERIMENTAL PROCEDURE

Samples are manufactured from EPON<sup>®</sup> 828 epoxy resin (diglycidyl ether of bisphenol A, DGEBA) with 12 pph Anacmine<sup>®</sup> DETA (Diethylenetriamine) curing agent with embedded microcapsules as outlined in Brown *et al.* [2]. A range of microcapsule size and concentrations are investigated. Microcapsule concentration is the weight fraction of microcapsules in the self-healing polymer composite. The standard deviation for microcapsule diameter is less than 35% of the mean value over the range of diameters investigated. Urea-formaldehyde microcapsules containing DCPD monomer are manufactured in-house, by the emulsion microencapsulation method (Fig. 1a) [4]. Shell wall thickness of the urea-formaldehyde microcapsules is between 160 and 220 nm for the full range of microcapsule diameters investigated (Fig. 1b). Self-healing specimens contain microcapsules and catalyst. Investigation of fracture mechanisms and fatigue behavior utilize neat epoxy specimens and specimens with embedded microcapsules.



**Figure 1** (a) Urea-formaldehyde microcapsules and (b) shell wall cross-section.

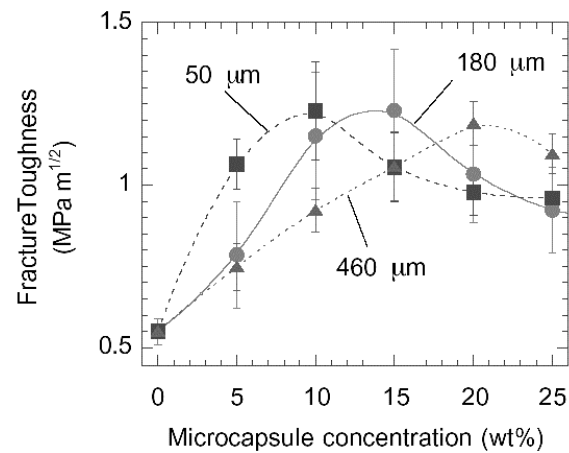
Using the protocol established by White *et al.* [1], healing efficiency is measured by carefully controlled fracture experiments for both the virgin and the healed material. These tests utilize a tapered double-cantilever beam (TDCB) geometry [2], which provides a crack-length-independent measure of fracture toughness. Fracture specimens are tested under displacement control, using pin loading and a 5  $\mu\text{m/s}$  displacement rate.

Fatigue crack propagation (FCP) studies are performed using an Instron DynoMight 8841 low load frame with 250 N load cell. A triangular frequency of 5 Hz is applied with a load ratio ( $R = K_{\min} / K_{\max}$ ) of 0.1. Crack lengths are measured optically. Crack growth rates are obtained from the number of cycles  $N$  required to grow a crack a distance  $a$  of approximately 1 mm for a given range of Mode-I stress intensity factor,  $\Delta K_I$ .

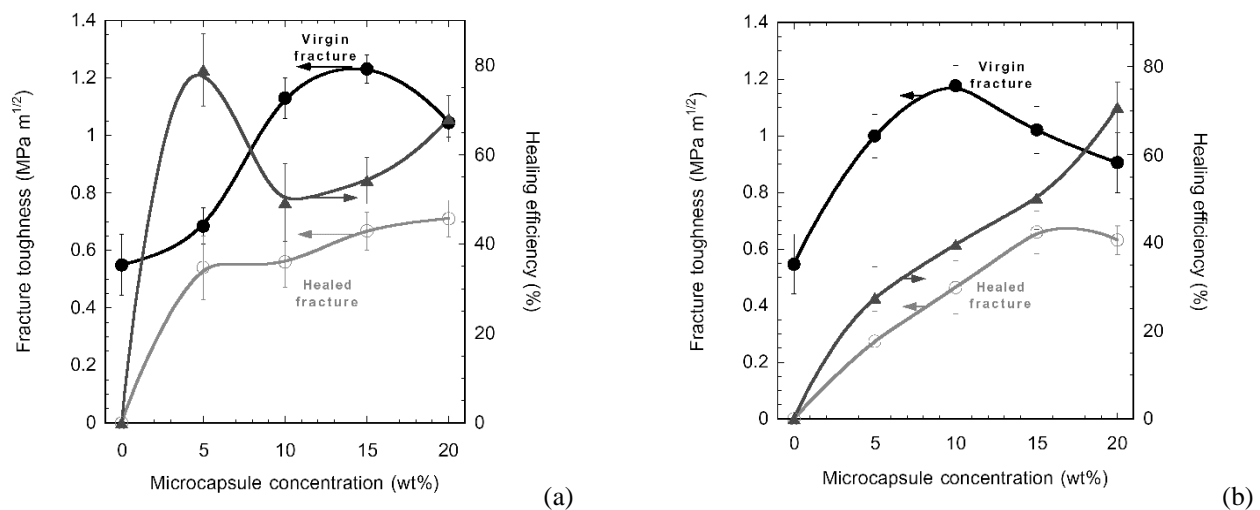
Fracture surface morphology is investigated with a Philips XL30 ESEM-FEG. After fracture the specimens are mounted and sputtered with gold/palladium with a Denton Vacuum Desk II TSC. SEM micrographs are obtained using 10kV secondary electrons in high vacuum mode and a spot size of 3 or 4.

