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. This paper investigates fracture mechanics issues consequential to the development and optimization of this new class of materials, with focus on toughening mechanisms induced by embedded microcapsules. The self-healing material under investigation is an epoxy matrix composite, which utilizes embedded microcapsules to store dicyclopentadiene (DCPD) as a healing agent. Fracture toughness is measured using a tapered double-cantilever beam (TDCB) test, which ensures controlled crack growth along the centerline of the brittle epoxy specimen. Effects of microcapsule size and concentration are studied with a view towards improving healing efficiency and understanding toughening mechanisms. Toughening is shown to result from a transition in the fracture mechanism of the epoxy matrix from cleavagelike brittle fracture to hackle markings on the fracture plane. Comparisons of urea-formaldehyde microcapsule toughening to that of silica microspheres, urea-formaldehyde particles and void inclusion are also discussed.

Keywords: self-healing, autonomic-healing, fracture toughness, microcapsule, void

INTRODUCTION

A novel approach has been demonstrated to improve the service life of thermosetting polymers through the addition of self-healing functionality [1]. 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. Recent breakthroughs in self-healing technology have resulted in a material capable of recovering up to 90% of its virgin fracture properties without external intervention [2]. The healing system under investigation has a three stage healing process, accomplished by incorporating a microencapsulated healing agent and a catalytic
chemical trigger in an epoxy matrix, shown in Figure 1. As a crack propagates through the polymer, (i) the embedded microcapsules are ruptured, (ii) a healing agent (Dicyclopentadiene, DCPD) is released into the crack plane, and embedded particles of Grubbs’ Ruthenium catalyst are exposed. Polymerization of DCPD (iii) is triggered by contact with the catalyst through ring opening metathesis polymerization (ROMP) and bonds the crack faces closed. Crack healing efficiency is assessed by adopting a measurement of the ability to recover fracture \[ \eta = \frac{K_{Ic,\text{healed}}}{K_{Ic,\text{virgin}}} \], (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.

In this paper, we present a comprehensive experimental investigation of microcapsule toughening in a polymer composite. Effects of microcapsule size and concentration on virgin fracture toughness are studied with a view towards improving healing efficiency and understanding toughening mechanisms. A fundamental requirement of a self-healing material is that the addition of self-healing functionality must not detrimentally affect the virgin fracture performance. The addition of microcapsules to a polymer matrix has a significant toughening effect [2] that must be understood and optimized for the self-healing application.

Investigation of particle reinforced composites in the literature has focused on two main toughening mechanisms: crack-pinning through the inclusion of impenetrable particles [4,5,6] and cavitation or microcracking through rubber toughening [7,8,9]. In crack pinning cleavage like brittle fracture is observed in the matrix and the propagating crack is constrained, or pinned, by the embedded particles. These inclusions force the crack front to bow out beyond the inclusions thus increasing the energy required to continue crack growth. Once the crack bows out by a critical amount the crack front snaps past the pinning inclusions. The primary indicator of crack pinning is the presence of tails on the fracture plane in the wake of the inclusion, which is due to this snap through. Two separate mechanisms have been proposed for inclusion of ductile, rubber particles: cavitation and microcracking. A triaxial stress state (plane strain) usually exists ahead of a crack, which tends to produce dilation. The bulk modulus of a rubber particle, with a Poisson’s ratio approaching 0.5, will be large and deformation will be difficult under triaxial stress conditions. In some cases the rubber particles have been shown to respond to the imposed stress field by debonding and internal cavitation, also called void growth. Other cases have been presented where inclusions act as points of stress concentration, which under triaxial stress conditions leads to shear yielding or microcracking in the matrix. For the case of microcracking, it has been shown for epoxy reinforced with silicon rubber that the fracture surface exhibits hackle marks on the fracture plane and are toughened with the addition of rubber particles up to a maxima [7].

