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Microencapsulation of a Reactive Liquid-Phase Amine for Self-Healing Epoxy Composites

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ABSTRACT: A method was developed for the preparation of microcapsules containing a reactive amine with potential applications in self-healing polymers. Amine core microcapsules were prepared by interfacial polymerization of an isocyanate and an amine stabilized by an inverse Pickering emulsion. Microcapsules were successfully isolated, dried, and redispersed in epoxy. Visualization of capsules in cured epoxy was carried out by the addition of fluorescent dye to the core material. Mass spectrometry of capsule core material indicated the presence of the desired starting material. Fill content was estimated at 55 wt % by thermogravimetric analysis, and titration of the capsule core material gave an amine equivalent weight of 254 g/mol NH_2. Capsules released the core material upon rupture and were able to cure epoxy to form a polymer film.

Introduction

Active materials incorporating self-healing functionality have been recently reported in the literature.[1−12] The first generation of microcapsule based self-healing polymers focused on a two-part system consisting of solid Grubbs' catalyst and microencapsulated *endo*-dicyclopentadiene (DCPD). This system utilizes ring-opening metathesis polymerization (ROMP) to rebond the faces of an epoxy specimen. Over 90% of the original material's fracture toughness, as assessed by K_{IC} measurements, is restored,[4] even though bonding between the substrate and the poly(DCPD) is not optimal. Microencapsulation of several other healing agents has also been employed, including a solvent-based approach to form new chemical bonds.[2] However, this approach requires chain mobility within the solid substrate that is enhanced by solvent diffusion and a substantially undercured resin to allow for mobility and further cross-linking to occur.

Several methods of microencapsulation have been reported in the literature. Capsule wall formation is typically achieved by condensation polymerization of monomers,[13,14] complex coacervation of large molecules,[15] or precipitation of polymer at an interface.[16] Microencapsulation of epoxy resin[17−20] and epoxy resins with a solvent[21] is a fundamental step toward self-healing in thermoset epoxies. Rosenbauer recently demonstrated a means of using interfacial polymerization of isocyanate and amine in a reverse-phase emulsion[22] to encapsulate a phosphate buffered saline solution and magnetite particles.

Much of the work in self-healing materials has focused on binary systems. In each of these systems, two components meet in the damage region and react, triggering the healing response. Microcapsules comprising the DCPD/Grubbs' system[13] and a siloxane-based system[3,23] have been extensively studied. Other binary self-healing techniques incorporate impregnated hollow glass fibers or embedded microchannels containing a vasculature of reactive monomer.[6,7,24−27] Because of the robustness of the microvascular preparation, a larger library of monomers, including reactive amines, may be employed in the vascular systems than has previously been possible in microencapsulated preparations.

Preparation of amine-containing microcapsules enables the creation of self-healing epoxies in which the microencapsulated healing agents contain the same chemistry as the bulk matrix. Motivated by this objective, we explore microencapsulation strategies to form a polymer shell around a reactive amine to produce a microencapsulated curing agent for epoxide-functionalized healing agents. Previous efforts to encapsulate curing agents has been met with some success: Zhang et al. reported on the encapsulation of a mercaptan and imidazole-based curing agent.[11,17,28] Drawing on work in water-in-oil and oil-in-oil emulsion stabilization,[29,30] we establish a protocol for interfacial polymerization of a small-molecule polyamine with a small-molecule diisocyanate to create a cross-linked polymer shell around an amine-containing core.

Experimental Section

Materials. Diethylenetriamine (DETA) was used as received from Air Products. Epon Resin 828 was used as received from Miller-Stephenson. DEH-52 curing agent, an adduct of Epon Resin 828 and DETA, was used as received from Dow Chemical. Toluene diisocyanate (TDI), decalin, Span 85, and polyisobutylene (PIB) were used as received from Sigma-Aldrich. Cloisite 20A nanoclay was used as received from Southern Clay Products. Rhodamine B was purchased as "FLT Industrial Red Dye" from Kingscote Chemicals.

Experimental Methods and Instrumentation. A stock suspension of 5 pph nanoclay in decalin was prepared, and the nanoclay was dispersed by sonication for 60 min in a water bath. Likewise, 40 g of PIB was added to 200 mL of decalin to form a 20 pph stock solution of PIB in decalin. The reactive core material was prepared as a 33 pph solution of DETA in DEH-52.