## FRACTURE AND SELF HEALING BEHAVIOR

The virgin fracture behavior and subsequent healing efficiency are investigated for a range of microcapsule size and concentrations. The virgin fracture toughness is plotted in Figure 2 for three different microcapsule diameters. A significant increase in fracture toughness occurs with increasing concentration of microcapsules for all three sizes. The concentration of microcapsules at which a maximum value occurs is strongly dependent on microcapsule diameter. For smaller microcapsules the maximum fracture toughness value occurs at a lower concentration. The literature suggests that smaller microcapsules supply greater surface area for a fixed concentration, thus producing greater shear yielding and increased fracture toughness [5]. At a fixed concentration, inter-particle spacing is also reduced with smaller microcapsules, increasing fracture toughness by transitioning the local matrix fracture behavior from plane-strain to plain-stress [6]. The shape of the curve is similar for all three microcapsule diameters. The diameter has only a slight effect on peak toughness value for the range studied.



**Figure 2** Effect of microcapsule concentration and diameter on fracture toughness.

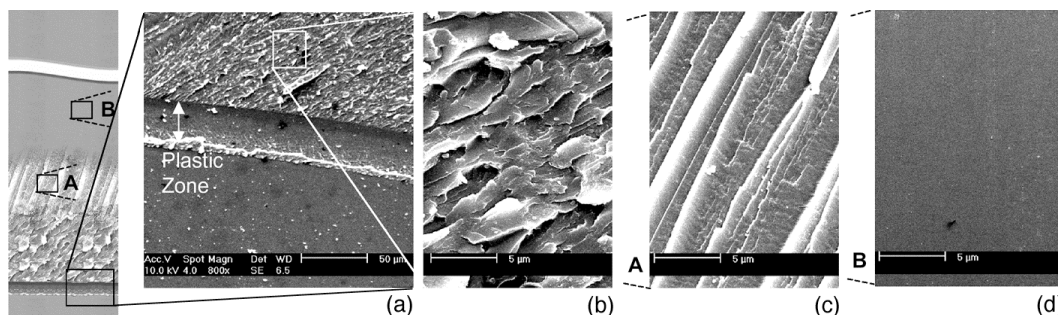


**Figure 3** Healing efficiency as a function of concentration for (a) 180  $\mu\text{m}$  and (b) 50  $\mu\text{m}$  diameter microcapsules.

The virgin and healed fracture behavior and healing efficiency are plotted in Figure 3 for samples containing 50 or 180  $\mu\text{m}$  diameter capsules and 2.5 wt% catalyst. Healed fracture toughness increases steadily with capsule concentration until reaching a plateau for both capsule diameters. The subsequent healing efficiency calculated via Eq. (1) depends more significantly on capsule diameter. The maximum healing efficiency for 180  $\mu\text{m}$  microcapsules occurs at low concentrations (5 wt%) just prior to the peak virgin fracture toughness. For 50  $\mu\text{m}$  microcapsules, high healing efficiency only occurs at higher microcapsule concentrations (20 wt%). As might be expected, a larger number of the smaller microcapsules are required to deliver an identical volume of DCPD healing agent. Over 70% recovery of virgin fracture toughness is obtained for both diameters through careful selection of microcapsule concentration.

