Robust, Double-Walled Microcapsules for Self-Healing Polymeric Materials

Mary M. Caruso,[†] Benjamin J. Blaiszik,[‡] Henghua Jin,[§] Stuart R. Schelkopf,[†] Dylan S. Stradley,[#] Nancy R. Sottos,[†,#,⊥] Scott R. White,[§,#,⊥] and Jeffrey S. Moore*,[†,#,⊥]

Department of Chemistry, 600 S. Mathews Avenue, Department of Mechanical Science and Engineering, 1206 W. Green Street, Department of Aerospace Engineering, 104 S. Wright Street, Department of Materials Science and Engineering, 1304 W. Green Street, and Beckman Institute, 405 N. Mathews Avenue, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

ABSTRACT Double-walled polyurethane/poly(urea-formaldehyde) microcapsules (PU/UF) are prepared for use in self-healing materials. This modified encapsulation procedure combines two chemistries to form more robust capsule shell walls in a single operation. Robust capsules are formed by this procedure as long as the aromatic polyisocyanate prepolymer is soluble in the core liquid and the core liquid is compatible with isocyanates. Compared to a standard UF encapsulation, the modified procedure results in capsules with an increase in shell wall thickness from 200 to 675 nm as a function of the amount of PU added to the core liquid. Thermal stability of PU/UF microcapsules prepared with varying amounts of PU is compared to UF microcapsules. Mechanical properties of the PU/UF microcapsules are assessed from single-capsule compression testing.

KEYWORDS: microcapsules • self-healing • polyurethane • poly(urea-formaldehyde) • thermal stability

INTRODUCTION

High temperatures and large shear stresses are common in the processing of polymeric materials and composites. Structural epoxy thermosets are typically cured between 100−200 °C and most thermoplastic materials are extruded under high shear stresses at temperatures greater than 150 °C (1). For self-healing materials based on encapsulated repair agents, these processing conditions require significant advancements in microcapsule stability (2, 3). The incorporation of solvent-filled microcapsules into polymers to impart self-healing (4) functionality can be problematic if the processing temperature of the polymer is near the boiling point of the core liquid or the degradation point of the microcapsule shell wall. Here, we report a method for the preparation of polyurethane (PU)/poly(urea-formaldehyde) (UF) microcapsules (PU/UF) in a single batch process. The method provides capsules that are highly stable at elevated temperatures when compared to standard UF microcapsules, while retaining the excellent interfacial bonding of UF microcapsules (5). The PU/UF capsules also demonstrate improved long-term stability at room temperature and increased ability to contain liquids that would readily diffuse out of UF microcapsules.

A variety of encapsulated repair agents have been incorporated into self-healing materials (6–10). UF microcapsules containing the liquid monomer dicyclopentadiene (DCPD) were utilized in the initial metathesis-based self-healing system (5, 6, 11–13). Upon crack damage to the epoxy composite, encapsulated DCPD was released from ruptured microcapsules into the crack plane where it contacted the embedded Grubbs' catalyst in the matrix to form poly(D-CPD). Other microcapsule-based self-healing systems include chemistry based on polydimethylsiloxane (8, 9, 14, 15), a tungsten-catalyzed metathesis of bicyclic monomers (16, 17), and activation of latent functional groups with common organic solvents (4) and epoxy-solvent mixtures (18). These previous studies have used capsules prepared either by in situ emulsion polymerization or interfacial polymerization techniques to produce single-walled, liquid-containing microcapsules.

Previous methods for the preparation of multiwalled capsules (19, 20) involve multiple, discrete steps: (1) interfacial reaction between isocyanates and polyols to build the PU shell wall; (2) rinsing and filtration of prepared PU microcapsules; and (3) redispersion in aqueous medium and deposition of a UF shell wall. Secondary nucleation onto the microcapsule exterior allows the UF microcapsules to bond to the matrix for efficient rupture in a self-healing composite, a major problem with PU single-walled capsules (21). In this work, PU/UF microcapsules filled with ethyl phenylacetate (EPA) core liquid are prepared by a single-batch process and characterized in terms of shell morphology, thermal stability, and failure strength as a function of PU prepolymer added. EPA was selected as the core solvent because of its ability to dissolve the PU prepolymer and its successful healing ability in solvent-promoted self-healing polymers (18, 22).

ARTICLE

The behavior of the PU/UF capsules is compared to that of UF microcapsules with the same core material.

