

Nanostructured Self-Healing Polymers and Composites

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2010 Final Report

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Summary

Through this research, we successfully demonstrated self-healing with submicron and nanoscale constituents. A summary of the research program is shown in Figure 1. The research was driven by basic science and engineering of new processing routes for nanoencapsulation of healing chemistries and seamless integration of the self-healing functionality into polymer and polymer composites. Major accomplishments described in this abstract include:

- Identified three promising healing chemistries and successfully encapsulated the components in submicron capsules.
- Functionalized the nanocapsules with a silica coating.
- Dispersed high concentrations of submicron and nanocapsules in epoxy
- Demonstrated modest healing in bulk epoxy specimen.
- Successfully integrated nanocapsules on glass and fiber surface for composite applications.
- Developed a new protocol and demonstrated preliminary fiber/matrix interfacial healing during a single fiber pullout test.

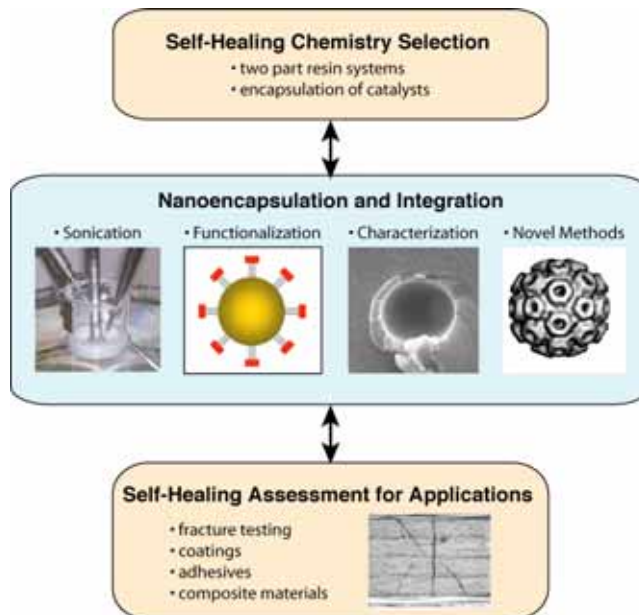


Fig. 1. Research tasks and integration.

SIGNIFICANT RESULTS

1. Self-Healing Chemistry for the Nanoscale

We have identified three potential healing chemistries that can be successfully scaled for healing at submicron length scales: (1) Grubbs catalyzed DCPD monomer, (2) one-part solvent-epoxy, and (3) two-part amine cured epoxy. We were able to demonstrate healing with the first two systems and believe the third chemistry also holds promise.

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14. ABSTRACT Through this research, we successfully demonstrated self-healing with submicron and nanoscale constituents. The research was driven by basic science and engineering of new processing routes for nanoencapsulation of healing chemistries and seamless integration of the self-healing functionality into polymer and polymer composites. Major accomplishments described in this report include - Identified three promising healing chemistries and successfully encapsulated the components in submicron capsules. - Functionalized the nanocapsules with a silica coating. - Dispersed high concentrations of submicron and nanocapsules in epoxy. - Demonstrated modest healing in bulk epoxy specimen. - Successfully integrated nanocapsules on glass and fiber surface for composite applications. - Developed a new protocol and demonstrated fiber/matrix interfacial healing with high efficiency during a single fiber pullout test.					
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1.1 Grubbs Catalyst ROMP Based Healing