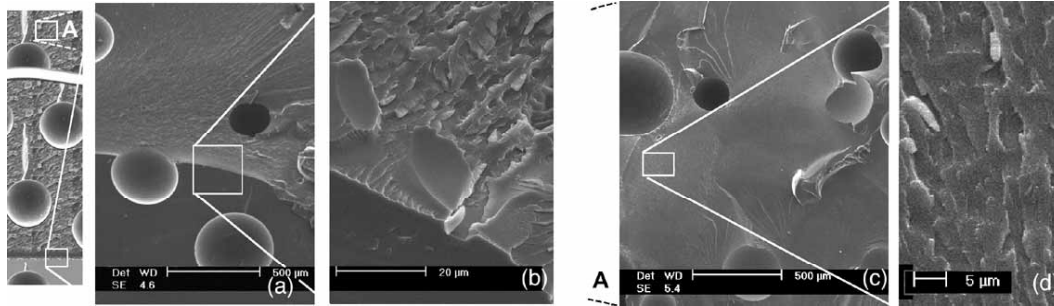
## FRACTURE MECHANISMS

The fracture mechanisms of neat epoxy are investigated as a control. Three distinct zones are distinguished in electron micrographs of the fracture plane in neat epoxy, shown in Fig. 4. A 37  $\mu\text{m}$  thick plastic zone is present at the location of the precrack tip, denoted in Fig. 4a. Based on the theoretical prediction of plastic zone size proposed by Irwin [7] the calculated plastic zone size,  $r_y$ , is  $\sim 40 \mu\text{m}$ . The surface of the fracture plane before the plastic zone is smooth, typical of cleavagelike brittle fracture. In the region just beyond the plastic zone, a series of hackle markings are present, enlarged in Fig. 4b. Within 1.5 mm of the plastic zone, the hackle markings transition into striations in the direction of crack propagation, shown in Fig. 4c and within 2.0 mm complete transition back to cleavagelike brittle fracture occurs, Fig. 4d. The size of this middle zone coincides roughly with the 3D zone size [8],  $r_{3D} \approx 2.2 \text{ mm}$ .



**Figure 4** Electron micrographs of fracture plane in neat epoxy. (a) Precrack tip location and plastic zone. (b) Hackle markings in the 3D zone. (c) Transition zone. (d) Brittle fracture plane (2 mm from plastic zone).

Electron micrographs of fracture planes containing embedded microcapsules indicate changes in fracture mechanism from that of neat epoxy. The plastic zone observed for neat epoxy is no longer present as a distinct band, shown in Fig. 5a. Rather there is a transition directly to hackle markings, Fig. 5b. In the case of embedded microcapsules, hackle markings become the dominant fracture plane topology. The degree of roughness appears largest close to the precrack tip, but hackle marking is observed over the entire crack plane, Fig. 5d.



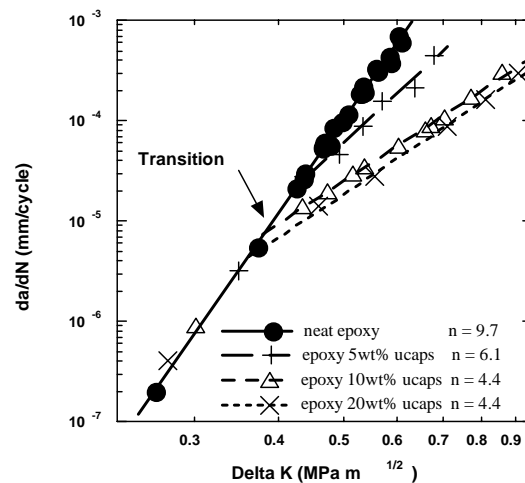
**Figure 5** (a) Precrack front in the presence of microcapsules, without a defined plastic zone (b). (c) Tails in the wake of microcapsules and (d) continued presence of hackle marking 30mm from precrack.

## FATIGUE

Fatigue response of the self-healing polymer is also investigated. Preliminary experiments on embedded microcapsules are plotted in Figure 6. The crack growth rate,  $da/dN$ , of epoxies has been extensively studied and found to be correlated with the applied range of Mode-I stress intensity factor,  $\Delta K_I$ , according to the Paris-Power Law,

$$\frac{da}{dN} = C_o \Delta K_I^n, \quad (2)$$

where  $C_o$  and  $n$  are material dependent constants. Reported values of  $n$  for epoxy are as high as 10 [9-11]. The addition of microcapsules increased the resistance to fatigue crack growth. Crack propagation in neat Epon 828/DETA follows  $n = 9.7$ . A transition point is observed in the FCP behavior of epoxy with microcapsules, below which microcapsules do not effect FCP. Above this threshold, approximately  $\Delta K_I = 0.4 \text{ MPa m}^{1/2}$ , epoxy with microcapsules exhibits a higher FCP resistance than neat epoxy. The observed reduction of  $n$  to a steady state value of 4.4 above 10 wt% microcapsules is similar to the behavior of rubber toughened epoxy [11].



**Figure 6** The effect of microcapsule concentration on the FCP behavior.

## CONCLUSIONS

The fracture and fatigue behavior of microcapsules embedded in epoxy were investigated towards the development of a self-healing polymer. The addition of microcapsules is shown to yield a 127% increase in virgin fracture toughness. The concentration of microcapsules at which maximum toughening occurs is dependent on microcapsule size. Maximum healing efficiency is measured when toughening of the virgin material is minimized, with recovery of over 90% of the virgin fracture toughness. Investigation of the fracture planes with electron microscopy indicated a change in fracture mechanism with the addition of microcapsules. Under fatigue loading a transition point is observed in the FCP behavior of epoxy with microcapsules. Above the threshold, resistance to FCP increased with increased microcapsule concentration.

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