EXPERIMENTAL SECTION

Materials. Ethyl phenylacetate (EPA), urea, ammonium chloride (NH_4Cl), resorcinol, and formaldehyde solution (formalin, 37 w/v%) were purchased from Sigma-Aldrich and used as received. The commercial polyurethane (PU) prepolymer, Desmodur L 75, was purchased from Bayer MaterialScience and used as received. Desmodur L 75 is a prepolymer solution in ethyl acetate with a reported equivalent weight of 315 g and an isocyanate content of 13.3 ± 0.4 wt %. Ethylene-maleic anhydride (EMA) copolymer (Zemac−400) powder with an average molecular weight of 400 kDa was graciously donated by Vertellus and used as a 2.5 wt % aqueous solution. Diglycidyl ether of bisphenol A resin (DGEBA or EPON 828) was used as received from Miller-Stephenson with the curing agent Ancamine DETA received from Air Products in a ratio of 12 parts per hundred (pph) curing agent to EPON 828 to form epoxy samples (EPON 828:DETA).

Characterization. Microcapsules were imaged using a Leica DMR Optical Microscope at various magnifications, and ImageJ software was used to measure capsule diameters from acquired images for each batch of capsules produced. Scanning electron microscopy (SEM, Philips XL30 ESEM-FEG) was used to image fracture surfaces of 5 wt % microcapsules in an EPON 828: DETA matrix cured at 35 °C for 24 h. SEM images were acquired after sputter-coating the sample with gold−palladium. The procedure to image capsule shell walls by AFM was based on examination of microtomed surfaces as follows: thin films of epoxy samples (EPON 828:DETA) containing 5 wt % microcapsules were ultramicrotomed into 300 nm thick slices and mounted onto glass slides for imaging. Atomic force microscopy (AFM) images were acquired on an Asylum Research MFP-3D AFM in tapping mode with BudgetSensors Tap300AL tips. Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851^e, calibrated with indium, aluminum, and zinc standards. Unless otherwise indicated, a heating rate of 10 °C min^{-1} was used in an atmosphere of nitrogen. For each experiment, the sample (ca. 5 mg) was accurately weighed (± 0.02 mg) into an alumina crucible. The mass loss was recorded during a heating cycle over the temperature range of 25 to 650 °C for a dynamic experiment. For isothermal experiments, the temperature was ramped from 25 to 180 °C (10 °C min^{-1}) and subsequently held at 180 °C for 2 h. Afterward, samples were heated from 180−600 °C (10 °C min^{-1}). Single-capsule compression testing was performed on a series of microcapsule batches with ≥8 capsules from each batch tested at a displacement rate of 5 μm s^{-1} using a previously described setup and procedure (23). For each experiment, a dry microcapsule was compressed between flat parallel plates and imaged through a stereo microscope (Nikon SMZ-2T) during testing while the load vs displacement behavior was recorded.

Encapsulation. The procedure to yield polyurethane/poly-(urea-formaldehyde) (PU/UF) microcapsules incorporates both shell components in a single batch process. In contrast to producing UF microcapsules (5, 22), the modified procedure combines in situ poly(urea-formaldehyde) microencapsulation with an interfacial microencapsulation (21, 24, 25) using a commercially available PU prepolymer (Desmodur L 75) following the procedure outlined in Figure 1. The amount of Desmodur L 75, denoted as "X" g in Figure 1, was varied in this work from 0 to 8 g. The prepolymer was dissolved into the desired core liquid (60 mL EPA) before adding to the stirred emulsion. In preparing PU/UF EPA capsules, the Desmodur L 75 easily dissolved into the solvent.
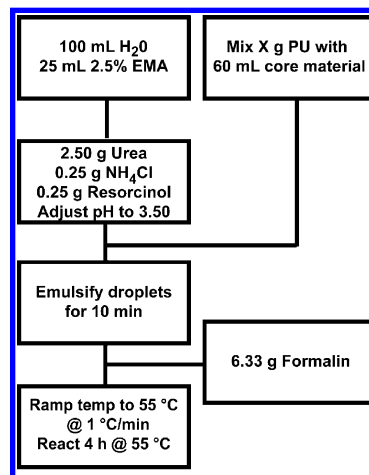

