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14. ABSTRACT
Our aim in the previous studies was to design polymeric composites and blends that would heal defects that were present within the material. We considered three distinct approaches, which involved:
1. Harnessing nanoparticles to heal cracks in layered composites
2. Using microcapules to deliver nanoparticles to damaged coatings
3. Exploiting photo-chemical reactions to create defect-free hierarchical structures
As we note below, our findings generated considerable interest in the scientific community. We are also initiating new studies

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Report Title

Using Theory and Simulation to Design Self-Healing Surfaces - Final Report

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As we note below, our findings generated considerable interest in the scientific community. We are also initiating new studies on controlling crack propagation in brittle materials. Herein, we provide a brief description of our research in each of these areas. (Papers acknowledging this grant are listed in the Bibliography section and start with the letter P).

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Number of Papers published in peer-reviewed journals: 11.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations:

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Number of Manuscripts:

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

FINAL REPORT

Title: Using Theory and Simulation to Design Self-Healing Surfaces
Funding: $300, 000 awarded for May 1, 2004 – May 1, 2007.

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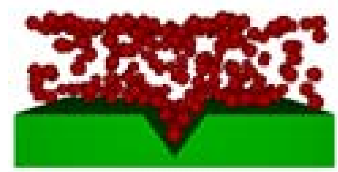

Fig. I. Nanoparticles in polymer film (not shown) driven into notch in surface (see P2)

Using a variety of computer simulations, including Monte Carlo simulations (P1), self-consistent field theory (P1) and molecular dynamics (P2-P3), we investigated the behavior of nanoparticle-filled polymer films near a substrate that contains a nanoscopic notch or crack (see Fig. I). We found that for sufficiently large nanoparticles that are compatible with the host matrix, entropic forces expel the nanoparticles from the polymer film and into the cracks (P1-P3). (In particular, the radius of the nanoparticles should be comparable to the radius of gyration for the chains.) The system behaves in an autonomous manner; no intervention is necessary to localize the particles at the damaged or defective sites. By using the results of our morphological studies as the input to the Lattice Spring Model (LSM), we determined the mechanical properties of the undamaged, damaged and healed states and thereby showed that mechanical properties of the healed system are substantially restored to those of the undamaged material (P1-P3).

In collaboration with Profs. T. Russell and T. Emrick at U. Mass., Amherst, we experimentally verified these theoretical predictions by showing that sufficiently large nanoparticles dispersed in a compatible polymer matrix migrated to a crack generated at the interface between the polymer and a silicon oxide layer (P4). The findings also confirmed the importance of entropic interactions in segregating the nanoparticles to the crack. The results from these studies point to a simple, novel means of fabricating self-healing systems that promise to improve the durability of multilayered composites. The paper describing our results appeared in *Nature Materials* (P4) and the findings sparked a significant amount of interest. In particular, *United Press International* (UPI) released a story on this research; this article can be found at: http://www.physorg.com/news11000.html).

During the period of this grant, we interacted with researchers at both the Natick (Dr. Steven Fosse) and Aberdeen (Dr. Rick Beyer) Army Research Labs to discuss how the findings could be most profitably used for Army applications. We note that the Army generated a call for SBIR (Small Business Innovation Research) proposals to facilitate the commercialization of self-healing materials that exploit the concepts outlined in our papers. A grant has in fact been awarded and thus, efforts are currently underway to fabricate these materials.

With respect to item 2 above, we developed a novel computational approach (P5) to simulate the rolling motion of fluid-driven, particle-filled microcapsules along heterogeneous, adhesive substrates to determine how release of the encapsulated nanoparticles could be harnessed to repair damage on the underlying surfaces (P6). We focused on a substrate that contains a crack or eroded surface coating, which prevents the otherwise mobile capsules from rolling along the surface. We isolated conditions where nanoparticles released from an arrested capsule can repair this damage and thereby enable the capsules to continue to move along the substrate. Figure II shows snapshots of the simulation at regular time intervals; the nanoparticles are drawn as blue dots. The capsule's shell is bounded by the outer and inner black lines. The solid black dot is added to reveal the rotation of the shell. The solid red curve shows the fractional occupation, Θ , of the substrate sites by the nanoparticles as a function of position along the surface. The dashed red lines mark the two edges of the initially damaged region. Through these studies, we established guidelines for designing particle-filled microcapsules that perform a "repair and go" function and could ultimately be used to restore the integrity of optical coatings (see article cited below).