Begheri and Pearson [8] used latex microcapsules in a DGEBA epoxy to simulate sites of precavitation while investigating rubber particle toughening. Though not explicitly stated, their data indicated that fracture toughness increased as microcapsule size decreased, for a fixed volume fraction. The shell wall thickness in these experiments was less than 10% of the microcapsule
diameter. For microcapsules of diameter less than 15 µm toughening was attributed to shear yielding at the crack tip, while for microcapsules of greater diameter a combination of shear yielding and microcracking was identified as the operative mechanism. Independent of diameter, all microcapsules were reported to rupture. Mouritz [10] used 100 µm diameter hollow polymer microcapsules to simulate voids in a glass fiber reinforced isophthalic polyester resin. Fracture toughness decreased dramatically with the addition of microcapsules. No information was provided regarding the microcapsule material, shell wall thickness or failure mode. Ahmad [11] investigated the behavior of thermoplastic microcapsules (50 µm to 140 µm diameter) in vinyl plastisol and found the elastic modulus was strongly dependent on microcapsule size. The microcapsules were Expancel®, a copolymer of vinylidene chloride, acrylonitrile and methylmethacrylate. Composites with smaller microcapsules had higher modulus than larger microcapsules for a given volume fraction.

Toda et al. [12] investigated the toughening effect of silica microcapsules in epoxy at 55 vol%. Silica microcapsules with a shell wall thickness 10% of the diameter were shown to generate a level of toughening comparable to that of identical diameter (13.3 µm) silica microspheres. The silica microcapsules were observed to debond rather than rupture, causing the crack to propagate predominantly in the matrix material. A composite with larger 29.5 µm diameter silica microspheres exhibited significantly lower fracture toughness but also failed predominantly by debonding. Zihlif and Ragosta [13] reported the addition of glass micro-balloons reduced the toughness of epoxy (DGEBA epoxy cured with V40) by 33% in impact fracture tests. The reduction in toughness was independent of the volume of glass microspheres from 5 to 55 vol%. Fracture surfaces in the neat epoxy contained primary cracks near the precrack tip and secondary cracks appearing as parabolic striations, taken to indicate plastic deformation and shear yielding. The epoxy containing glass microspheres had brittle fracture surfaces. This change in fracture mechanism and reduction in fracture toughness were claimed to result from the change in physical structure of the material due to the incorporating of glass microcapsules. In contrast, Azimi et al. [14] reported that hollow glass spheres increase the fracture toughness $K_\text{IC}$ of DGEBA epoxy cured with piperadine by approximately a factor of two, from 0.90 MPa m$^{1/2}$ to 2.03 MPa m$^{1/2}$. Results from the literature are inconclusive as to the effect of embedded microcapsules on fracture toughness. This paper investigates the toughening effect of embedded urea-formaldehyde microcapsules in epoxy. The fracture modes of neat epoxy and epoxy containing microcapsules are reviewed by electron microscopy.

**SAMPLE PREPARATION AND TEST METHOD**

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, which ensures controlled crack growth along the centerline of the brittle specimen. The TDCB fracture geometry, developed by Mostovoy et al. [15], provides a crack-length-independent measure of fracture toughness

$$K_\text{IC} = \alpha P_c,$$

which requires knowledge of only the critical fracture load $P_c$ and geometric term $\alpha$. The geometric term $\alpha$ is determined experimentally by the Irwin–Keys [16] method as discussed in Brown et al. [2]. The TDCB sample geometry shown in Figure 2 is a modification to a geometry developed by Beres et al. [17], for which $\alpha = 11.2x10^3$ m$^{3/2}$ [2]. Combining Equations (1) and (2) the healing efficiency is rewritten as

