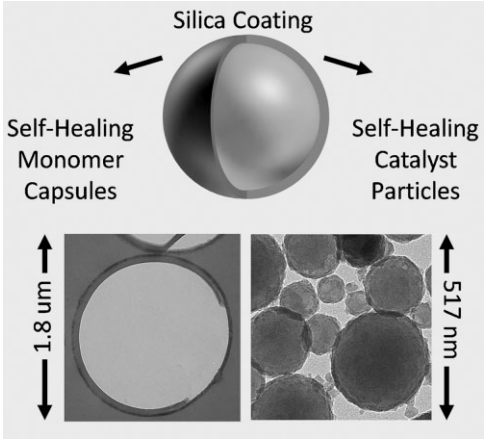
Silica-Protected Micron and Sub-Micron Capsules and Particles for Self-Healing at the Microscale[a]

Aaron C. Jackson, Jonathan A. Bartelt, Kamil Marczewski, Nancy R. Sottos, Paul V. Braun*

A generalized silica coating scheme is used to functionalize and protect sub-micron and micron size dicyclopentadiene monomer-filled capsules and polymer-protected Grubbs' catalyst particles. These capsules and particles are used for self-healing of microscale damage in an epoxy-based polymer. The silica layer both protects the capsules and particles, and limits their aggregation when added to an epoxy matrix, enabling the capsules and particles to be dispersed at high concentrations with little loss of reactivity.



Introduction

Extending the lifetime of engineering materials is an important challenge for many applications. Self-healing offers an autonomic solution to this challenge; the incorporation of healing agents into a material gives the material the ability to heal after a damage event. An early example of a self-healing polymeric system was realized by incorporating a microencapsulated healing agent and catalyst particles in a polymer matrix.[1] Upon a damage event, the advancing crack ruptures the dicyclopentadiene (DCPD) filled capsules and exposes Grubbs' catalyst particles. The DCPD fills the crack plane and dissolves the exposed catalyst, initiating polymerization via a ring opening metathesis. The polyDCPD fills the crack plane, bonding the two surfaces of the crack plane together. This concept has shown promise for a range of applications including self-healing composites[2,3] and self-healing coatings.[4] Self-healing has also been realized by embedding vascular systems within a material[5] or developing polymers with functional moieties that can elicit a self-healing response.[6,7] In the majority of the capsule-based healing systems to date, the capsules and healing agents have ranged from 10 to 100 μm in diameter.[1–3,8–9] This size range is ideal for healing of large cracks, but not for healing of micron and sub-micrometer size damage events. To heal very small damage events, micron size, and smaller healing agents present an advantage.

Small size-scale self-healing components are of particular interest in systems where the typical crack size is too small to rupture larger capsules. Fiber reinforced composites, thin films, and thermoplastic polymers are three examples where sub-micron defects are found, and thus, micron size or smaller self-healing components could be

P. V. Braun, A. C. Jackson, J. A. Bartelt, K. Marczewski, N. R. Sottos
Department of Materials Science and Engineering, Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA
Fax: 217-333-2736; E-mail: pbraun@illinois.edu

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beneficial. In fiber-reinforced composites, the spacing between fibers is often well below a micron.[10] Similarly, for thin film applications, polymer films are often only micrometers thick. In both of these cases, self-healing components must fit into the space available. Finally, the damage induced by crazing in thermoplastic polymers may be insufficient to rupture larger capsules, but perhaps smaller capsules can be ruptured by crazes. Here, we demonstrate the potential of a micron-scale self-healing system building upon earlier work on self-healing using larger encapsulated DCPD monomer and Grubbs' catalyst.[1]

