FATIGUE OF SELF-HEALING POLYMERS: MULTISCALE ANALYSIS AND EXPERIMENTS

S. R. White[1], S. Maiti[1], A.S. Jones[2], E.N. Brown[2,3], N.R. Sottos[2], and P.H. Geubelle[1]
[1]Department of Aerospace Engineering, University of Illinois, Urbana, IL 61801 USA
[2]Department of Theoretical and Applied Mechanics, University of Illinois, Urbana, IL 61801 USA
[3]Present Address: Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM, 87545

ABSTRACT

Self-healing polymers were recently developed at the University of Illinois by incorporating a microencapsulated healing agent and chemical catalyst in a polymer matrix. Whenever damage occurs, the repair process is triggered and after sufficient healing time the inherent strength and toughness of the material is recovered. Self-healing polymers are designed to heal the microcracks that occur naturally during fatigue, thereby preventing large-scale cracks from forming. In this paper we report on the fatigue response of self-healing epoxy and show that under certain conditions fatigue cracks can be permanently arrested when the chemical kinetics of healing are much faster than the mechanical kinetics of crack growth. To understand the complex role that various kinetic processes have on the ultimate fatigue behavior of self-healing polymers we have developed a multiscale analytical model of fatigue crack growth from molecular dynamic (MD) simulations of the curing reaction of the healing agent to a cohesive volumetric finite element (CVFE) description of the self-healing polymer system. We show that good agreement with experiments can be obtained by properly calibrating the cohesive law that is used in the CVFE simulations. Our cohesive law describes the natural competition between progressive degradation of the cohesive properties associated with the fatigue process and their restoration through self-healing. Ultimately, the cohesive law and its kinetic description will be directly linked to MD level simulations of the healing process.

1 INTRODUCTION

The natural process of fatigue in brittle polymers and composite leads to microcracking and other forms of micro-damage [1-3]. Eventually these microcracks coalesce to form large-scale cracks that propagate and lead to ultimate failure. The traditional approach to these problems has been to increase the inherent toughness of brittle polymers through addition of reinforcement phases or elastomers, or to repair the article once the cracks are large and of a critical size.

A new self-healing materials system was recently developed [4-6] that offers an alternative to these traditional approaches. Whenever damage occurs in a self-healing polymer, the repair process is triggered automatically and after sufficient healing time, the inherent strength and toughness of the material is recovered. Self-healing polymers are designed to heal microcracks that occur naturally during fatigue, thereby preventing large-scale cracks from forming. As a result, the fatigue life and the useful mechanical function of these materials are significantly extended.

2 MICROCAPSULE SELF-HEALING CONCEPT

The self-healing concept is shown in Fig. 1. A microencapsulated healing agent is embedded along with a catalyst into a polymer matrix. When damage occurs in the polymer a crack propagates through the matrix rupturing the microcapsules in the crack path. The ruptured microcapsules release the healing agent which is then drawn into the crack through capillary action. Once the healing agent within the crack plane comes into contact with the embedded catalyst, a chemical reaction is triggered and polymerization of the healing agent occurs. Afterwards, the crack faces are bonded and the strong singularity at the crack tip is relieved.

During fatigue the interplay of mechanical and chemical

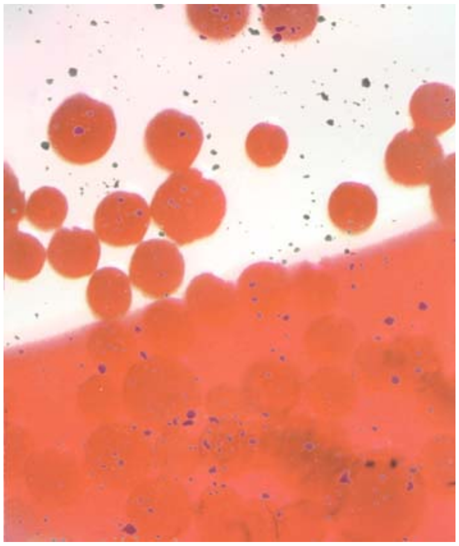

Fig. 1. Self-healing epoxy polymer.
A microencapsulated healing agent (labeled with red dye) is released into the fracture plane behind the propagating crack front that dissects the image from left to right. The capsules in front of the crack (top of image) remain unbroken. (E. Brown, Univ. of Illinois, 2001).

kinetics governs the efficiency of self-healing and whether any retardation of crack growth rate or extension of life is achieved. For example, if mechanical kinetics dominates then the crack growth rate is relatively fast and any chemistry that is triggered along the crack plane is not allowed to reach completion. The growing crack essentially experiences no influence of self-healing functionality beyond the beneficial effects of microcapsule-induced toughening alone [ref]. On the other hand, if chemical kinetics dominates then the crack growth rate is relatively slow and the chemistry that is triggered by the growing crack reaches sufficient completion before the crack grows beyond the local influence zone. In this case the functionality of self-healing is achieved and crack growth rates can be reduced and perhaps fully arrested.

