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14. ABSTRACT
A set of multi-scale materials systems design tools focused on issues relevant to self-healing structural composites have been developed by a research team from the University of Illinois and the University of Michigan. Our vision was to create a computational framework for materials systems design spanning from atomistic to macroscopic (structural) length scales, supported and validated by a set of experiments conducted at various scales. Although special emphasis in the present project has been placed on the modeling of the fatigue response of a self-healing composite, the approach adopted in this project yielded tools that have broad applicability for generic fracture and fatigue problems in modern engineering materials. This paper summarizes our accomplishments of the past three years primarily on the macroscale numerical and experimental aspects of the program. On the numerical side, we have focused on the development, implementation and validation of a cohesive failure model able to capture at the structural level the fatigue retardation effect of the healing agent on the cyclic response of the self-healing composite.

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ABSTRACT

A set of multiscale materials systems design tools focused on issues relevant to self-healing structural composites have been developed by a research team from the University of Illinois and the University of Michigan. Our vision was to create a computational framework for materials systems design spanning from atomistic to macroscopic (structural) length scales, supported and validated by a set of experiments conducted at various scales. Although special emphasis in the present project has been placed on the modeling of the fatigue response of a self-healing composite, the approach adopted in this project yielded tools that have broad applicability for generic fracture and fatigue problems in modern engineering materials. This paper summarizes our accomplishments of the past three years primarily on the macroscale numerical and experimental aspects of the program. On the numerical side, we have focused on the development, implementation and validation of a cohesive failure model able to capture at the structural level the fatigue retardation effect of the healing agent on the cyclic response of the self-healing composite. The model captures both the adhesive (or "bridging") effect of the healing agent along the crack faces during the loading phases and the crack closure (or "wedging") effect associated with the presence of an additional material between the contacting fracture surfaces during the unloading phase. A novel multiscale cohesive model based on the mathematical theory of homogenization has been proposed to relate the macroscopic cohesive failure relations between cohesive tractions and displacement jumps to continuum or microscale models of damage. On the experimental side, a fatigue-life-extension protocol was established for characterizing healing efficiency of the self-healing epoxy under cyclic loading. These experiments provided a necessary database for validation of the macroscale CVFE fatigue simulations and demonstrated the ability to achieve self-healing under cyclic loading conditions.
1. Objectives

The objective of this research project has been to develop a set of multiscale materials systems design tools focused on issues relevant to self-healing structural composites. A research team composed of faculty from the University of Illinois (UIUC) and the University of Michigan (UM) was assembled with broad expertise in all aspects of the proposal, from microscale simulations to macroscopic experiments. The research work has been comprehensive and highly integrated, building upon knowledge at each time and length scale considered.

Our vision has been to create a computational framework for materials systems design spanning from atomistic to macroscopic (structural) length scales and properly validated with relevant experimental databases. Our approach yields tools that have broad applicability for generic fracture and fatigue problems in modern engineering materials. The research over the three-year duration of the MEANS project has concentrated on structural polymer composites with self-healing capability. Such materials are multifunctional possessing not only the ability to perform a structural function, but can also repair internal damage in an autonomic fashion. Specifically we have developed:

*Multiscale physics-based design and modeling* – coupled analytical tools based on the underlying physical and chemical principles involved for use in modeling the self-healing process from the molecular (monomer) level to the macroscopic (structural) level,

*Experimental database for self-healing materials* – perform carefully controlled experiments of model systems and self-healing composites to develop appropriate databases for use in validation of models at a variety of length and time scales,

*Generic computational design tools for materials engineering* – the analysis tools which have been developed have broader application than self-healing including enhancing fatigue life and fracture resistance in brittle composites, reaction kinetics for polymers and process modeling, and damage modeling in structural materials.
2. Development of a Multi-Scale CVFE Scheme for Macro-Scale Fatigue Simulations

One of the key objectives of this project has been to develop a flexible computational tool able to model at the macro-scale the fatigue failure of polymeric components, with special emphasis on self-healing polymeric media. The approach adopted in this project is based on a special form of the cohesive modeling of fracture, in which the failure is assumed to take place in a very narrow zone ahead of the propagating crack front. The main attractiveness of this approach is the fact that it can readily be combined with conventional finite element schemes, allowing for great flexibility in loading conditions, geometrical complexity and material constitutive response. The combination of conventional ("volumetric") finite elements with interfacial ("cohesive") elements is often referred to as cohesive-volumetric finite element (CVFE) schemes and has shown great success in capturing a wide range of quasi-static and dynamic fracture events, especially in brittle systems.