Realization of a micron size-scale self-healing system is limited by several challenges. First, synthesis of monomer containing capsules or catalyst containing particles approximately 1 μm in diameter is not trivial. Although Blaiszik et al.[11] fabricated sub-micron DCPD-filled capsules, previous Grubbs' catalyst encapsulation methods have only produced stable particles larger than 50 μm.[8] In these encapsulation methods, wax particles protected the catalyst from deactivating species such as amines and alcohols.[12,13] However, smaller wax particles tend to aggregate during synthesis and have poor thermal stability. Second, the DCPD-filled capsules reported by Blaiszik et al. are highly aggregated when dry and are not easily dispersed in an epoxy matrix by mechanical stirring. Blaiszik et al. suspended micron size capsules in a volatile solvent and then added this mixture to the epoxy resin followed by evaporation of the solvent from the resin. Even using this procedure, aggregation was still a problem above capsule loadings of 3 wt.-%. Capsules and particles dispersed well in epoxy at concentrations approaching 20 wt.-% are desirable for self-healing applications. Third, as the encapsulation size decreases, the surface area to volume ratio increases and the shell wall thickness of micron size capsules decreases.[11] As a result, capsule stability is critical. The capsules should retain their contents for an extended period both in the dry state and once incorporated into a polymer matrix. Finally, new testing methods are needed to evaluate healing at smaller size-scales. Recovery of interfacial shear strength was recently demonstrated for micron size capsule-functionalized glass fibers[10] in an epoxy matrix, but evaluation of small size-scale self-healing in bulk polymers remains a challenge.

In this research, each challenge is addressed in order to develop a strong framework for future self-healing at smaller size-scales. First, micron size polymer-protected catalyst particles are built using emulsion solvent evaporation similar to the methods used to produce drug delivery devices.[14,15] Polymer particles made using this method are routinely micron size and smaller while maintaining a good dispersion. In addition, polymer particles are potentially more stable than wax at all temperatures while still dissolving in DCPD. Second, a generalized silica coating procedure is developed to address the issues of stability and dispersion in a matrix for both the DCPD capsules and catalyst particles. Silica chemistries are well studied, often utilize mild synthetic conditions,[16–19] are amenable to functionalization,[20,21] and silica is a potentially good diffusion barrier. Although there are several silica condensation chemistries available,[16–19] it is expected that a fluoride-catalyzed silica condensation chemistry[19] minimizes deactivation and loss of the healing agent while building a non-porous, continuous shell. Finally, self-healing of micron size capsules and particles is demonstrated using tapered double-cantilever beam (TDCB) specimens similar to previous work.[9,22] However, since the small size of the capsule limits the amount of healing agent that can be delivered to the crack plane,[9] a force is applied across the generated crack in order to narrow the crack and simulate small size-scale cracks.[2,23]

Experimental Part

Materials

Dicyclopentadiene (DCPD) was purchased from Alfa Aesar (90 + %, stab. with 150–200 ppm *p-tert*-butyl catechol). The DCPD was distilled to remove stabilizer, cyclopentadiene, and any oligomeric units that might be present. Grubbs' catalyst, ammonium chloride, polystyrene (PS, MW = 280 000), poly(methyl methacrylate) (PMMA, MW = 120 000), tetraethylorthosilicate (TEOS), and tetrabutylammonium fluoride (TBAF, 75 wt.-% in water) were purchased from Sigma–Aldrich. TBAF was diluted to 0.75 wt.-% for use. Cetyltrimethylammonium bromide (CTAB) was purchased from Acros. Formaldehyde solution (37 wt.-% formaldehyde in water) and monobasic potassium phosphate were purchased from Fisher Chemicals. Ethylene maleic anhydride copolymer was donated by Zeeland chemicals (EMA, MW = 400 000). EPON 828 was purchased from Miller Stephenson and diethylaminetriamine (DETA) was received from Dow Chemical.

Fabrication of Self-Healing Components

Micron size polymer capsules were synthesized based on the procedure by Blaiszik et al.[11] Briefly, an aqueous phase was prepared containing EMA solution, urea, resorcinol, and ammonium chloride. Distilled DCPD was added to the solution and emulsified by an impeller blade at 900 rpm. While stirring, the solution was sonicated (750 W Ultrasonic Homogenizer, Cole Parmer) at 40% intensity for 90 s. Formaldehyde was added and the reaction temperature was increased to 55 °C at 60 °C min^{-1} and held at 55 °C for 4 h. Uncoated capsules were dried by centrifugation followed by freeze drying for 3 d.