FIGURE 1. Microencapsulation protocol for the preparation of PU/UF capsules. The amount of Desmodur L 75 prepolymer solution ("X") varied from 0 to 8 g.
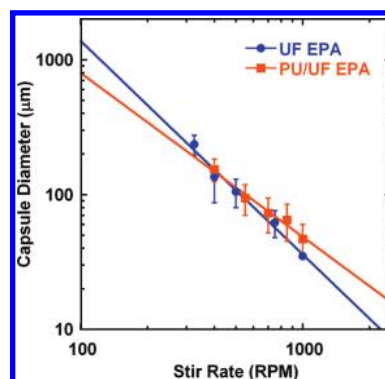

FIGURE 2. Log−log plot of microcapsule diameter as a function of stir rate for capsules where the core material is EPA alone or EPA mixed with 1.5 g PU (Desmodur L 75 prepolymer). The average diameter and one standard deviation (error bars) are plotted on the basis of measurements of at least 100 capsules for each batch.

RESULTS AND DISCUSSION

Microcapsule Preparation. Following the modified encapsulation procedure shown in Figure 1, PU/UF capsules of various sizes were produced by changing the stirring speed. Figure 2 reveals the size range of PU/UF EPA capsules produced with a constant amount of PU prepolymer. The capsule diameter is compared to UF EPA capsules for a range of stir rates (5). The addition of PU prepolymer does not significantly change the mean size of the resultant PU/UF EPA microcapsules from the sizes of the produced UF EPA capsules.

Capsule Shell Wall Morphology. The addition of the PU prepolymer results in PU/UF microcapsules with thicker shell walls than UF capsules. Moreover, two distinct shell morphologies are observed when the PU prepolymer is added to the core. SEM imaging of the epoxy surfaces (Figure 3a) reveals an abrupt change in texture that suggests a distinct double-wall morphology. AFM imaging of a PU/UF EPA capsule prepared with the highest amount of PU used in this study (7.5 g) is presented in Figure 3b. A color map was created from raw AFM phase images, which displayed a difference in phase for the two regions. These regions were designated as different shell walls based on a
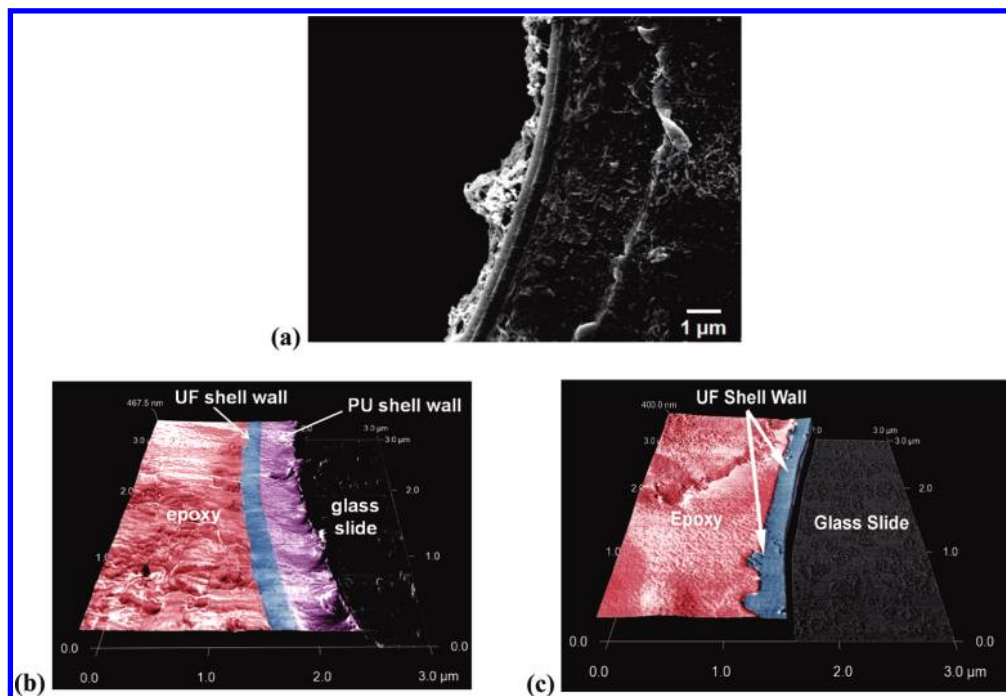
FIGURE 3. (a) SEM image of an epoxy sample showing the double wall morphology for a PU/UF EPA capsule with core material containing 7.5 g PU; (b) and (c) AFM phase images with a 3D representation of a microtomed epoxy sample showing the capsule shell wall morphology of a PU/UF EPA capsule with 7.5 g PU and (a) UF EPA capsule, respectively.
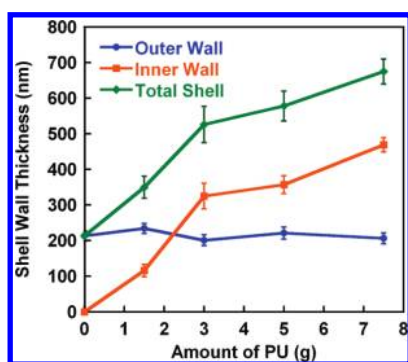