The first step in the development of cohesive models for the fatigue response of self-healing composites has been the derivation of a cohesive model able to capture the fatigue response of conventional (i.e., non self-healing) polymeric materials, which are usually characterized by a very high fatigue sensitivity. Indeed, for this materials, the exponent \( n \) appearing in the classical Paris' Law

\[
\frac{da}{dN} = C (\Delta K)^n,
\]

takes a very high value (typically 8 to 10) versus 3 to 4 for metals. In (1), \( da/dN \) denotes the crack advance per cycle, and \( \Delta K \) the range in stress intensity factor \( K \) reached during the cycling loading of the structure. An evolution law for the cohesive stiffness during the reloading phase of the cyclic loading has been introduced in the cohesive failure law to generate a natural degradation of the cohesive strength (Maiti and Geubelle, 2005a). Figure 1 shows a comparison between the numerical and experimental measurements of the fatigue response of epoxy (Maiti and Geubelle, 2005a).

Figure 1. Experimental measurements (symbols) and numerical prediction (solid curve) of the fatigue response of epoxy (Maiti and Geubelle, 2005a).

Figure 2. Modification of the fatigue cohesive failure model to account for the presence of the healing agent between the crack faces (Maiti and Geubelle, 2005b).
experimental Paris' law curves of a room-temperature-cured epoxy. The measurements were obtained as part of the experimental thrust described in Section 3. The cohesive failure model for fatigue has then been implemented in a generic semi-implicit CVFE code able to simulate a wide variety of fatigue crack propagation problems.

The second step of this part of the research effort has focused on the modification of the cohesive failure model to account for the effect of the healing agent on the fatigue crack propagation in a self-healing composite. Two key phenomena contribute to the crack retardation observed in the self-healing composite: the first one is the adhesive effect of the curing healing agent on the crack faces during the reloading phase of the load cycle. As the healing agent comes in contact with the catalyst disperses in the polymeric matrix, it polymerizes and progressively creates an adhesive bond between the two crack faces. The second key phenomenon is the crack closure effect associated with the presence of the polymerizing healing agent between the crack faces during the unloading phase of the loading cycle.

Based experimental observations, the crack closure effect was shown to be dominant and has therefore been the focus of our initial cohesive modeling efforts, summarized in Figure 2. After the complete failure of a material point, a wedge of thickness $\Delta_n$ is inserted behind the crack front and affects the propagation of the fatigue crack through premature contact between the crack faces. This simple model allows the capture of one of the key experimental observations: at high load level, little to no healing is observed, while at lower loading levels, substantial life extension is obtained for the self-healing composite (Fig. 3).

However, in its initial implementation, the self-healing cohesive failure model did not incorporate any dependence of the cohesive response of the healing agent on its cure kinetics. In other words, the polymerization time scale of the healing agent was assumed to be much smaller than the failure time scale associated with the propagation of the fatigue crack. This simplification did not allow for the capture of another key experimental observation, i.e., the competition between the healing kinetics and fatigue failure length scales. Under high load level, the crack was observed to propagate too fast for any healing to take place. On the other end of the spectrum, under very low cyclic load levels, the polymerization of the healing agent behind the slowly advancing crack front had ample time to take place and complete crack arrest was detected. At intermediate loading levels, the two time scales are of similar order and partial healing is observed.
To account for this competition between time scales and capture the critical importance of rest periods, we have modified the cohesive modeling by incorporating an additional degree of freedom, the degree of cure $\alpha$, along the fracture plane. In its initial implementation, an explicit dependence of the cohesive parameters (and, in particular, the stiffness of the curing healing agent) was assumed. However, we have recently obtained this dependence through lower-level MD and coarse-grained discrete simulations performed at the U. of Michigan by John Kieffer and his student (Maiti et al., 2005). An illustrative result taken from this more recent work can be found in Figure 4, which shows the effect of the duration of the rest period on the fatigue crack propagation in a self-healing Double Cantilever Beam (DCB) specimen.