Coated capsules were made by first removing excess reactants through centrifugation and redispersing them in 40 mL of water. In a second solution, monobasic sodium phosphate (0.2 g), ammonia chloride (0.05 g), and dilute TBAF solution (12 mL) were mixed in water (20 mL). The capsule solution was mixed into the second solution using an impeller blade at 500 rpm. Finally, TEOS

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(1 mL) was added and the reaction was stirred over night. The coated capsules were centrifuged, and then freeze dried for 3 d.

Composite polymer particles containing Grubbs' catalyst were prepared using an emulsion solvent evaporation technique similar to those described in literature.[12,13] First, CTAB (0.4 g) and dilute TBAF (18 mL) were dissolved in water (120 mL) at room temperature and stirred with a stir bar at medium speed. Next, PS (0.8 g), PMMA (0.4 g), and Grubbs' catalyst (0.08 g) were dissolved in methylene chloride (16 mL). For particles containing polystyrene and catalyst, PS (0.8 g) and catalyst (0.08 g) were dissolved in methylene chloride (16 mL). The organic phase was poured into the aqueous phase, emulsified for 1 min, and then sonicated for 30 s. The emulsion was stirred overnight with nitrogen flowing over the sample to assure evaporation of the methylene chloride. To add a silica coating, TEOS was added to the solution and allowed to react for 1 d. The final particles were centrifuged and then freeze dried for 4 d affording a dry powder.

Analysis of Self-Healing Components

Morphology of the DCPD capsules and catalyst particles was analyzed via SEM (Philips XL30 ESEM-FEG) and TEM (Philips CM200). A microtoming process was used to prepare cross sections of DCPD capsules for TEM analysis. Fill content of the capsules was determined using thermal gravimetric analysis (TGA) and elemental analysis. TGA was performed using a Mettler-Toledo TGA 851e under nitrogen atmosphere and a heating rate of 10 °C min^{-1}. Elemental Analysis was performed on a CE440 by Exeter Analytical. Rheology experiments and NMR were used to characterize the activity of Grubbs' catalyst in the catalyst particles. Because the coated catalyst particles did not dissolve in organic solvents, the silica was etched in an aqueous hydrofluoric acid solution. Etched particles were dissolved in deuterated methylene chloride with a trimethoxybenzene standard for NMR. Etched particles were dissolved in DCPD at 0.0167 g · mL for qualitative gel tests. More details for the fill content and activity of the self-healing components can be found in the Supplementary Information.

Self-Healing Composites

All self-healing samples were prepared by mixing EPON 828 and diethylenetriamine (DETA) at 12 pph DETA in EPON 828. Vacuum was applied to the resin/hardener mixture for 10 min before adding the encapsulated healing agents. After the encapsulated healing agents were added, vacuum was reapplied for 5 min. The final mixture was poured into the appropriate mold and cured for 24 h at room temperature followed by 24 h at 35 °C. Short-groove tapered double cantilever beam (TDCB) specimens were prepared as described previously[9] but with the changes described in the Supplementary Information. After testing the virgin samples and determining their virgin fracture toughness, the samples were clamped across the crack and allowed to heal for 24 h before testing them for their healed fracture toughness. For injected healing tests, DCPD (5 μL) was injected into the crack plane before applying pressure to the sample. At least three samples were tested for each data point.

Results and Discussion

Coated Grubbs' Catalyst Particles

Grubbs' catalyst-containing PS particles produced using the emulsion solvent evaporation method maintain the purple color of activated Grubbs' catalyst and have an average diameter of 1.5 μm. The gel time for the polymerization of DCPD is similar for both catalyst-containing PS particles and unprotected catalyst when mixed into DCPD at similar catalyst (as opposed to catalyst particle) concentrations (Supporting Information Figure S1). This assures that DCPD dissolves PS and that the catalyst retains its activity after synthesis. However, PS provides insufficient protection when the particles are exposed to the DETA curing agent in our epoxy system. When incorporated into epoxy, their color changes from purple to yellow, indicating deactivation by the amine curing agent.