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

(3)
Samples were prepared by mixing EPON® 828 epoxy resin (diglycidyl ether of bisphenol A, DGEBA) with 12 pph Anacmine® DETA (Diethylenetriamine) 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 microcapsules on the virgin fracture properties, varying weight percent of microcapsules were mixed into the resin prior to pouring. Urea-formaldehyde microcapsules containing DCPD monomer were manufactured in-house, by the emulsion microencapsulation method outlined by Brown et al [18]. By controlling the mixing speed, microcapsules with diameters ranging from 10 µm to 1 mm were fabricated. Shell wall thickness of the urea-formaldehyde microcapsules was between 160 and 220 nm for the full range of microcapsule diameters investigated. A study of the effect of void content on fracture toughness was performed. Voids were introduced by aggressive mixing of the resin before it was poured into the mold. The effects of silica microspheres, debonded microspheres, and urea-formaldehyde microparticle on fracture toughness were investigated. Inclusions were mixed into the resin prior to pouring. Fracture specimens were tested under displacement control, using pin loading and a 5 µm/s displacement rate. Samples were tested to failure, measuring compliance and peak load. A representative load–displacement curve is shown in Figure 2 for the in situ healing case. Virgin fracture is brittle in nature, while the healed fracture exhibits prolonged stick-slip.

**VIRGIN FRACTURE BEHAVIOR**

Understanding the effects of microcapsules on the virgin fracture toughness is essential for design and development of self-healing polymers. The amount of toughening depends on the concentration and diameter of microcapsules in the composite. Figure 3a contains a plot of measured fracture toughness as a function of microcapsule concentration for three different diameter capsules: 50 µm, 180 µm, and 460 µm. 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 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. Characteristic tails originating from broken spheres in the fracture plane, as shown in Figure 3b, indicate a crack pinning toughening mechanism may be operative. Successful crack pinning is generally observed with rigid reinforcing particles, such as silica [19]. However, the level of
toughening observed in Figure 3a far exceeds that reported for glass microspheres at comparable volume fractions. For the same diameter (30 \( \mu \text{m} \)) and volume (10 vol\%) of inclusions, glass beads yield an increase in toughness of \( \sim 20\% \) [19], compared to a 127\% increase in toughness for 10 vol\% of 30 \( \mu \text{m} \) microcapsules. We investigated fracture surfaces in neat epoxy and epoxy with embedded microcapsules to understand why the observed level of toughening occurs.

TOUGHENING MECHANISMS

**Neat Epoxy**

The fracture behavior of neat epoxy is investigated first as a control. Three distinct zones are distinguished in electron micrographs of the fracture plane in neat epoxy, shown in Figure 4. A 37 \( \mu \text{m} \) thick plastic zone is present at the location of the precrack tip, denoted in Figure 4a. Based on the theoretical prediction of plastic zone size proposed by Irwin [20]

\[
r_y = \frac{1}{2\pi} \left( \frac{K_{IC}}{\sigma_{YS}} \right)^2,
\]

where \( K_{IC} \) is 0.55 MPa m\(^{1/2}\) and the yield stress \( \sigma_{YS} \) is 35 MPa, 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 Figure 4b. Such markings have been reported in epoxy when shear stresses dominate the fracture process and attributed to coalescence of many tension-induced microcracks inclined at an angle to the overall fracture plane [21]. Within 1.5 mm of the plastic zone, the hackle markings transition into striations in the direction of crack propagation, shown in Figure 4c and within 2.0 mm complete transition back to cleavagelike brittle fracture occurs, Figure 4d. The size of this middle zone coincides roughly with the 3D zone size propose by Rosakis and Ravi-Chandar [22], \( r_{3D} \approx 2.2 \text{ mm} \).

**Epoxy with Embedded Microcapsules**

Next, fracture surfaces of samples with microcapsules are investigated. Electron micrographs of fracture planes containing embedded microcapsules indicate two changes in fracture mechanism from that of neat epoxy. First, the 37 \( \mu \text{m} \) plastic zone observed for neat epoxy is no longer present as a distinct band, shown in Figure 5a. Rather there is a transition directly to hackle markings, Figure 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 markings were observed over the entire crack plane (Figure 5c). In the case of neat epoxy and all other inclusion investigated—silica microspheres, urea-formaldehyde microparticles, debonding microcapsules and voids—the hackle markings were found to be restricted to a small region near the crack tip. The mechanism of microcrack-toughening, which is associated with the presence of hackle markings, is discussed by Karger-Kocsis and Friedrich [23].