Finally, in addition to the coupling with the MD and coarse-grained discrete models obtained at U. Michigan, we have also developed during the last year of the project a multiscale homogenization framework allowing for the extraction of the macroscopic cohesive models from microscale models of the failure processes. This represents a major advance in the development of cohesive failure models, which are usually chosen in a purely phenomenological fashion for mathematical simplicity (bilinear, exponential, trapezoidal, etc.). The multiscale cohesive framework we have developed allows the analyst to extract in a physically and mathematically consistent fashion the macroscopic cohesive traction-separation laws from lower-scale continuum or discrete models of the failure processes taking place in a representative volume element (RVE). Two approaches have been considered for the transfer of microscopic quantities to the macroscale: an energetic approach

![Figure 4. Effect of the duration of the rest period on the fatigue crack propagation in a DCB specimen made of self-healing epoxy.](image)

![Figure 5. Multiscale cohesive model, showing the extraction of the macroscopic cohesive failure law (top figure) based on the microscale analysis of damage evolution in an adhesive RVE composed of 14 stiff particles embedded in a brittle matrix.](image)
based on Hill’s lemma equating the virtual work done by the microscopic stress fields in the RVE to that done by the macroscopic cohesive tractions, and the other relying on an extension of the mathematical theory of homogenization. A preliminary example of such a multiscale study is presented in Figure 5, which shows the link between the microscale distribution of damage present in an adhesive RVE subjected to mixed-mode loading and the resulting macroscopic traction-separation relation for the normal (red curve) and tangential (green curve) cohesive tractions. Although still preliminary, these results suggest great potentials for this method in improving the physical justification behind cohesive models, not only under fatigue loading, but also for quasi-static and dynamic fracture cases.

3. Macro-scale Validation: Self-Healing Fatigue Experiments

Characterization of self-healing performance under fatigue loading is more complex than monotonic fracture due to dependence on the applied stress intensity range $\Delta K_I = K_{max} - K_{min}$, the loading frequency $f$, the ratio of applied stress intensity $R=K_{max}/K_{min}$, as well as the healing kinetics and any rest periods. Our experimental program was divided into several thrusts to systematically investigate many of these variables and provide validation during the development of the CVFE macroscale fatigue code.

In the first thrust, completed in year 1, we fully characterized the fatigue response of the neat epoxy and the influence of microcapsules on fatigue crack propagation with the effects of self-healing precluded. The addition of microcapsules significantly decreased the fatigue crack growth rate and increased the fatigue life nearly three fold above a transition value of the stress intensity factor (Brown et al., 2005a). The Paris exponent decreased from $n=10$ for neat epoxy to $n=4$ for concentrations greater than 10 wt% microcapsules. These experiments

![Fig. 6. Fatigue life extension in self-healing polymers. a. Case of high stress intensity ($\Delta K=0.72$ MPa$\sqrt{m}$) where mechanical kinetics dominate and rapid crack growth occurs. By incorporating periodic rest periods (training) the crack is retarded and fatigue life is extended. b. Case of intermediate applied stress intensity ($\Delta K=0.61$ MPa$\sqrt{m}$) where life extension is greater for faster healing kinetics, in great contrast to a neat epoxy sample. c. Case of relatively low stress intensity ($\Delta K=0.50$ MPa$\sqrt{m}$) where chemical (healing) kinetics dominate and slow crack growth occurs. In the self-healing specimen, crack growth is arrested.](image)
provided a necessary database for validation of the initial CVFE fatigue simulations, as shown in Fig. 1 for neat epoxy.

The second thrust, completed in year 2, focused on \textit{in situ} self-healing of fatigue damage. A fatigue-life-extension protocol was established for characterizing healing efficiency of the self-healing epoxy under cyclic loading (Brown \textit{et al.}, 2005b, 2005c). Three different levels of applied range of stress intensity \(\Delta K_i\) were prescribed: one low-cycle fatigue case and two high-cycle fatigue cases. Low-cycle fatigue refers to the fatigue regime where \(\Delta K_i\) approaches \(K_{IC}\) and rapid crack growth causes sample failure after very few cycles (< 10,000 cycles). High-cycle fatigue refers to the fatigue regime of low \(\Delta K_i\), relatively slow crack growth rate and longer fatigue life (> 10,000 cycles).

Under low-cycle-fatigue conditions, crack propagation in the self-healing epoxy proceeds at a constant rate comparable to a control sample with no self-healing. To achieve successful self-healing, the healing agent released into the crack plane must have enough time to polymerize. If the crack growth rate is too fast, little or no healing is achieved. To facilitate healing under these conditions, rest periods were incorporated into the loading cycle. Fatigue loading was stopped after a small amount of crack growth (5000 cycles) and allowed to heal under load at \(K_{max}\) for 10 hr. Figure 6a shows the regression and retardation of a fatigue crack achieved by using successive rest periods to allow sufficient time for self-healing. The polymerized healing agent formed a wedge at the crack tip during healing (see cover image), leading to artificial crack closure and fatigue-life extension of over 350%.