In order to produce more stable particles, PMMA is added to the PS catalyst particles, and the resulting particles are coated with silica. PMMA or silica alone does not protect the catalyst when the particles are incorporated into epoxy resin. However, the composite particles containing PS, PMMA, and silica maintain their purple color in the epoxy resin. These composite particles are approximately 0.4 μm in diameter and have a uniform 20 nm thick shell of silica surrounding them (Figure 1a,b). SEM shows that the particles may be acorn shaped suggesting that the PMMA only partially encapsulates the polystyrene. NMR and a qualitative gel test show that the Grubbs' catalyst contained in the particles is active. In ^{1}H NMR, a carbene peak observed at 20 ppm is characteristic of active Grubbs' catalyst (Figure 1c). When etched and dissolved in DCPD, the core of these composite particles gelled DCPD confirming catalyst activity.

Coated DCPD Capsules

Uncoated DCPD capsules have limited use due to aggregation when incorporated in polymer matrices and when dried to a powder. Typically, polymer brushes or charge stabilization can be used to minimize aggregation.[24] We hypothesized that a silica coating would provide a functional layer to develop these strategies, reducing aggregation. In addition, silica can potentially improve capsule stability (discussed further in the Supplementary Information). The coated and uncoated capsules were both spherical with an average diameter of 1.5 μm as measured using SEM (Supporting Information S2). Figure 2 shows a TEM image of a representative cross-section of coated capsules in epoxy prepared by microtome. The DCPD and part of the polyureaformaldehyde (PUF) shell wall are removed during the microtoming process. The PUF shell wall is 20-25nm thick and the silica shell wall is 20-40nm

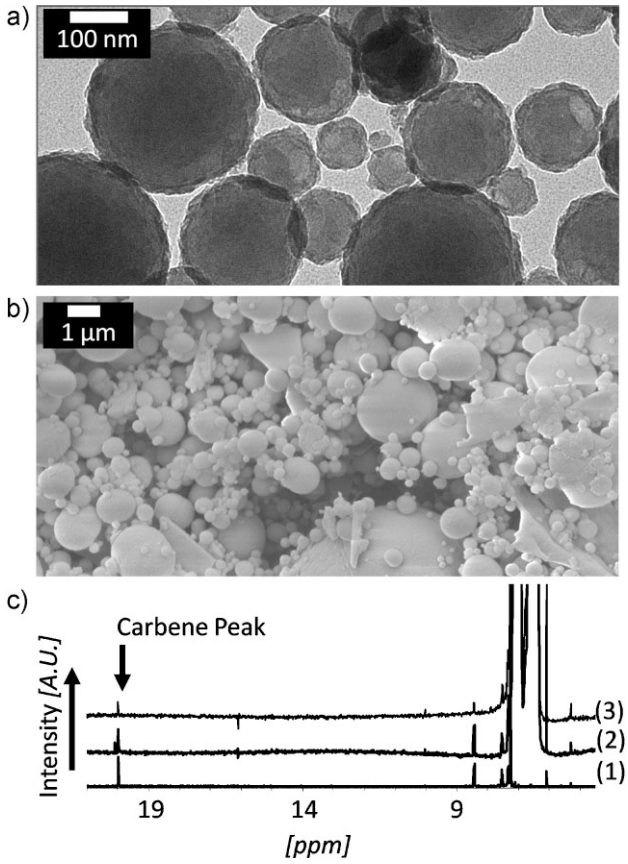

Figure 1. The morphology of the core-shell catalyst particles as observed via (a) TEM and (b) SEM. (c) ^{1}H NMR spectrum of as received Grubbs' catalyst (1), catalyst in polystyrene (2), and etched particles of catalyst in polystyrene, poly(methyl methacrylate), and silica (3).