FIGURE 4. Average thicknesses of PU/UF EPA capsule shell wall components and total shell thickness as a function of the amount of PU added to the EPA core material. At least 30 measurements using ImageJ were taken using one AFM phase image per data set for the average thickness and error bars show one standard deviation of the measurements for one image.

series of images taken as the amount of PU was systematically increased (see the Supporting Information, Figure S1). Based entirely on their location, the inner texture is assigned as the PU shell wall and the outer texture is assigned as the UF shell wall. The precise chemical composition of these textures is presently unknown. As a control, an AFM image of a UF EPA capsule shows only one phase with a uniform texture consistent with a single wall and a color map was also added to this image in order to make this concept more evident (Figure 3c). Capsule shell wall thicknesses are measured from a series of AFM phase images using ImageJ analysis software. The average thicknesses are presented in Figure 4 and show that as the amount of PU prepolymer added to the core increased, the size of the inner wall, which is presumably a PU layer formed by interfacial polymerization, also increased. The outer wall is most likely a UF layer formed by the in situ polymerization reaction; the thickness

of this outer wall does not change within observational scatter (Figure 4). In contrast, the UF EPA capsules show only one capsule wall. Additional images for PU/UF EPA capsules with varying amounts of PU are provided in the Supporting Information (Figure S1).

Thermogravimetric Analysis. The thermal stability of PU/UF EPA capsules was analyzed by TGA. Onset temperatures of mass loss for these capsules in a dynamic experiment were higher than UF EPA capsules (see the Supporting Information, Figure S2). The fill content of microcapsules from dynamic TGA experiments can be determined, and assuming the mass of the shell wall is negligible, the mass loss for these capsules is >90%. This behavior is consistent from batch to batch of UF EPA microcapsules and PU/UF EPA microcapsules. To demonstrate the long-term stability of these capsules at room temperature, we tested UF and PU/UF EPA capsules after 1 year (Figure S2). Both capsules absorbed water as evidenced from the initial mass loss around 100 °C. The PU/UF EPA capsules are still more stable over time since the sharp drop in mass loss occurs at a temperature close to the boiling point of EPA, whereas the UF EPA capsules show a gradual mass loss at elevated temperatures. A similar analysis of capsule quality was performed on DCPD capsules in Blaiszik et al. (26).

However, a dynamic TGA experiment does not provide data on the amount of core mass lost when the capsules are exposed to high temperatures for an extended period of time. Thus, the better experiment to simulate capsule stability during commercial polymer processing was an isothermal protocol in which the temperature was ramped from room temperature to 180 °C and then held constant at 180 °C for 2 h. Representative traces for EPA capsules are shown
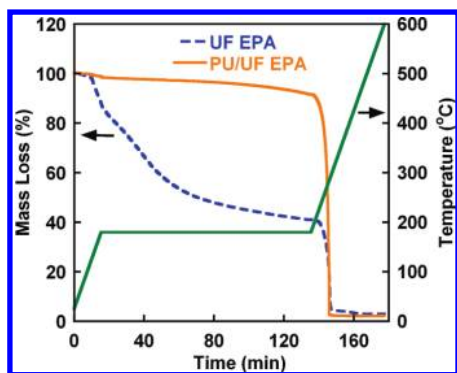
FIGURE 5. Representative isothermal TGA curves for UF EPA capsules (dashed line) and PU/UF EPA capsules (solid line) plotted versus the temperature profile (25 to 180 °C at 10 °C min⁻¹), held at 180 °C for 2 h, and then heated from 180−600 at 10 °C min⁻¹). The average diameter of the capsules tested was 150 μm and 1.5 g of PU was added to the PU/UF capsules.
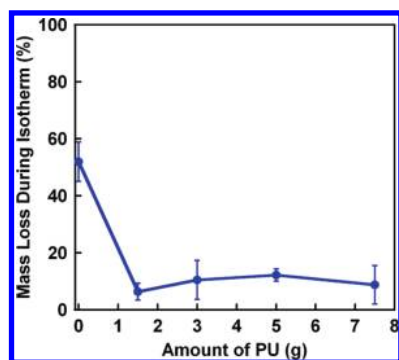