We have developed a sonication based-emulsion technique to produce DCPD filled UF capsules as small as 200 nm in diameter [1]. Capsules containing DCPD monomer were prepared by *in situ* polymerization of urea and formaldehyde using a modified process of Brown *et al.* [2]. The sonication horn of an ultrasonic homogenizer was placed in the solution for 3 minutes with continuous mixing at 800 RPM. The resulting capsules with a core material of pure DCPD had a mean diameter of $1.56 \pm 0.50 \mu\text{m}$ measured by focused extinction and $1.65 \pm 0.79 \mu\text{m}$ via SEM measurements (Fig. 2a). The mean shell wall thickness was $77 \pm 25 \text{ nm}$. Through the use of chemical co-stabilizers to limit Ostwald ripening, we were able to reduce the capsule diameter even further. Hexadecane significantly reduced the capsule diameter with only a small reduction in available healing agent (80% size decrease, 5% healing agent decrease). The smallest batch of capsules, had a mean diameter of $220 \pm 113 \text{ nm}$ measured by SEM, and was achieved with 10 wt% hexadecane costabilizer. Images of the nanocapsules show spherical capsules, free of surface debris with well-formed shell walls (Fig. 2b). CHN data was used to estimate the DCPD and UF content of the capsules [1]. The average microcapsule DCPD content by mass was 78.4%, corresponding to a mean capsule fill percentage of 94% by volume.

We also developed an encapsulation procedure to reduce the size scale of the Grubbs catalyst, while maintaining reactivity. Using a one-pot synthesis method, solid Grubbs catalyst was encapsulated in polystyrene beads, directly followed by silica shell protection. This method enabled functionalization of the particles (similar to the DCPD capsules), thus resulting in better dispersion and better stability. The Grubbs catalyst filled polystyrene particles were less than 200 nm in diameter (Fig. 2c). NMR and rheology confirmed that the catalyst remained active with a gel time similar to that of as-received Grubbs catalyst when mixed into DCPD.

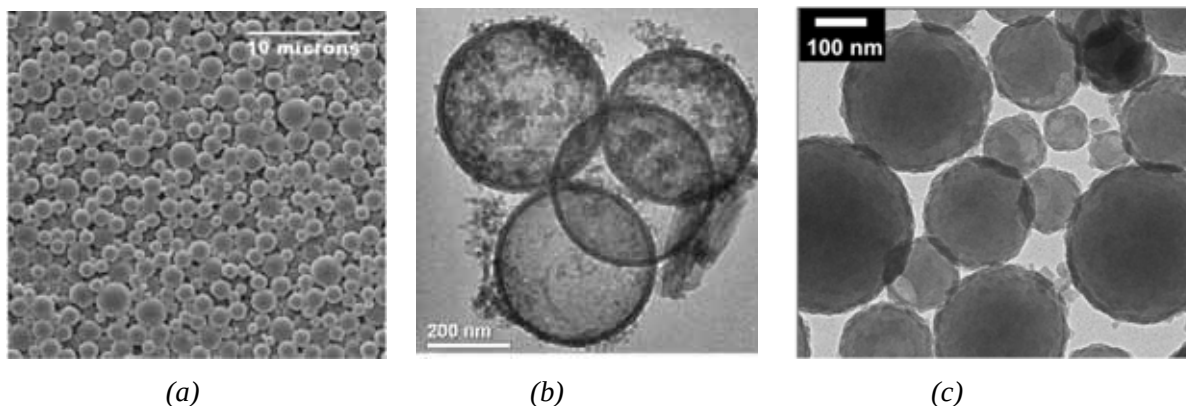


Fig. 2. (a) Distribution of 1.5 mm diameter capsules filled with DCPD healing agent, (b) TEM image showing the core-shell morphology of the nanocapsules, (c) TEM image of Grubbs catalyst particles encapsulated in PS.

1.2 One Part Solvent-Epoxy Based Healing

Microcapsules containing a solvent and reactive epoxy resin hold promise for the development of cost-effective, low toxicity, and low flammability self-healing materials [3,4]. We have developed a robust *in situ* encapsulation method for protection of a variety of oil soluble solvents and reactive epoxy resins by a thin, polymeric, urea-formaldehyde (UF) shell. Capsules as small as 300 nm in diameter were achieved through additional sonication and

stabilization procedures [5]. The presence of both the epoxy resin and solvent core components was confirmed by differential scanning calorimetry (DSC) measurements, and the relative amount of epoxy and solvent in the liquid core was determined by thermal gravimetric analysis (TGA). The capsules were shown to satisfy the requirements for use in self-healing materials including thermal stability, the ability to survive composite processing, and efficient *in situ* rupture for delivery of healing agent. These capsules were used to functionalize high performance fibers for interfacial healing studies (Section 3).

