FATIGUE CRACK PROPAGATION IN A SELF-HEALING POLYMER COMPOSITE

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ABSTRACT

A novel approach is explored for improving the fatigue life of thermosetting polymers through the addition of self-healing functionality. Thermosetting polymers are used in a wide variety of applications ranging from composite structures to adhesive joints to microelectronic packaging. Due to their low strain-to-failure these polymers are highly susceptible to damage in the form of cracks. Fatigue loading is particularly problematic, giving rise to the initiation and propagation of small cracks deep within the structure where detection is difficult and repair is virtually impossible. These cracks often lead to catastrophic failure of the material. A strategy based on recent developments in self-healing technology is utilized to autonomically repair fatigue cracks and extend the service-life of polymeric components. The material under investigation is an epoxy matrix composite, which utilizes embedded microcapsules to store a healing agent and an embedded catalyst. A propagating crack exposes particles of catalyst and ruptures the microcapsules, which release healing agent into the crack plane. Polymerization of the healing agent is triggered by contact with the catalyst, which bonds the crack faces closed.

A comprehensive experimental program is carried-out to assess the fatigue behavior of a self-healing polymer. The inherent fatigue characteristics of the material are measured using two types of control samples: unfilled neat epoxy and epoxy with embedded microcapsules. Fatigue crack propagation in neat epoxy and epoxy with embedded microcapsules is accurately captured by the Paris power-law. The Paris Law exponent n is strongly dependent on the content of microcapsules, varying from 9.7 for neat epoxy to approximately 4.5 above 10 wt% microcapsules. A control healing experiment is performed by injected precatalyzed DCPD healing agent in a fatigue crack. Once cured, crack growth is arrested in the healed sample, significantly increasing sample life. *In situ* healing experiments are in progress

1. INTRODUCTION

A novel approach to recover the fracture properties of thermosetting polymers has been introduced by White et al. [1]. Healing is achieved by incorporating a microencapsulated healing agent and a catalytic chemical trigger within a polymer matrix. A propagating crack ruptures the microcapsules and exposes catalyst particles. Crack opening draws the healing agent into the crack plane, where contact with the catalyst phase initiates polymerization. The polymerized healing agent reestablishes structural integrity across the crack plane. Conclusive demonstration of self-healing is obtained with a healing agent based on the ring-opening metathesis polymerization (ROMP) reaction [1]. Dicyclopentadiene (DCPD), a highly stable monomer with excellent shelf life, is encapsulated in urea-formaldehyde (UF) microcapsules. A small volume fraction of microcapsules is dispersed in an epoxy matrix along with Grubbs' transition metal catalyst. This self-healing epoxy is able to recover over 90% of its virgin fracture toughness [2].

In addition to providing an efficient mechanism for self-healing, the presence of DCPD-filled UF microcapsules also significantly increases the inherent fracture toughness of the epoxy. Under monotonic loading the average maximum toughness with microcapsules is 127% greater than neat epoxy. Fracture of the neat epoxy is brittle, exhibiting a mirror fracture surface. The addition of microcapsules produces a transition of the fracture plane morphology to hackle markings. The increased toughening associated with fluid-filled microcapsules is attributed to increased hackle marking and subsurface microcracking not observed for solid particle fillers [3]. In the present work, we investigate the behavior of the self-healing polymer under fatigue loading. The crack growth rate da/dN of epoxies is related to the applied range of Mode-I stress intensity factor ΔK_I according to the Paris-Power Law,

$$\frac{da}{dN} = C_o \Delta K_I^{\,n}, \tag{1}$$

where C_o and n are material dependent constants.