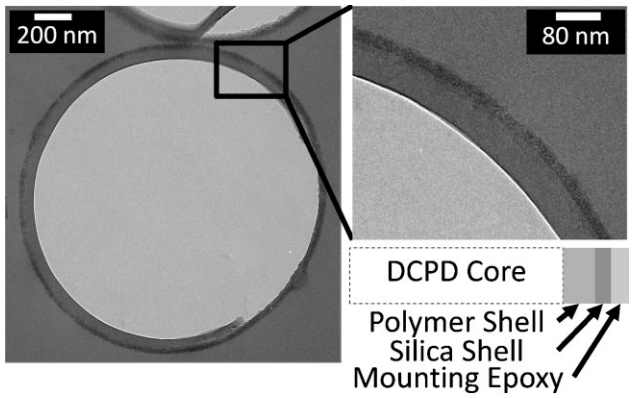

Figure 2. A representative TEM image of a microtomed cross-section of a silica coated DCPD-filled capsule. The DCPD core is removed during the microtoming process.

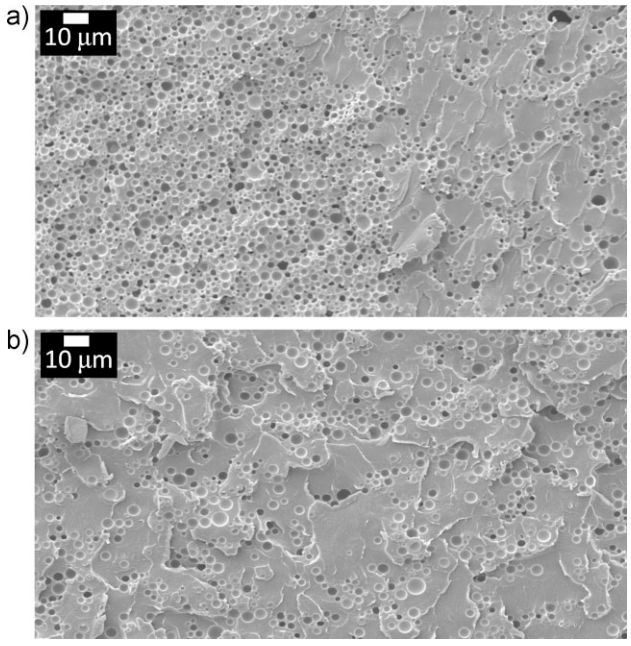

Figure 3. SEM of a fracture surface of an EPON 828/DETA epoxy containing (a) uncoated, and (b) coated capsules at 10 wt.-%. Capsules are mixed into the uncured resin/hardener mixture as a dry powder.

thick. TGA and elemental analysis confirm that DCPD is retained in the coated capsules at between 55 wt.-% and 70 wt.-% depending on the synthesis conditions of the sample (Supporting Information S3). TGA analysis also demonstrates that the micron size capsules retain almost all of their DCPD after being stored at room temperature for 7 d, providing sufficient time to incorporate them into an epoxy.

The importance of the silica shell is most apparent when comparing the dispersion of coated capsules to the dispersion of uncoated capsules in an epoxy matrix. As mentioned previously, uncoated capsules could not be incorporated into epoxy at concentrations higher than 3 wt.-%. Additionally, micron size uncoated capsules could not be dried without significant aggregation. Centrifuging and freeze drying the aqueous solution of coated capsules resulted in a free flowing powder of individual capsules. This powder could be incorporated into epoxy at significantly higher concentrations than the uncoated capsules. A comparison of uncoated capsules and coated capsules dispersed in epoxy at 10 wt.-% is shown in Figure 3. We have successfully dispersed coated capsules into epoxy at up to 20 wt.-%.

Self-Healing in Bulk Epoxy

The self-healing efficacy of this micron size capsule and catalyst system is tested in short-groove TDCB specimens similar to previous research (Supporting Information Figure S5).[9] To simulate small size-scale self-healing, pressure is applied across the crack via a clamp. This

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provides approximately 20-30 lbs of force and reduces the crack width along portions of the crack to 1 μm or less (Supporting Information Figure S6).