1.3 Two Part Amine-Epoxy Based Healing

Microencapsulation of a reactive amine represents a leap forward in self-healing chemistry in an epoxy matrix. As most advanced composite materials rely on the ring-opening reaction of epoxide with amine, a two-part healing chemistry that incorporates identical material to the existing matrix is desirable. Present research demonstrated that an amine phase can be emulsified and a thin shell can be formed around the amine droplet. Microcapsules were isolated and dried to a flowable powder capable of curing epoxy *ex situ*. Mean capsule diameter was controlled between 12-50 μm by agitation rate. Microcapsules were fully characterized for amine content and curing behavior. Dynamic scanning calorimetry of microcapsules with epoxy indicated 25% of the capsule mass is chemically available as a curing agent. [6] Qualitative *ex situ* healing was demonstrated at elevated temperatures. The capsules were also capable of curing epoxy using a solvent-mediated system, where dissolved epoxy is carried to the capsule region and reacts with capsule material. Work is still in progress to establish the healing efficiency of these systems.

2. Capsule Stabilization and Dispersion in Epoxy

To stabilize the smaller capsules/particles and prevent agglomeration, we developed a method to grow a silica shell around the PUF capsules. The silica shell growth procedure is based on a fluoride-catalyzed regrowth procedure used in literature [7]. The resulting coated capsules have a silica shell that varies in thickness between 20nm and 50nm and contains approximately 60 wt% DCPD. Uncoated capsules prepared similar to the coated capsules contain a similar quantity of DCPD. TEM of capsule cross-sections prepared by microtome sectioning show a solid silica shell in direct contact with the PUF capsule surface (Fig. 3a). The DCPD has evaporated, and is thus not visible in the cross-section. High concentrations of the silica-coated capsules were incorporated into an epoxy matrix, with excellent dispersion, at up to 20 wt% (Fig. 3b).

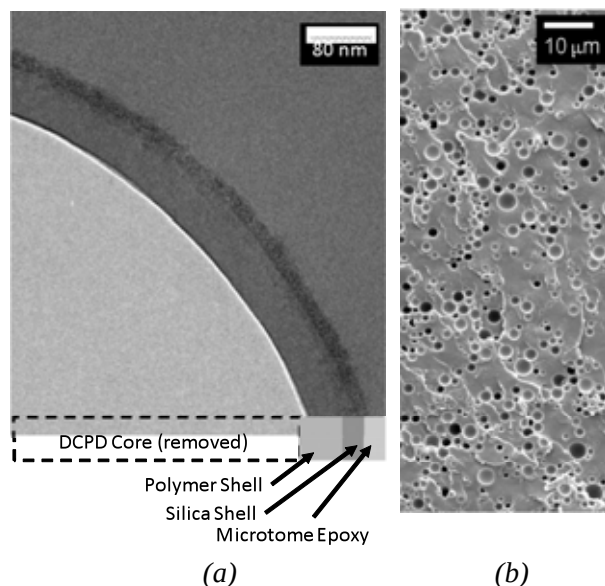


Fig. 3. (a) TEM of a capsule cross-section prepared by microtome sectioning. The PUF shell is ca. 50 nm thick, while the silica coating is 20-50 nm thick depending on the sample. (b) SEM of 20 wt% silica coated, DCPD filled nanocapsules in epoxy.