The water-in-oil emulsion was prepared by adding 5 g of the nanoclay suspension, 10 g each of the PIB stock and core stock, and 30 g of decalin and emulsifying at 1500 rpm with a Caframo digital mixer with a three-blade agitator for 10 min.

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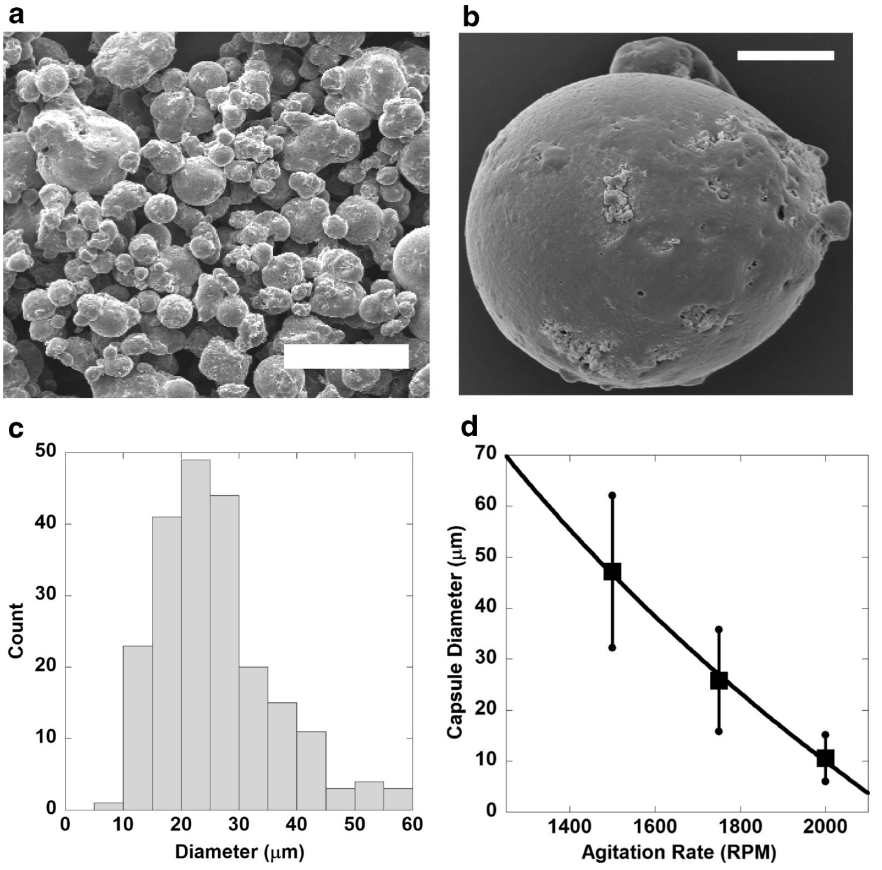

Figure 1. (a) Electron micrograph of dried amine-filled capsules prepared at 1750 rpm. The scale bar is 50 μm. (b) Electron micrograph of a single capsule showing small adhesions to an overall spherical capsule. The scale bar is 10 μm. (c) Size distribution of microcapsules prepared at 1750 rpm. Average capsule diameter is 26 ± 10 μm. (d) Plot of size distributions by agitation rate. Increased agitation rate results in smaller microcapsule diameter. Error bars correspond to 1 SD of the data.

The shell-forming reaction was carried out by syringe pump injection of 20 mL of a 20 wt % solution of TDI in decalin at 0.5 mL/min. The polyurea condensation was allowed to proceed at room temperature with continued agitation for 72 h.

Following shell wall synthesis, the capsules were rinsed in decalin to remove excess polyisobutylene, rinsed in ethyl acetate to coacervate the polyisobutylene chains, and subsequently decanted and freeze-dried to remove any remaining solvent. The capsules were recovered by this method in excess of 80% yield based on total capsule weight relative to the amine weight. Capsules were then analyzed by optical microscopy, thermogravimetric analysis, electrospray ionization−mass spectrometry, and scanning electron microscopy.