3 MACROSCALE FATIGUE EXPERIMENTS ON SELF-HEALING POLYMERS

Fatigue experiments present a considerable challenge in managing the multitude of interaction variables such as stress amplitude, frequency, temperature, etc. At present, we have completed preliminary investigations of fatigue crack propagation in self-healing epoxy with embedded microcapsules. In these experiments, the crack growth rate, *da/dN*, is measured as a function of the applied Mode-I stress intensity factor, ΔK_I, and fit to the well known Paris-Power Law,

$$\frac{da}{dN} = C_0 \Delta K_I{}^n, \tag{3}$$

where C_0 and n are material constants, a denotes crack length, and N is the number of loading cycles. The dramatic effect of embedded microcapsules on fatigue crack growth rate, with the ability to self-heal precluded, is plotted in Fig. 2 and compared with a neat epoxy control sample (no microcapsules). A transition is observed in the crack propagation behavior, below which microcapsules do not affect fatigue crack propagation. Above this threshold, epoxy with microcapsules exhibits a significantly higher resistance to crack growth compared to neat epoxy. The Paris exponent reduces from n=10 for neat epoxy to n=4 for concentrations greater than 10 wt% microcapsules [7].

Overall, the data in Fig. 2 show that in addition to increasing the quasi-static fracture toughness [5], embedded microcapsules also significantly improve the dynamic fatigue response of epoxy. The addition of 10 wt% microcapsules alone can increase the fatigue life of the polymer over three-fold. In more recent fatigue tests on samples with in-situ healing capability, fatigue loading of a sample with 20 wt% microcapsules and catalyst demonstrated a significant enhancement of fatigue life. As shown in Fig. 3, fatigue crack growth was arrested for $4\text{x}10^5$ cycles, extending the fatigue life over 3 times that of the control sample [8,9].

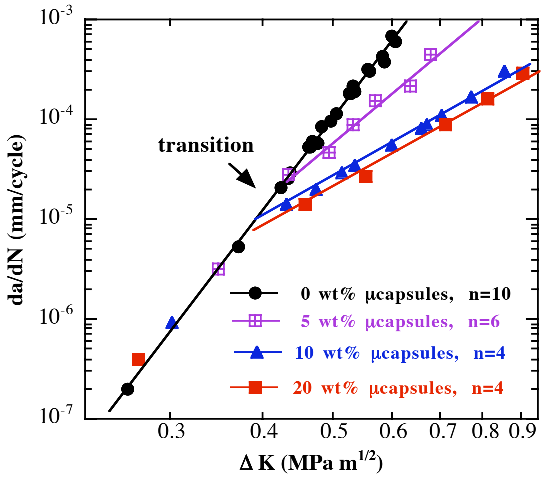

Fig. 2. Effect of microcapsule concentration on the fatigue crack propagation rate.

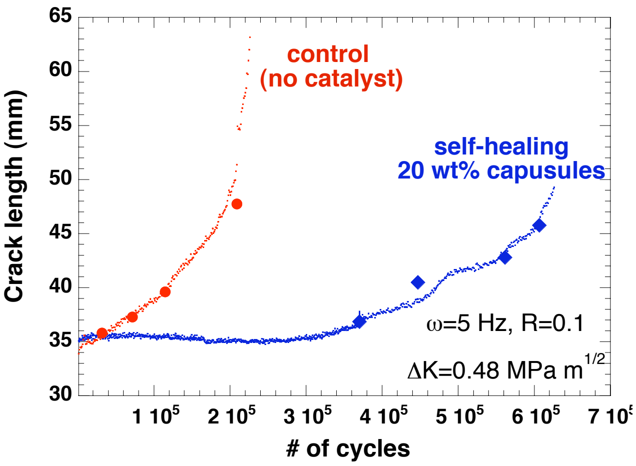

Fig. 3. Crack tip position versus number of cycles to failure for self-healing sample compared to control.

4 MODELING SELF-HEALING DURING FATIGUE

Understanding the competition between mechanical and chemical kinetics is crucial to the design of self-healing systems for fatigue applications. However, the physical phenomena governing this problem occur over many length scales from the molecular (polymerization rates and interfacial bonding) to the macroscopic (crack extension and failure). Our approach has been to develop a multiscale simulation tool that couples molecular dynamics and course grained models to finite element descriptions of a self-healing polymer (Fig. 4). This tool is supported by focused experiments at various length scales to support and validate the models under development. Molecular dynamic and coarse-grained models have been the focus of research efforts of our colleague at the University of Michigan (J. Kieffer). In this paper we focus our attention on the macroscopic description of the problem and supporting experiments.