3. Self-Healing in Bulk Specimens

Self-healing of these components in bulk polymers was evaluated by modifying previously developed fracture testing protocols developed to accommodate the small size of the self-healing components. TDCB samples prepared based on previous work [8] showed no healing because the crack size was too large. However, by applying force to the specimen, the crack width could be decreased in some regions. The decrease in crack width was sufficient to see a recovery of mechanical properties. SEM of the crack plane confirmed that new material had deposited during the healing period (Fig. 4). Controls suggested that a component of the healing was due to catalyst encapsulating polymer dissolving in the DCPD and depositing in the crack plane. No solvent healing was observed between DCPD and excess groups in the epoxy confirming earlier work [3,4].

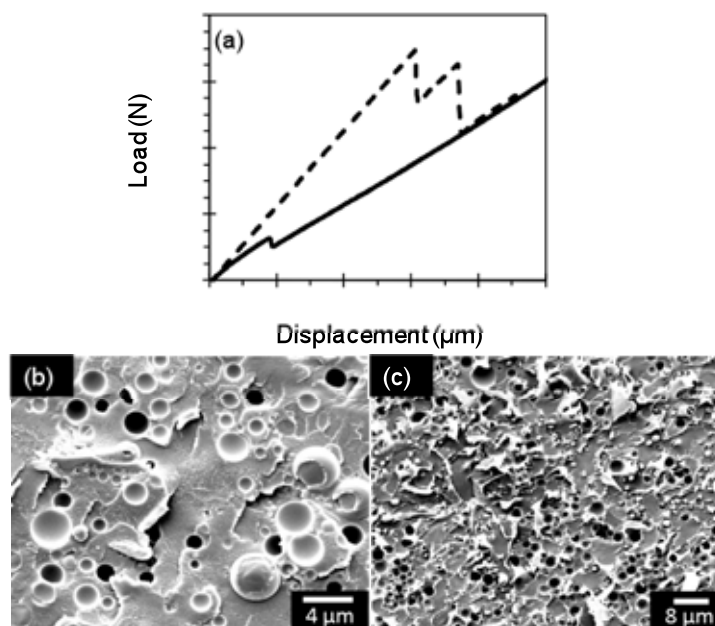


Fig. 4. Load Displacement curve for a sample containing 15wt% capsules and 7wt% catalyst particles(a). The surfaces of the crack plane of these samples is observed before (b) and after (c) healing.

4. Self-Healing Interfaces

Although healing was observed in bulk specimens, the nanoscale constituents are better suited to healing more localized crack damage. Fiber/matrix interface debonding is a critical reliability issue and presents an ideal target for our healing systems. We developed a new protocol to investigate recovery of interfacial shear strength in model single fiber composites. Microbond specimens consisting of a single self-healing functionalized fiber embedded in a microdroplet of epoxy (Fig. 5), were used to test the virgin and healed fiber-matrix interfacial properties.

A method was developed for sequestration of DCPD healing agent filled microcapsules and Grubbs' catalyst to the reinforcement-matrix interface. Figure 6 shows standard glass fibers functionalized with urea-formaldehyde (UF) capsules containing monomeric DCPD healing agent. The extent of this functionalization was defined as ρ , the number of capsules per surface area of the fiber.

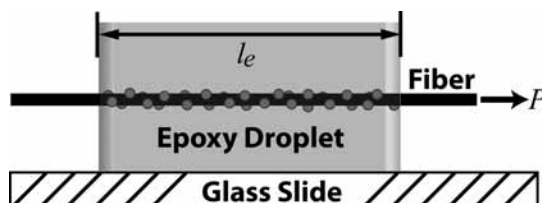


Fig. 5. Schematic of microbond specimen geometry for single fiber interfacial healing studies.