2. EXPERIMENTAL PROCEDURE

The fatigue crack propagation behavior of microcapsule-filled epoxy was investigated using a tapered double-cantilever beam (TDCB) test. Side grooves ensured controlled crack growth along the centerline of the brittle specimen. The TDCB geometry, developed by Mostovoy et al. [4], provided a crack-length-independent relationship between applied stress intensity factor K_I and load P,

$$K_I = \alpha P, \tag{2}$$

which only required knowledge of the geometric term α. For the TDCB sample geometry in Fig. 1, α = 11.2x10^3 m$^{-3/2}$ was determined experimentally as discussed by Brown et al. [2].

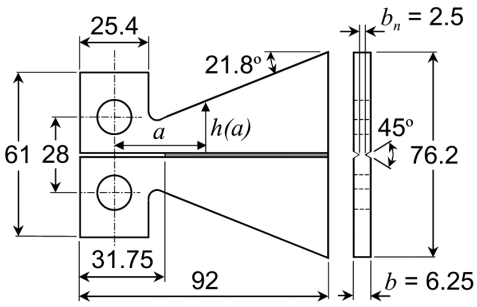

Figure 1 Tapered double-cantilever beam (TDCB) geometry [2].

Urea-formaldehyde microcapsules containing DCPD monomer (Fig. 2) were manufactured with diameters of 53 ± 19 μm and 183 ± 43 μm using the emulsion in situ polymerization microencapsulation method outlined by Brown et al [5]. Shell wall thickness was 190 ± 30 nm for all batches. Tapered double-cantilever beam specimens were cast from EPON® 828 epoxy resin (DGEBA) and 12 pph Ancamine® DETA (diethylenetriamine) curing agent with a prescribed concentration of microcapsules. 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. A razor blade was gently tapped into a molded starter notch to generate a sharp precrack.

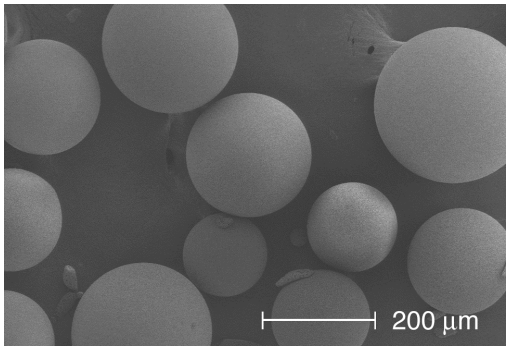

Figure 2. ESEM image of UF microcapsules containing DCPD core [4].

Fatigue crack propagation studies were performed using an Instron DynoMight 8841 low load frame with 250 N load cell. A triangular frequency of 5 Hz was applied with a load ratio ($R = K_{min}/K_{man}$) of 0.1. Crack lengths were measured optically. Crack growth rates were 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 ΔK_I.

3. FATIGUE CRACK GROWTH

The effect of embedded microcapsule size and concentration on fatigue crack growth is shown in Fig. 3. 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 ΔK_I according to the Paris-Power Law given in Eq. (1). Reported values of Paris Law exponent for epoxy are as high as n = 10 [6-8]. Crack propagation in neat Epon 828/DETA (no microcapsules) is measured to follow n = 9.7. The addition of microcapsules increases the resistance to fatigue crack growth. A transition point is observed in epoxy with microcapsules, below which microcapsules do not effect fatigue crack growth rate. Above this threshold, approximately ΔK_I = 0.4 MPa $m^{1/2}$, epoxy with microcapsules exhibits a higher resistance to fatigue crack growth than neat epoxy, accompanied by a reduction of the Paris Law exponent n. The observed reduction of n with microcapsule concentration above the transition is independent of microcapsule diameter (Fig. 4). For concentrations greater than 10 wt% microcapsules, n has a steady state value of approximately 4.5. Similar fatigue behavior has been reported for rubber toughened epoxy [8].