FIGURE 6. Average mass loss during a 2 h isothermal TGA at 180 °C for EPA microcapsules (average capsule diameter = 50 μm) with varying amounts of PU. The average value is plotted from 2−3 independent runs and error bars indicate one standard deviation.

in Figure 5. UF capsules (made without the addition of PU) lost a significant amount of mass (ca. 60%) during the 2 h isotherm, while the PU/UF capsules lost only ca. 10%. This dramatic improvement in thermal stability was also analyzed as a function of PU added to the core liquid and is summarized in Figure 6 for the PU/UF EPA capsules prepared. The data point for 0 g PU added to the core is shown as a control. Capsule size was not observed to affect the mass percent lost during these isothermal experiments (see Supporting Information, Table S1).

Microcapsule Mechanical Compression Testing.
The mechanical properties of capsule shell walls have been determined through single-capsule compression experiments for polyurethane (21, 27), melamine-formaldehyde (28), gelatin (29), and urea-formaldehyde (23, 29) microcapsules. Following the same procedure as described in Keller et al. (23), single microcapsules were compressed between parallel plates and the load vs displacement data was acquired until capsule rupture occurred. A representative plot for a UF EPA capsule (dashed line) and a PU/UF EPA capsule (solid line) is shown in Figure 7a. When capsules of similar diameter are compared, the PU/UF EPA capsules had higher loads to failure than the UF capsules. Furthermore, as the amount of PU added to the EPA core increased and average capsule diameter was held constant, the failure strength also increased (Figure 7b). The dashed line on the plot indicates the failure strength of UF DCPD capsules tested by Keller et al. at a similar capsule diameter (23). A summary of all results for EPA capsules tested at different diameters with a constant amount of PU added to the core (1.5 g for EPA) is given in the Supporting Information (Table S2). The normalized failure strength decreased as capsule diameter increased, which corresponds to the trend observed in prior compression studies (29).

CONCLUSIONS

A modified encapsulation procedure that combines the interfacial polymerization of PU and the in situ polymerization of UF was used to prepare liquid-filled microcapsules with two distinct shell walls. The commercial polyurethane prepolymer (Desmodur L 75) was dissolved in the EPA core liquid prior to adding this mixture to the aqueous phase during the encapsulation procedure. TGA analysis of these double-walled microcapsules showed improved stability at high temperatures (180 °C for 2 h) compared to single-walled microcapsules with the same core liquid. Additionally, the second inner shell wall leads to PU/UF EPA microcapsules with improved mechanical properties as evidenced by capsule compression studies. At this point, the exact chemistry of the inner capsule wall is unknown and its further characterization is the subject of future work in our laboratory. Nevertheless, this modified encapsulation method may be extended to a variety of core liquids or prepolymers, and will be useful for maintaining capsule integrity when added to polymers that are subsequently cured or processed
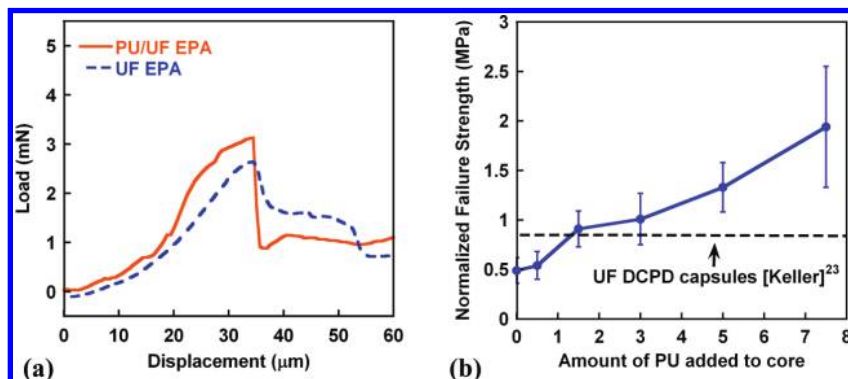

FIGURE 7. (a) Representative load−displacement curves for single-capsule compression testing of EPA capsules. The average capsule diameter size was 125 ± 15 μm and the PU/UF EPA contained 1.5 g of PU. (b) Normalized failure strength of EPA capsules as a function of the amount of PU added to the core material. The average capsule diameter size was 57 ± 3 μm for the results shown.

at higher temperatures than room-temperature epoxy systems, thus expanding the scope of self-healing polymers.