The healed peak loads of various samples and a typical load displacement curve for a full self-healing system are presented in Figure 4. Healing efficiency, defined as the healed peak load divided by the virgin peak load,[1] was used in previous studies but is not adopted here since the virgin peak load varies significantly depending on which self-healing components are added (Supporting Information Figure S7). Instead, the healed peak load is used to compare samples. For a sample containing capsules and catalyst particles (CCap + CGr), the average healed peak load is 15.0 N. Unlike the fracture surface of the sample before healing (Figure 4c), the fracture surface of a healed sample has a thin film across a fraction of the crack surface (Figure 4d). Samples containing catalyst particles alone show no healing and no film was found. Solvent healing, a mechanism described previously,[25] could occur if the polystyrene dissolves in the DCPD and redeposits in the crack plane, bonding the surfaces back together. To test this hypothesis, we evaluated samples containing capsules and polymer particles (CCap + CPoly). The polymer particles are prepared using the same procedure used to make catalyst particles but no catalyst is added to the organic phase. As shown in Figure 4a, these samples show an average healed peak load of 10.4 N. The difference between catalyst containing samples and catalyst-free samples is statistically significant. Samples containing only catalyst particles or polymer particles were also tested and injected with DCPD to mimic capsule rupture. The healed peak loads of these samples follow a similar trend as the samples containing both monomer and catalyst healing agents. This suggests that, while solvent-induced healing does account for a portion of the recovered mechanical properties, the presence of the catalyst significantly improves recovery of mechanical properties. More analysis of the mechanical properties can be found in the Supplementary Information.

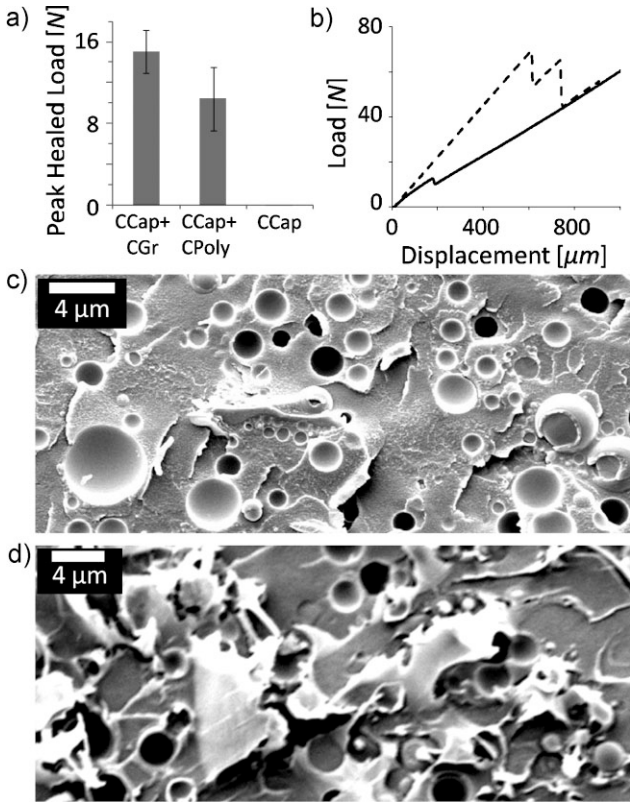

Figure 4. (a) Peak healed loads for short groove TDCB specimens as shown in Figure S5b containing capsules and catalyst particles (15 wt.-% CCap; 7 wt.-%, CGr), capsules and polymer (catalyst free) particles (15 wt.-% CCap; 7 wt.-% CPoly), or only capsules (15 wt.-%, CCap), (b) Typical load displacement curve of a full sample (CCap + CGr) with both the virgin (dashed line) and healed (solid line) fracture. (c) SEM of the crack of a sample containing capsules and catalyst particles surface prior to healing. (d) SEM of the crack surface of a similar sample after healing. A polymerized polyDCPD film can be seen on the crack surface.

Conclusion

Encapsulated healing agents have been compartmentalized in silica coated micron size capsules and particles for use in applications where larger capsules and particles are impractical or inefficient. Micron size polymer particles containing Grubbs' catalyst were developed to protect the catalyst and complement the micron size DCPD capsules that had been previously developed.[11] Both were coated with silica through a fluoride-catalyzed silica condensation chemistry to add a protective and functional layer to the capsules and particles. This significantly improved dispersion of the capsules and catalyst particles in epoxy. In addition, the coated capsules and catalyst particles were successfully incorporated into epoxy without significant loss of healing agent. A modest recovery of mechanical properties was observed through self-healing.