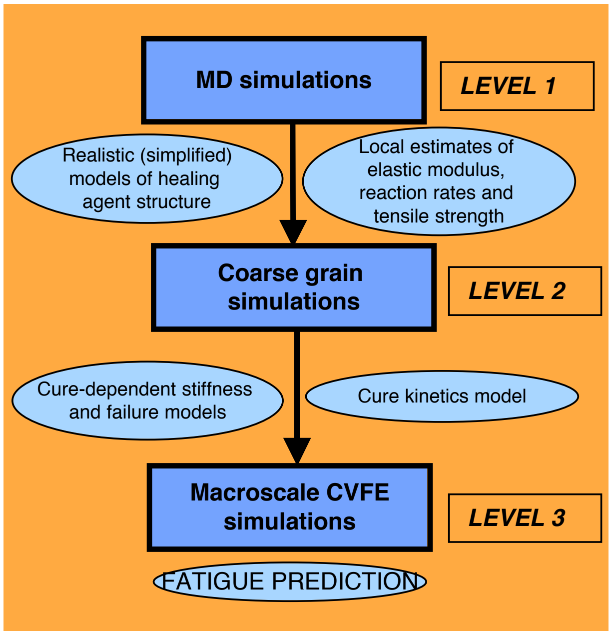

Fig. 4. Multiscale modeling of fatigue of self-healing polymer composites.

A two-dimensional explicit quasi-static cohesive volumetric finite element (CVFE) code has been developed for the study of fatigue crack propagation in self-healing materials. The CVFE formulation relies on conventional constant strain or linear strain triangular elements and on linear or quadratic cohesive elements placed on the initial crack plane. In this initial implementation, the volumetric elements are chosen as linearly elastic and the failure process is assumed to be in mode I (i.e., of tensile type). The cohesive failure model adopted in this study is an extension of the phenomenological model proposed by Nguyen [10] for the simulation of fatigue crack growth in metals. The original model has been modified to account for the larger value of the Paris' Law exponent (typically 10, versus 3 or 4 for many metals). By introducing a simple evolution law for the cohesive stiffness under loading conditions, we achieve a progressive degradation of the cohesive strength as illustrated in Fig. 5 and the associated Paris's law curve shows very good agreement with the experimental measurements performed on neat and microcapsule-filled epoxy.

The introduction of the healing agent in the material yields a natural competition between the progressive degradation of the cohesive properties associated with the fatigue response and their "restoration" through the cure kinetics of the healing agent. To account for this effect, we have introduced an additional degree of freedom at all integration points along the cohesive failure zone in our CVFE code. This new degree of freedom is the time dependent degree of cure α, whose evolution is described by a first-order cure kinetic relation

$$\frac{d\alpha}{dt} = f(\alpha, T), \tag{2}$$

where the cure- and temperature-dependent function $f(\alpha, T)$ has been obtained experimentally for the DCPD/Grubbs' catalyst system used in our self-healing composite [11]. The two parameters defining the cohesive failure law (the failure strength and the fracture toughness) have then been modified to account for the evolution of the degree of cure α. This influence of the cure kinetics on the cohesive properties is one of the key information to be provided by molecular dynamics and coarse grain simulations being performed at the University of Michigan. In the meantime, we use a simple explicit dependence of these fracture parameters on the degree of cure, yielding the fracture response presented in Fig. 6. Although preliminary, these results clearly illustrate the

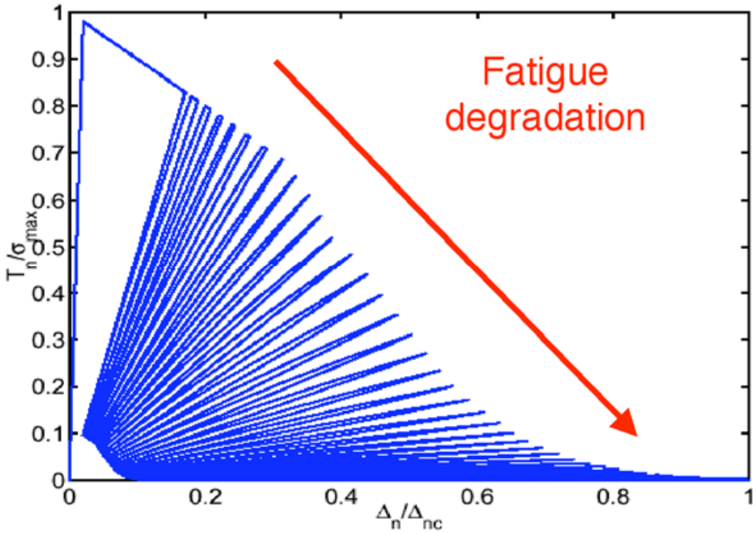

Fig. 5. Degradation of the cohesive failure properties under cyclic loading: evolution of the relation between the cohesive traction (T_n) and the crack opening displacement (Δ_n) normalized by their respective critical values.

retardation effect of the healing process on the fatigue crack propagation and the potential for self-healing polymers to provide extended life in fatigue loading regimes.