Supporting Information Available: Additional AFM images, TGA curves, shell thickness measurements, and results from capsule compression in a tabular format (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Fried, J. R. *Polymer Science and Technology*, 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 2003.
(2) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. *Chem. Rev.* **2009**, *109*, 5755–5798.
(3) White, S. R.; Caruso, M. M.; Moore, J. S. *MRS Bull.* **2008**, *33*, 766–769.
(4) Caruso, M. M.; Delafuente, D. A.; Ho, V.; Sottos, N. R.; Moore, J. S.; White, S. R. *Macromolecules* **2007**, *40*, 8830–8832.
(5) Brown, E. N.; Kessler, M. R.; Sottos, N. R.; White, S. R. *J. Microencapsulation* **2003**, *20*, 719–730.
(6) White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. *Nature* **2001**, *409*, 794–797.
(7) Blaiszik, B. J. Ph. D. Thesis, University of Illinois at Urbana−Champaign, Urbana, IL, 2009.
(8) Cho, S. H.; Andersson, H. M.; White, S. R.; Sottos, N. R.; Braun, P. V. *Adv. Mater.* **2006**, *18*, 997–1000.
(9) Keller, M. W.; White, S. R.; Sottos, N. R. *Adv. Funct. Mater.* **2007**, *17*, 2399–2404.
(10) Wilson, G. O.; Moore, J. S.; White, S. R.; Sottos, N. R.; Andersson, H. M. *Adv. Funct. Mater.* **2008**, *18*, 44–52.
(11) Brown, E. N.; Sottos, N. R.; White, S. R. *Exp. Mech.* **2002**, *42*, 372–379.
(12) Brown, E. N.; White, S. R.; Sottos, N. R. *J. Mater. Sci.* **2004**, *39*, 1703–1710.
(13) Kessler, M. R.; Sottos, N. R.; White, S. R. *Compos., Part A* **2003**, *34*, 743–753.
(14) Beiermann, B. A.; Keller, M. W.; Sottos, N. R. *Smart Mater. Struct.* **2009**, *18*, 085001−7.
(15) Cho, S. H.; White, S. R.; Braun, P. V. *Adv. Mater.* **2009**, *21*, 645–649.
(16) Kamphaus, J. M. Ph.D. Thesis, University of Illinois at Urbana−Champaign, Urbana, IL, 2007.
(17) Kamphaus, J. M.; Rule, J. D.; Moore, J. S.; Sottos, N. R.; White, S. R. *J. R. Soc. Interface* **2008**, *5*, 95–103.
(18) Caruso, M. M.; Blaiszik, B. J.; White, S. R.; Sottos, N. R.; Moore, J. S. *Adv. Funct. Mater.* **2008**, *18*, 1898–1904.
(19) Li, G.; Feng, Y.; Gao, P.; Li, X. *Polym. Bull.* **2008**, *60*, 725–731.
(20) Watanabe, A.; Hayashi, T. *Microencapsulation Techniques of Fuji Photo Film Co. Ltd., and Their Applications*; Dekker: New York, 1976.
(21) Yang, J.; Keller, M. W.; Moore, J. S.; White, S. R.; Sottos, N. R. *Macromolecules* **2008**, *41*, 9650–9655.
(22) Blaiszik, B. J.; Caruso, M. M.; McIlroy, D. A.; Moore, J. S.; White, S. R.; Sottos, N. R. *Polymer* **2009**, *50*, 990–997.
(23) Keller, M. W.; Sottos, N. R. *Exp. Mech.* **2006**, *46*, 725–733.
(24) Benita, S., Ed. *Microencapsulation: Methods and Industrial Applications*, 2nd ed.; Informa Healthcare: New York, 2005.
(25) Kondo, A. *Microcapsule Processing and Technology*; Dekker: New York, 1979.
(26) Blaiszik, B. J.; Sottos, N. R.; White, S. R. *Compos. Sci. Technol.* **2008**, *68*, 978–986.
(27) Liu, K. K.; Williams, D. R.; Briscoe, B. J. *Phys. Rev. E.* **1996**, *54*, 6673–6680.
(28) Zhang, Z.; Saunders, R.; Thomas, C. R. *J. Microencapsulation* **1999**, *16*, 117–124.
(29) Sun, G.; Zhang, Z. *Int. J. Pharm.* **2002**, *242*, 307–311.

AM100084K