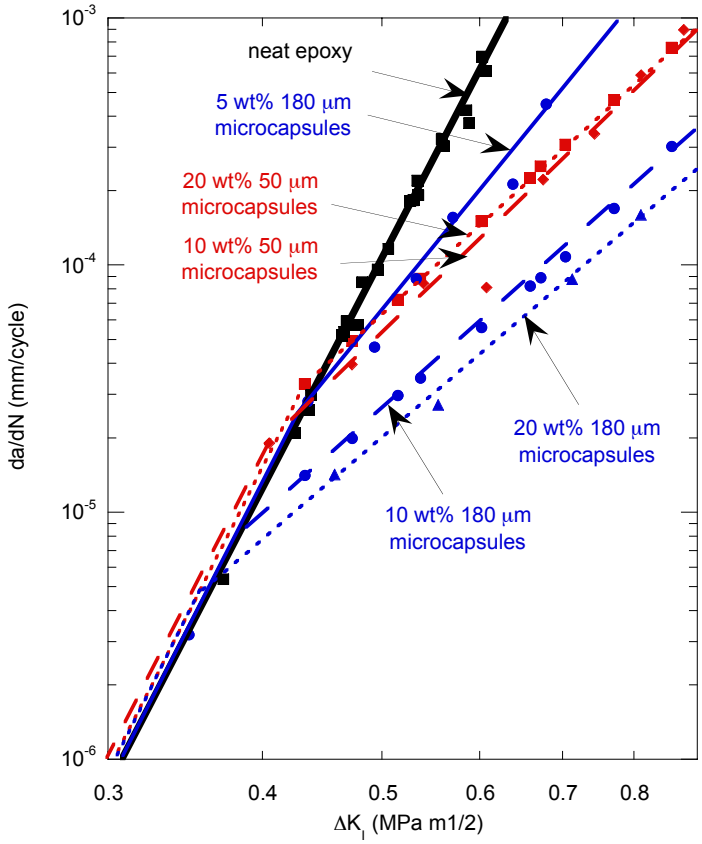

Figure 3. The effect of microcapsule concentration on the FCP behavior.

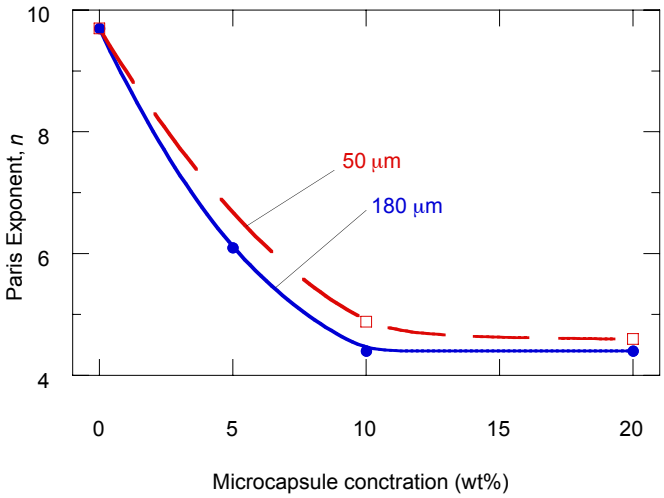

Figure 4. The effect of microcapsule concentration on Paris Law exponent, n.

