SELF-HEALING POLYMER COMPOSITES FOR EXTENDED FATIGUE LIFE

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Summary An extensive experimental investigation is carried out to assess the fatigue response of a self-healing polymer composite. Mode-I fatigue crack propagation is measured for a range of material parameters and loading conditions. Significant fatigue life extension and permanent fatigue crack arrest are achieved at moderate crack growth rates.

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. We utilize a strategy based on recent developments in self-healing technology [1-3] to autonomically repair fatigue cracks and extend the service-life of many polymeric components. The material under investigation is an epoxy matrix composite (EPON 828 cured with 12pph DETA), which utilizes embedded microcapsules [4] to store a healing agent and embedded Grubbs catalyst [5]. 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, reestablishing structural integrity across the crack plane. The fatigue-crack propagation behavior is investigated using the tapered double-cantilever beam (TDCB) specimen with constant range of applied stress intensity factor ΔK. All measurements are made with a loading frequency of 5 Hz and load ratio $R = K_{min}/K_{max}$ of 0.1. Samples are cast in a silicon mold, cured for 24 hrs at room temperature followed by 24 hrs at 30°C, and then precracked with a razor blade.

FATIGUE CRACK GROWTH PRECLUDING SELF-HEALING

Fatigue crack propagation in neat epoxy, epoxy with embedded microcapsules, and epoxy with embedded catalyst is accurately captured by the Paris power law. The effect of embedded microcapsule size and concentration on fatigue crack growth is shown in Fig. 1. The addition of microcapsules significantly reduces the crack growth rate above a transition ΔK_T. Above the transition, 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. Similar retardation behavior has been reported for epoxy with embedded rubber particles [6].

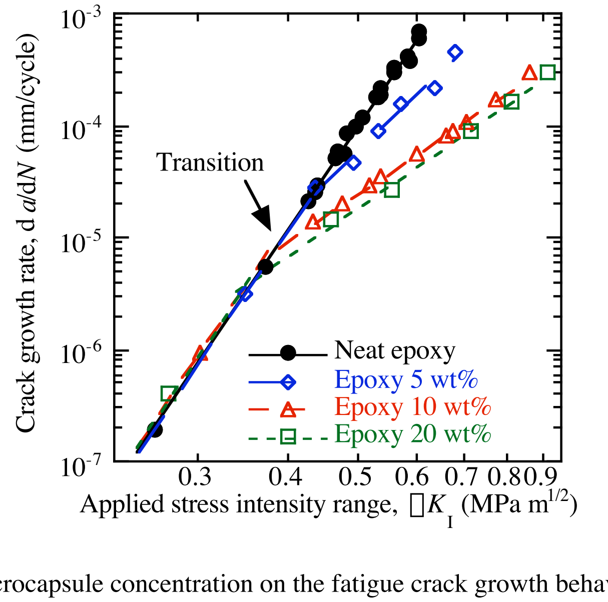


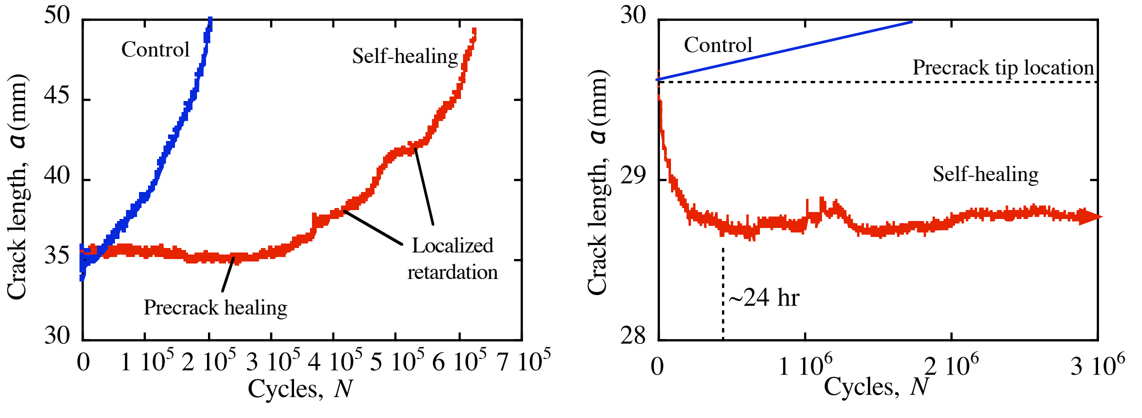
Figure 1. Influence of microcapsule concentration on the fatigue crack growth behavior for 180 μm diameter microcapsules.