Using the microbond test configuration shown in Fig. 5, damage was initiated at the fiber-matrix interface, rupturing the attached capsules and releasing the healing agent into the crack. A custom-made single fiber-testing frame was built and mounted under an optical microscope to provide simultaneous load-displacement and direct optical observation of crack propagation during debonding and subsequent healing events. Representative pullout curves are shown in Fig. 7a, including the virgin curve (blue), the healed curve (red) demonstrating recovery of interfacial shear strength, and a plain glass fiber control sample (black). Figure 7b summarizes the achieved healing results in terms of healing efficiency, defined as the ratio of peak interfacial shear strength of the healed sample to that of the virgin sample, for DCPD-Grubbs' single fiber self-healing. A maximum healing efficiency of 0.44 was achieved for self-healing (SH) samples functionalized with DCPD monomer filled capsules ($\rho=0.23$) and Grubbs' catalyst (Fig 6b). These results were published in *Advanced Functional Materials* and featured on the cover [9].

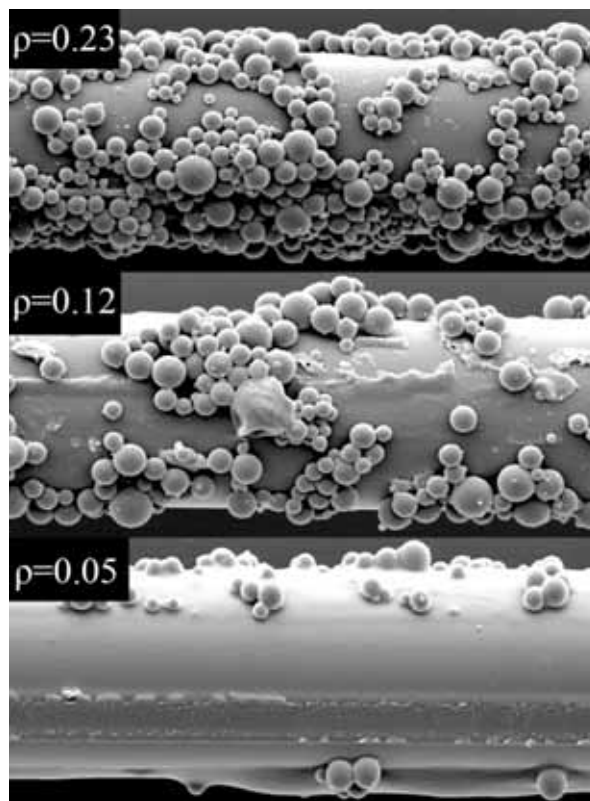


Fig. 6. (a) SEM micrographs of fibers functionalized with Grubbs' catalyst and with various capsule area densities, ρ [Capsules $\cdot \mu\text{m}^{-2}$],

While these results with DCPD healing agent and Grubbs' catalyst are promising, the interfacial bond strength between polyDCPD and glass and polyDCPD and epoxy is relatively weak. The new resin-solvent self-healing system described earlier holds great promise to increase the critical interfacial bond strength, simplify the healing chemistry to a one-part system, and enable healing with nanoscale capsules. For resin-solvent interfacial self-healing, capsules containing a one-part resin-solvent self-healing blend were successfully functionalized onto the surface of a standard glass fiber. Healing agent release into the crack plane was triggered by interfacial damage, similar to the DCPD-Grubbs' interfacial self-healing. Healing efficiencies of over 50% have been already achieved with this new system. Optimization of the resin to solvent ratio and capsule concentration are in progress.