Under high-cycle-fatigue conditions, the applied range of stress intensity \(\Delta K_i\) is reduced, decreasing the inherent crack growth rate and increasing the number of cycles to sample failure.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Images}
\caption{ESEM images of recrystallized Grubbs' catalyst polymorphs created by: (a) vacuum evaporation, (b) precipitation in acetone, (c) freeze drying. Corresponding healing performance: (d) dissolution rates of the catalysts and (e) typical healed response during Mode I fracture.}
\end{figure}
In this regime, the healing agent has sufficient time to polymerize and can effectively retard crack growth or completely arrest the crack (Fig. 6c). This result is in excellent agreement with the predictions in Fig. 3.

The fatigue data described above reveal the extraordinary result that periodic exposure to stress can lead to significant life extension in a self-healing polymer. In the third and final thrust, completed in year 3, we explored the interplay between mechanical kinetics of crack propagation and chemical kinetics in achieving life extension under different fatigue loading conditions. We demonstrated that the healing chemistry can be tuned by changing the morphology of the Grubbs catalyst (Jones et al., 2005). Several polymorphs of the catalyst were created through vacuum evaporation, precipitation in acetone and freeze drying, as shown in Fig. 7. These recrystallized forms of the catalyst had significantly higher dissolution rates than the as received catalyst from Sigma-Aldrich (Fig. 7d). Increased dissolution rates led to faster healing kinetics and improved healing performance in quasi-static fracture tests (Fig. 7e). Under fatigue loading at intermediate $\Delta K_I$ levels, self-healing systems that were chemically tuned to have faster healing kinetics provided greater life extension (Fig. 6b) than those with slower kinetics. Overall, if the healing kinetics are sufficiently rapid, fatigue cracks are effectively arrested as the material is cycled.
4. Personnel Supported

Faculty: Scott R. White, Nancy R. Sottos, Philippe H. Geubelle
Post-docs: Spandan Maiti (currently faculty member at Michigan Tech) and Alan Jones (currently faculty member at IUPUI)
Student: Eric Brown (until 9/03 – currently at Los Alamos National Lab – support was supplemented by additional industry funds)

5. References


6. Publications

Journal Papers


Conference Proceedings


Technical Conference, ed. by C.T. Sun and H. Kim, CD-ROM, 175, Oct. 21-23. ***Received 2002 ASC Best Paper Award ***


7. Interactions/Transitions

7.1 Conference Presentations and Seminars


Brown, E.N. Fatigue Behavior of a Self-Healing Polymer Composite, Beckman Institute Nanohour, Beckman Institute, Nov. 20, 2002, Urbana, IL.


7.2 Air Force Lab Collaborations

We wrote a MEANS2 proposal in collaboration with Dr. Ajit Roy from AFRL-WPAFB. The proposal focused on the multiscale design of multifunctional adhesives, and used some of the developments involved in the MEANS1 project.

We have recently completed a Phase I STTR with AFRL/VSSV on the use of self-healing technology for cryogenic fuel tanks. These tanks are prone to leakage caused by microcracking as they cycle between cryogenic conditions and elevated temperatures. We are teamed with a small company, CU Aerospace, on a phase-II STTR proposal with AFRL to produce test articles suitable for cryo-testing at test facilities at Kirtland, AFB. We are currently awaiting review of the proposal. The macroscale modeling will be used in that effort to design optimal self-healing materials for cryotank applications.

7.3 Transitions

None to report.

8. Patent Disclosures

None to report.

9. Honors/Awards

Prof. Scott White was named the Donald Biggar Willett Professor of Engineering (2005-).

Prof. Scott White was named a University Scholar for the UIUC (2005-08).

Prof. Nancy Sottos was named the Donald Biggar Willett Professor of Engineering (2005-).

Prof. Nancy Sottos received the Hetenyi Award from the Society for Experimental Mechanics (2004).
Postdoctoral research associate Alan Jones received a travel grant from the US National Committee on Theoretical and Applied Mechanics (2004).

Graduate Student Eric Brown received a Director’s Fellowship to pursue postdoctoral studies at Los Alamos National Lab (2003).

Prof. Nancy Sottos was named as Editor, *Experimental Mechanics* (2003—).

Prof. Scott White was named a Willett Faculty Scholar (2002-05) for the College of Engineering, University of Illinois.

Prof. Nancy Sottos was named a University Scholar (2002-05) for the University of Illinois.

Prof. Nancy Sottos was named to the Editorial Board of Composite Science and Technology (2002—).

Prof. Philippe Geubelle was named a Bliss Faculty Scholar (2005-2008) for the College of Engineering, University of Illinois