IN SITU SELF-HEALING

Fatigue crack retardation and arrest from self-healing functionality result from crack-tip shielding mechanisms. Hydrodynamic pressure generated initially by uncured, liquid healing agent reduces both the loading and unloading of the crack tip. After polymerization, the fully cured healing agent forms a polymer wedge at the crack tip, which inhibits loading of the crack tip through adhesive mechanisms and unloading the crack tip through artificial-crack closure. Healing efficiency of the self-healing epoxy under cyclic loading is characterized with a fatigue-life-extension protocol [7],

$$\eta = \frac{N_{healed} - N_{control}}{N_{control}}, \qquad (1)$$

where N_{healed} is the total number of cycles to failure for the self-healing sample and $N_{control}$ number of cycles to failure for a similar sample without healing. Under high-cycle fatigue (moderate ΔK_I), Fig. 2a, and low-cycle fatigue (high ΔK_I) when a rest period was employed, *in situ* healing extended fatigue life though temporary crack arrest and retardation. *In situ* self-healing permanently arrested crack growth under low-cycle fatigue conditions at low ΔK_I, Fig. 2b, and at moderate ΔK_I when a rest period was employed.



(a) (b)

Figure 2. Crack length against fatigue cycles of *in situ* sample tested to failure in (a) the high-cycle fatigue regime, $\eta = 213\%$. $\Delta K_I = 0.338$ MPa m$^{1/2}$ and (b) the threshold regime, $\eta = \infty$. $\Delta K_I = 0.270$ MPa m$^{1/2}$.

CONCLUSIONS

A self-healing polymer was developed that improves the reliability of thermosetting polymers by initiating a healing process in response to damage. Fatigue-life extension was achieved by a combination of crack-tip shielding mechanisms induced by self-healing functionality. Viscous flow of the healing agent in the crack plane initially retarded crack growth. Polymermization of the healing agent, resulted in a long-term crack closure effect, which prevented unloading of the crack tip, reduced the crack length and retarded additional crack growth. A material able to autonomically respond to fatigue crack growth represents a milestone in the development of safer, longer-lasting materials.

References

[1] White, S. R., Sottos, N. R., Geubelle, P. H., Moore, J. S., Kessler, M. R., Sriram, S. R., Brown, E. N., Viswanathan, S.: Autonomic Healing of Polymer Composites. *Nature* **409**: 794–797, 2001.
[2] Brown, E. N., Sottos, N. R., White, S. R.: Fracture Testing of a Self-Healing Polymer Composite. *Experimental Mechanics* **42**: 372–379, 2002.
[3] Kessler, M. R., Sottos, N. R., White, S. R.: Self-Healing Structural Composite Materials. *Composites A* **34**: 743–753, 2003.
[4] Brown, E. N., Kessler, M. R., Sottos, N. R., White, S. R.: In Situ Poly(urea-formaldehyde) Microencapsulation of Dicyclopentadiene. *J. Microencapsulation* **20**: 719–730, 2003.
[5] Rule, J. D., Moore, J. S.: ROMP Reactivity of *endo*- and *exo*-Dicyclopentadiene. *Macromol*. **35**: 7878–7882, 2002.
[6] Azimi, H. R., Pearson, R. A., Hertzberg, R. W.: Fatigue of Rubber-Modified Epoxies: Effect of Particle Size and Volume Fraction. *J. Mater. Sci*. **31**: 3777–3789, 1996.
[7] Brown, E. N.: Fracture and Fatigue of a Self-Healing Polymer Composite Material. *PhD Thesis*, UIUC Dept. Theoretical & Applied Mech., 2003.