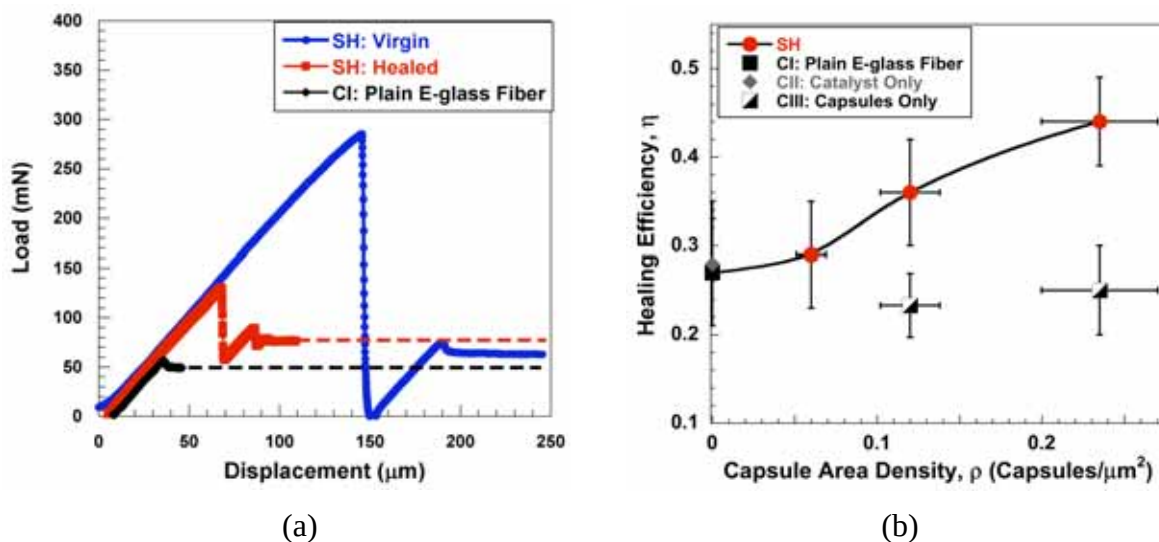


Fig. 7 (a) Representative pullout curves showing the virgin curve (blue), the healed curve (red), and the control healed curve of a plain E-glass fiber. (b) Healing efficiency DCPD-Grubbs' catalyst coated fibers (●), plain fiber control (■), catalyst only control (◆), and capsule only control (▲). Vertical error bars represent 95% confidence interval.

4. REFERENCES

1. Blaiszik, B.J., Sottos, N.R. and White, S.R. Nanocapsules for Self-Healing Materials, *Comp. Sci. Tech.* **68**, 978-986 (2008).
2. Brown, E.N., Kessler, M.R., Sottos, N.R. and White, S.R. In situ poly(urea-formaldehyde) microencapsulation of dicyclopentadiene. *J. Microencapsulation*, **20**, 719-730 (2003).
3. Caruso, M.M., Delafuente, D.A., Ho, V., Moore, J.S., Sottos, N.R., and White, S.R., Solvent-Promoted Self-Healing Materials, *Macromolecules* **40**, 8830-8832 (2007).
4. Caruso, M.M., Blaiszik, B.J., White, S.R., Sottos, N.R., Moore, J.S., Full recovery of fracture toughness using a non-toxic solvent-based self-healing system, *Advanced Functional Materials, Cover Feature*, **18**, 1898-1904 (2008).
5. Blaiszik, B., Caruso, M., McIlroy, D., Moore, J., White, S., and Sottos, N.R., Microcapsules filled with reactive solutions for self-healing materials, *Polymer*, **50**, 990-997 (2009).
6. McIlroy, D.A., Blaiszik, B.J., Caruso, M.M., White, S.R., Moore, J.S., Sottos, N.R. Microencapsulation of a Reactive Liquid-Phase Amine for Self-Healing Epoxy Composites, *Macromolecules*, **43** 4 1855-1859 (2010)
7. Jackson, A.C., Blaiszik, B.J., McIlroy, D., Sottos, N.R., Braun, P.V., New Capsule Chemistries for Nanoscale Self-healing, *Polymer Preprints*, **49**, (2008).
8. J. D. Rule, N. R. Sottos, S. R. White, *Polymer*. **2007**. *48*. 3520-3529
9. Blaiszik, B.J., Baginska, M., White, S.R. and Sottos, N.R. Autonomic Recovery of Fiber/Matrix Interfacial Bond Strength in a Model Composite, *Advanced Functional Materials*, **20**, 3547-3554 (2010). *Cover Feature*.