**Voids and Alternate Inclusions**

Close investigation of the fracture planes in Figures 3 and 5 reveal that the tails in the wake of the microcapsules form a step as shown in Figure 6a. Due to the discontinuity of the crack front in the presence of the microcapsule, the crack front on either side of the capsule divides causing a difference in elevation. In order to regain continuity after rupturing the microcapsule, the two crack faces reconnect by forming a step. In contrast, the tails associated with crack pinning by solid silica microspheres, shown in Figure 6b, form a delta. The tails form as the debonding crack, progressing along the interface of the inclusion, follows the lowest energy path when snap-through forces it to rapidly catch up with the bowed crack fronts.

Preliminary studies were performed to investigate the effect of voids, microcapsule bond strength, and urea-formaldehyde microparticles on fracture toughness. Voids were introduced by aggressive mixing of the epoxy resin. Void content, varying from 0.5 to 15 vol\%, was measured by optical

![Figure 5](image-url)  
**Figure 5** (a) Precrack front in the presence of microcapsules, without a defined plastic zone (b). (c) Tails in the wake of microcapsules and (inset) continued presence of hackle marking 30mm from precrack.
microscopy in the vicinity of the precrack tip. Voids dramatically decreased the fracture toughness, shown in Figure 7a. The main fracture plane features, with the presence of voids, were similar to those of neat epoxy. A distinct 35 µm thick plastic zone exists as shown in Figure 7b. The plastic zone exists along the entire length of the precrack front. Where voids intersect this front, the plastic zone size remains unchanged. The 3D zone, where hackle markings were observed, was less than 2 mm, consistent with neat epoxy. In the 3D zone however, the presence of voids locally changed the fracture mechanism, causing small regions of cleavagelike brittle fracture (inset in Figure 7b). The resulting reduction in the total area of hackle marks may account for part of the decline in fracture toughness with the inclusion of voids. The one similarity between voids and microcapsules was the appearance of step tails in their wake. This indicates that the presence of these tails does not necessarily indicate a major toughening mechanism.

Microcapsules with smooth surface morphology were manufactured and coated with Buehler release agent (20-8185-016) and Miller Stephenson PTFE release agent (MS-122DF). These microcapsules, designated as debonded, were easily pulled from cured epoxy and were observed to debond rather than rupture on the fracture plane. The fracture toughness decreased (Figure 7a) with increasing concentration of poorly bonded microcapsules.

Urea-formaldehyde microparticles were manufactured by an emulsion technique similar to the microcapsules. While urea-formaldehyde particles did toughen the epoxy matrix (Figure 7a), the increase was much less than achieved by microcapsules. No tails were observed on the fracture plane and the crack propagated through the equator of the particles rather than along the interface, as in the case of silica microspheres.

![Figure 6](a) Step tail in wake of microcapsule and (b) delta tail in wake of silica microsphere.

![Figure 7](a) Relative effects on fracture toughness of microcapsules, voids and microparticles and (b) electron micrograph of voids.
CONCLUSIONS

The fracture toughness of epoxy was significantly increased by the embedding of thin-walled urea-formaldehyde microcapsules. The extent of toughening was strongly dependent on the concentration and size of the microcapsules, the concentration for maximum toughening decreasing for smaller microcapsule diameters. Microcapsules were shown to trigger a change in the fracture mechanism of the epoxy matrix. Fracture plane features transitioned from cleavagelike brittle fracture to hackle markings. The capsules had to be well bonded to the matrix for this toughening to occur. Microcapsules behaved differently than voids in both their affect on fracture mechanisms and on the resulting fracture toughness.

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