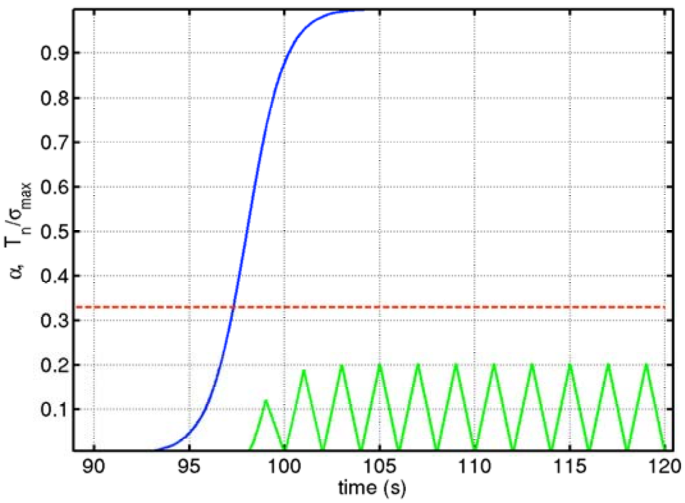

Fig. 6. Simulation of self-healing during fatigue. The degree of cure (blue) rises exponentially and coincides with recovery of load carrying capability as demonstrated by the increase in normal traction (green) across the crack face. The dashed line (red) denotes gelation of the healing agent and onset of structural recovery.

5 CONCLUSIONS

Self-healing polymers and composites can potentially extend the useful service life of components subject to mechanical fatigue. We have developed a multiscale simulation tool to study the propagation of fatigue cracks in self-healing polymers in order to more fully understand the role that both chemical and mechanical kinetics play in life extension. Preliminary experimental results show that incorporation of microcapsules in epoxy leads to retardation of crack growth rates during fatigue. We have also demonstrated that self-healing functionality can extend the fatigue life of epoxy when the kinetics of healing are sufficiently rapid (in comparison to the mechanical kinetics of crack growth). A macroscopic description of fatigue propagation based on cohesive volumetric finite elements has shown good agreement with preliminary data. In this model the degradation of cohesive properties with cyclic deformation is balanced by the recovery of properties during healing.

6 REFERENCES

1. Gamstedt, E. K. and Talrega, R. (1999). *J. Mat. Sci*. **34**, 2535.
2. Pecht, M. G., Nguyen, L. T., and Hackim, E. B. (1995). *Plastic-Encapsulated Microelectronics*. John Wiley & Sons, New York.
3. Lee, L. H. (1991). *Adhesive Bonding*. Plenum Press, New York.
4. White, S.R., Sottos, N.R., Geubelle, P.H., Moore, J.S., Kessler, M.R., Sriram, S.R., Brown, E.N., and Viswanathan, S. (2001). *Nature*. **409**, 794.
5. Brown, E.N., Sottos, N.R., White, S.R. (2002) *Experimental Mechanics*. **42**, 372.
6. Kessler, M.R., Sottos, N.R., White, S.R. (2003). *Composites Part A*. **34**, 743.
7. Brown, E.N., Moore, J.S., White, S.R., and Sottos, N.R. (2003a). Fracture and fatigue behavior of a self-healing polymer composite, ed. by G. Schmid, U. Simon, S.J. Stranick, S.M Arrivo, and S. Hong, *Bioinspired Nanoscale Hybrid Systems*, MRS Symposia Proceedings (C11.22), Materials Research Society [Boston, Dec. 2-6 2002], **735**.
8. Brown, E. N., Sottos, N. R. and White, S. R. (2003b) Fatigue crack propagation in a self-healing polymer composite. *Proceedings of SEM Annual Conference on Experimental and Applied Mechanics*, Charlotte NC, Society for Experimental Mechanics, CD-ROM, June 2-4 (2003).
9. Brown, E. N., Sottos, N. R. and White, S. R. (2003c) Fatigue crack propagation in a self-healing polymer composite. Proceedings of the 14th International Conference on Composite Materials (ICCM), San Diego, CA, Society of Manufacturing Engineering, CD-ROM, July 14-18.
10. Nguyen, O., Repetto, E.A., Ortiz, M. and Radovitzky, R.A. (2001) *International Journal of Fracture*, **110**, 351.
11. Kessler, M.R. and S.R. White. (2002). *J. Pol. Sci. A: Pol. Chem.* **40,** 2373.