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851^e, calibrated by indium, aluminum, and zinc standards. Unless otherwise indicated, a heating rate of 10 °C/min was used in an atmosphere of nitrogen. For each experiment, ~5 mg of sample were accurately weighed (±0.02 mg) into an alumina crucible. The mass loss was recorded during a heating cycle over the temperature range of 25−650 °C.

Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC821^e using a nitrogen atmosphere to measure heat flow (positive exothermal) from 25 to 400 °C at a heating rate of 10 °C/min.

Mass spectrometry (EI-MS) was performed by electrospray ionization on a 70-VSE through the Mass Spectrometry Facility, SCS, University of Illinois.

Scanning electron micrography (SEM) was performed on Au/Pd sputter-coated samples on a Philips XL-30 FEG at the Imaging Technology Group at the Beckman Institute.

Optical micrographs were acquired by Micropublisher CCD camera with fluorescence and analyzed using NIH ImageJ software.

Solution viscosity was measured by a TA Instruments AR-G2 rheometer with 25 mm diameter aluminum parallel plate geometry at 200% strain in an oscillation frequency sweep from 0.1 to 100 Hz (see Supporting Information).

Titration experiments were performed using a 100 μL Hamilton syringe containing 1.000 N HCl solution from Fisher Scientific. Bromothymol blue was used as the indicator.

Results and Discussion

Reverse Emulsion Stabilization. Stabilization of an inverse emulsion presents a challenge in microcapsule synthesis. Initial work focused on chemical surfactants, such as the sorbitol-based Span series,[29] which were unable to provide the necessary structural stability to prevent emulsified droplets from joining in solution rather than forming a stable microcapsule system. Span 85 was used to create an emulsion that appeared stable; however, when TDI was added, stable microcapsules were not formed. In order to provide the necessary stabilization, we adopted a hydrophobically modified nanoclay to form a Pickering emulsion at the polar−nonpolar boundary. Because the nanoclay platelets are several orders of magnitude larger than a chemical surfactant, their presence at the polar−nonpolar interface provided for excellent droplet stabilization.[30]

Wall Polymerization Rate. The reaction rate between shell wall components is critical to the formation of stable microcapsules. TDI is a highly reactive industrial chemical used in the synthesis of polyurethanes. TDI reacts readily with amines at room temperature to form polyureas. The reaction rate of isocyanates with amines is much faster than the rate of isocyanates with alcohols or water;[31] this results in complete

consumption of TDI and polyurea formation at the interface. Bolus addition of TDI to the emulsion was unsuccessful, whereas gradual addition of a TDI solution permitted oligomer formation and precipitation at the emulsion interface, subsequently leading to solidification of the polyurea wall around the amine core. We hypothesize that a single large delivery of TDI caused the emulsified droplets to coalesce, whereas slow addition permitted shell formation. Amine-terminated oligomer formation is stoichiometrically limited in favor of high molecular weight condensation polymerization.

Microcapsule Size Distribution. The prepared microcapsules were examined by optical and electron microscopy (Figure 1). Electron micrographs showed the capsules to be spheroid with some slight irregularities due to the platelet aspect of the nanoclay incorporated in the wall (Figure 1b). The mean capsule diameter, measured by electron microscopy, was $26 \pm 10\,\mu$m (Figure 1a), and a distribution of sizes is given in Figure 1c.

Typically, microcapsule diameter is influenced by agitation rate (Figure 1d).[1,32] Compared to previous work with a less viscous solution,[32] these capsules are several times larger at 1500 rpm but exhibit similar size to previous capsules prepared at higher speeds. This is likely due to a shear thinning of the continuous phase. Furthermore, because of the increased viscosity of the continuous phase, a critical stir rate exists for our system. Stirring at speeds slower than 1000 rpm did not distribute the isocyanate efficiently through the reaction beaker, causing clumping of soft capsules and precipitation of irregular, semisolid material. Agitation rates between 1250 and 2000 rpm had a moderate effect on mean capsule diameter. Viscosity of the stock solution was also critical to capsule formation.[33] When insufficient PIB was added to the emulsion (less than 1.5 g), no microcapsules formed. Instead, bulk polymer was collected from the reaction vessel. Rheological testing of the stock solution gave a viscosity of 15 400 cP at 25 Hz oscillation, corresponding to the 1500 rpm stir rate. Thus, the solution viscosity is substantially elevated relative to neat decalin, resulting in extended lifetime for the emulsion droplets.