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[1] S. R. White, N. R. Sottos, Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, E. N. Brown, S. Viswanathan, *Nature* **2002**, *409*, 794.

[2] M. K. Kessler, N. R. Sottos, S. R. White, *Compos. Part A.* **2003**, *34*, 743.
[3] A. J. Patel, N. R. Sottos, E. D. Wetzel, S. R. White, *Compos. Part A.* **2010**, *41*, 360.
[4] S. Cho, H. M. Anderson, S. R. White, N. R. Sottos, P. V. Braun, *Adv. Mater.* **2006**, *18*, 997.
[5] K. S. Toohey, N. R. Sottos, J. A. Lewis, J. S. Moore, S. R. White, *Nat. Mater.* **2007**, *6*, 581.
[6] C. R. Hickenboth, J. S. Moore, S. R. White, N. R. Sottos, J. Baudry, S. R. Wilson, *Nature* **2007**, *446*, 423.
[7] X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. Nutt, K. Sheran, F. Wudl, *Science* **2002**, *295*(5560), 1698.
[8] J. D. Rule, E. N. Brown, N. R. Sottos, S. R. White, J. S. Moore, *Adv. Mater.* **2005**, *17*, 205.
[9] J. D. Rule, N. R. Sottos, S. R. White, *Polymer* **2007**, *48*, 3520.
[10] B. J. Blaiszik, M. Baginska, S. R. White, N. R. Sottos, *Adv. Func. Mater.*, **2010**, DOI: 10.1002/adfm.201000798.
[11] B. J. Blaiszik, N. R. Sottos, S. R. White, *Compos. Sci. Technol.* **2008**, *68*, 978.
[12] G. O. Wilson, K. A. Porter, H. Weissman, S. R. White, N. R. Sottos, J. S. Moore, *Adv. Synth. Catal.* **2009**, *351*, 1817.
[13] M. B. Dinger, J. C. Mol, *Organometallics* **2003**, *22*, 1089.
[14] K. J. Pekarek, J. S. Jacob, E. Mathiowitz, *Nature* **1994**, *367*, 258.
[15] R. Gref, Y. Minamitake, M. T. Peracchina, V. Trubetskoy, V. Torchilin, R. Langer, *Science* **1994**, *263*, 1600.
[16] C. Graf, D. L. J. Vossen, A. Imhof, A. van Blaaderen, *Langmuir* **2003**, *19*, 6693.
[17] N. F. Steinmetz, S. N. Shah, J. E. Barclay, G. Rallapalli, G. P. Lomonosoff, D. J. Evans, *Small* **2009**, *5*, 813.
[18] C. E. Fowler, D. Khushalani, S. Mann, *Chem. Commun.* **2001**, 2028.
[19] S. Bégu, R. Durand, D. A. Lerner, C. Charnay, C. Tourné-Péteilh, J. M. Devoisselle, *Chem. Commun.* **2003**, 640.
[20] Y. L. Liu, C. Y. Hsu, M. L. Wang, H. S. Chen, *Nanotechnology* **2003**, *14*, 813.
[21] J. A. Howater, J. P. Youngblood, *Langmuir* **2006**, *22*, 11142.
[22] E. N. Brown, N. R. Sottos, S. R. White, *Exp. Mech.* **2002**, *42*, 372.
[23] E. L. Kirkby, V. J. Michaud, J.-A. E. Månson, N. R. Sottos, S. R. White, *Polymer* **2009**, *50*, 5533.
[24] T. Cosgrove, *Colloid Science*, Blackwell Publishing, Oxford, UK 2005, Ch 2, 8.
[25] M. M. Caruso, D. A. Delafuente, V. Ho, N. R. Sottos, J. S. Moore, S. R. White, *Macromolecules* **2007**, *40*, 8830.

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