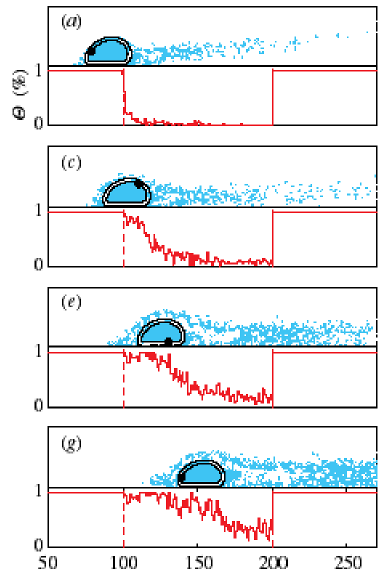

Fig. II

Again, the findings captured peoples' interest and a story describing our findings appeared in the online version of the *New Scientist.* The story, which is entitled "Artificial blood cells' could heal surfaces", can be found at http://www.newscientisttech.com/article.ns?id=dn10231.

Item 3 addresses a different type of repair, namely the removal of defects structures within a spatially periodic material. In particular, we used computer simulations to establish an approach for creating defect-free, periodically ordered thin films (P7-P9) and bulk polymers (P10). The process is initiated by shining a spatially uniform light over a photosensitive AB binary blend, which thereby undergoes both a reversible chemical reaction and phase separation. We then introduce a well-collimated, higher intensity light source. Rastering this secondary light over the sample locally increases the reaction rate and causes formation of defect-free, spatially periodic structures. In effect, the rastering light "combs" out the defects in the material. These binary structures resemble either the lamellar or hexagonal phases of microphase-separated diblock copolymers. We then add a non-reactive homopolymer C, which is immiscible with both A and B. We show that this component migrates to regions that are illuminated by the secondary, higher intensity light, allowing us to effectively write a pattern of C onto the AB film. Rastering over the ternary blend with this collimated light now leads to hierarchically ordered patterns of A, B and C. In this manner, one can create hierarchically patterned materials that exhibit periodicity over two distinct length scales. Figure III shows an image from the simulations; C is in green, A is in red and B is in blue. The approach points to a novel means of patterning with homopolymers, which normally do not self-assemble into periodic structures. The findings also point to a facile process for manufacturing high quality polymeric components in an efficient manner. We note that our first paper on this system (P7) was selected as an **Editor's Choice** in *Science* (see *Science*, **310** (2005) 946).

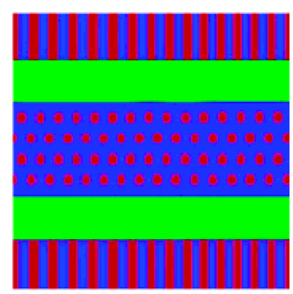

Fig. III

We are now embarking on new studies aimed at establishing guidelines for controlling crack propagation in brittle materials. In the first of these studies (P11), we used a computational model for mode I fracture to characterize the relationship between different features of the fractured material, such as crack roughness, fractal dimension, and fragment size distributions. We found that regions of different roughness in the crack lead to different mechanisms for the subsequent fragmentation of the material. We observed two robust power laws that characterize the size distribution of smaller and larger fragments and related these measurements of the fragment size distribution to the local roughness of the cracks. We are currently determining how the Poisson's ratio of the material will affect the crack propagation. These studies will yield the fundamental insight into the fracture process that will be useful in formulating approaches for influencing both the extent and the direction of the crack propagation.

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