4. REPAIR BY INFILTRATION

Preliminary experiments to determine the ability of the ROMP based healing reaction to heal a fatigue crack involved manual injection of catalyzed healing agent in the crack plane. Three TDCB fracture specimens were manufactured and precracked to identical crack length. One sample was manufactured with neat epoxy, two samples were manufactured with 10 wt% 180 μm diameter microcapsules. Fatigue cracks were grown in each sample under Mode-I stress intensity factor range, ΔK_I = 0.473 MPa $m^{1/2}$, frequency = 5 Hz, and load ratio R = 1. In two control samples –– one neat sample and one sample with microcapsules — the fatigue crack was grown until sample failure. Crack tip position is plotted versus number of cycles in Fig. 5. The neat epoxy sample failed after 3.07 x 10^5 cycles. The embedding of microcapsules extended the fatigue life of the specimen over three fold to 1.04 x 10^6 cycles. As a controlled healing experiment a crack was grown for 30 hours in the final sample containing microcapsules. After 30 hours, fatigue loading was interrupted and the sample held at constant K_{max}. DCPD was mixed with Grubbs catalyst at a ratio of 2 g per liter and injected into the crack plane. Fatigue loading was reestablished after a 10 hour cure period. The original crack tip position in epoxy and the interface boundary position between polyDCPD and epoxy, defined as the new crack tip, are both plotted versus number of cycles in Fig. 5. The positions of the original and new crack tips were both completely arrested for 6.0 x 10^6 cycles. Once an interfacial crack initiated between the polyDCPD and epoxy, it rapidly propagated to the position of the initial epoxy crack tip. Crack growth in the neat epoxy commenced at its prehealed growth rate. Sample failure occurred after 7.1 x 10^6 total applied cycles, over twenty-three times the fatigue life of the neat epoxy sample.

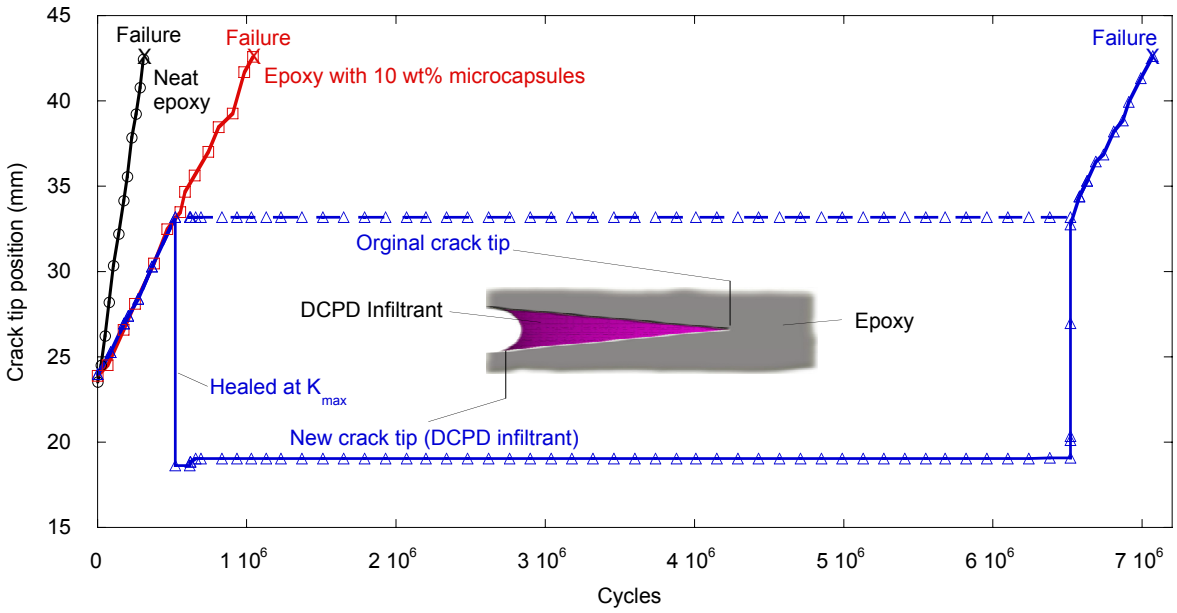

Figure 5. Crack tip position versus number of cycles for control samples and sample repaired by infiltration.

5. CONCLUSIONS

The inherent fatigue characteristics of a self-healing epoxy were investigated. In this preliminary study, the ability to self-heal was precluded and experiments focused on the effect of embedded microcapsules on fatigue performance. Under fatigue loading a transition point is observed in the fatigue crack growth behavior of epoxy with microcapsules. Above the threshold, fatigue crack growth in epoxy is retarded by embedded microcapsules. Infiltration of precatalyzed DCPD healing agent into the crack plane arrests fatigue crack growth and substantially increases fatigue life.

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