JOURNAL PUBLICATIONS RESULTING FROM THIS GRANT

- Jackson, A.C., Bartelt, J.A., Marczewski, K., Sottos, N.R. and Braun, P.V. Silica-Protected Micron and Sub-Micron Capsules and Particles for Self-Healing at the Microscale, *Macromolecular Rapid Communications*, **32**, 82-87 (2011). DOI: 10.1002/marc.201000468
- Blaiszik, B.J., Baginska, M., White, S.R. and Sottos, N.R. Autonomic Recovery of Fiber/Matrix Interfacial Bond Strength in a Model Composite, *Advanced Functional Materials*, **20**, 3547-3554 (2010). DOI: 10.1002/adfm.201000798. *Cover Feature*.
- Blaiszik, B.J., Kramer, S.L.B., Olugebefola, S.C., Moore, J.S., Sottos, N.R. and White, S.R. Self-Healing Polymers and Composites, *Annual Review of Materials Research*, **40**, 179-211 (2010). DOI: 10.1146/annurev-matsci-070909-104532
- Caruso, M.M., Blaiszik, B.J., Jin, H., Schelkopf, S.R., Stradley, D.S., Sottos, N.R., White, S.R. and Moore, J.S. Robust Double-Walled Microcapsules for Self-Healing Polymeric Materials, *Applied Materials and Interfaces*, **2**, 1195-1199 (2010).
- McIlroy, D.A., Blaiszik, B.J., Caruso, M.M., White, S.R., Moore, J.S. and Sottos, N.R. Microencapsulation of a reactive liquid-phase amine for self-healing epoxy composites, *Macromolecules*, **43**, 1855-1859 (2010). DOI: 10.1021/ma902251n
- Moll, J.L., White, S.R. and Sottos, N.R., A self-sealing fiber-reinforced composite, *Journal of Composite Materials*, **44**, 2573-2585 (2010). DOI: 10.177/0021998306356605
- Beiermann, B., Keller, M.W. and Sottos, N.R., Self-healing flexible laminates for resealing of puncture damage, *Smart Materials and Structures*, **18**, 085001 (2009). DOI: 10.1088/0964-1726/18/8/085001
- Blaiszik, B., Caruso, M., McIlroy, D., Moore, J., White, S., and Sottos, N.R., Microcapsules filled with reactive solutions for self-healing materials, *Polymer*, **50**, 990-997 (2009). DOI: 10.1016/j.polymer.2008.12.040
- Caruso, M.M., Blaiszik, B.J., White, S.R., Sottos, N.R., and Moore, J.S., Full recovery of fracture toughness using a nontoxic solvent-based self-healing system, *Advanced Functional Materials*, **18**, 1898-1904 (2008). DOI: 10.1002/adfm, *Cover Feature*.
- Blaiszik, B.J., Sottos, N.R. and White, S.R. Nanocapsules for Self-Healing Materials, *Comp. Sci. Tech.*, **68**, 978-986 (2008). DOI: 10.1016/j.compscitech.2007.07.021
- Youngblood, J. and Sottos, N.R., Bioinspired materials for self-cleaning and self-healing, *MRS Bulletin*, **33**, 732-741 (2008).
- Yang, J., Keller, M.W., Moore, J.S., White, S.R. and Sottos, N.R., Microencapsulation of Isocyanates for Self-Healing Polymers, *Macromolecules*, **41**, 9650-9655 (2008). DOI: 10.1021/ma801718v.
- Rule, J.D., Sottos, N.R. and White, S.W., Effect of microcapsule size on the performance of self-healing materials, *Polymer*, **48**, 3520-3529 (2007).
- Keller, M.K., White, S.R. and Sottos, N.R., A self-healing poly(dimethyl siloxane) Elastomer, *Adv. Func. Materials*, **17**, 2399-2404 (2007).