Microscopy of Prepared Microcapsules. Capsules were examined by optical microscopy. Capsules were generally spheroid, with significant adhesions resulting in shape irregularity (Figure 2a). After drying, capsules could be ruptured by applying force to a coverslip. Capsule rupture caused an observable release of core liquid. Additional syntheses were performed with rhodamine B dye incorporated in the amine core phase. The dye was sequestered to the shell wall, as observed under fluorescence. When force was applied to the dyed capsules, a substantial amount of core material was released as evidenced by a layer of viscous liquid surrounding the fluorescent shell wall (Figure 2b).

Capsule Analysis. Capsule fill content was assessed by thermogravimetric analysis (Figure 3). The stock solution used for the encapsulation showed two distinct weight loss peaks corresponding to DETA and the oligomeric component of DEH-52 (Figure 3a). Thermal analysis of the microcapsules (Figure 3b) and differential thermal analysis (Figure 3c) have clearly resolved peaks matching the stock DETA and DEH-52.

Significant weight loss was also seen corresponding to the polyurea wall material (onset 230 °C, 42%). The residual mass of 6% at elevated temperatures corresponds to inorganic clay and reduced carbon. The capsules were found to be 55 mass % reactive amine core material. Future refinement of the technique will reduce the wall material and enhance the mass fill content.

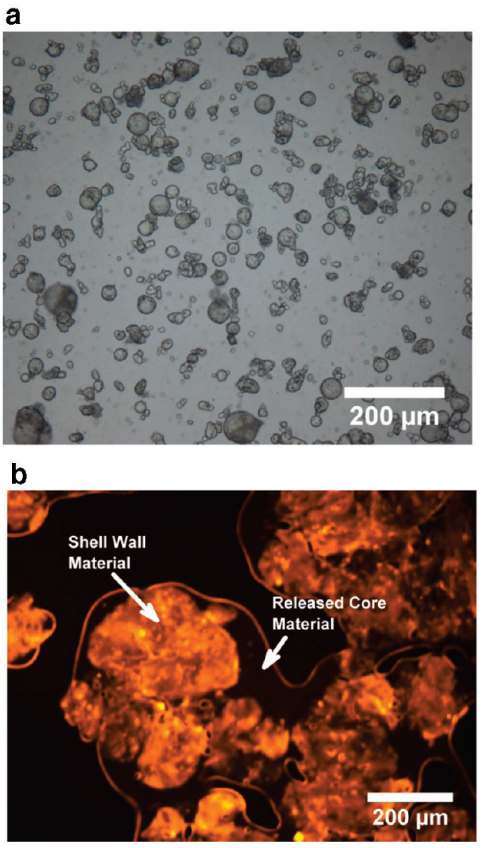

Figure 2. (a) Optical micrograph of capsules in solution illustrating typical shape and adhesions between formed capsules. (b) Fluorescence micrograph illustrating release of core material from within dry capsules following applied pressure.

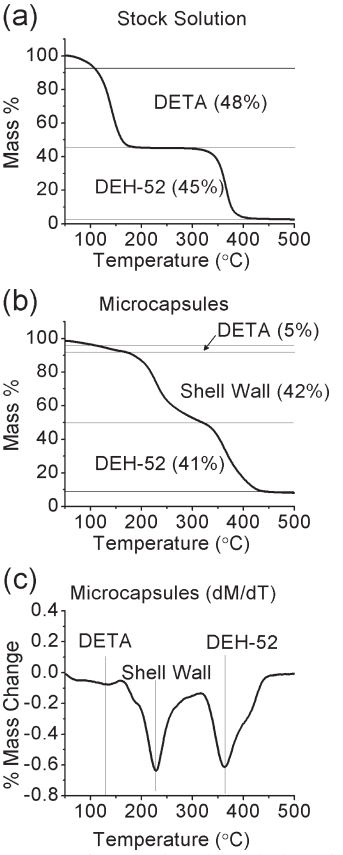

Figure 3. Thermograms of (a) stock amine solution, (b) microcapsules, and (c) differential thermal analysis of microcapsules.

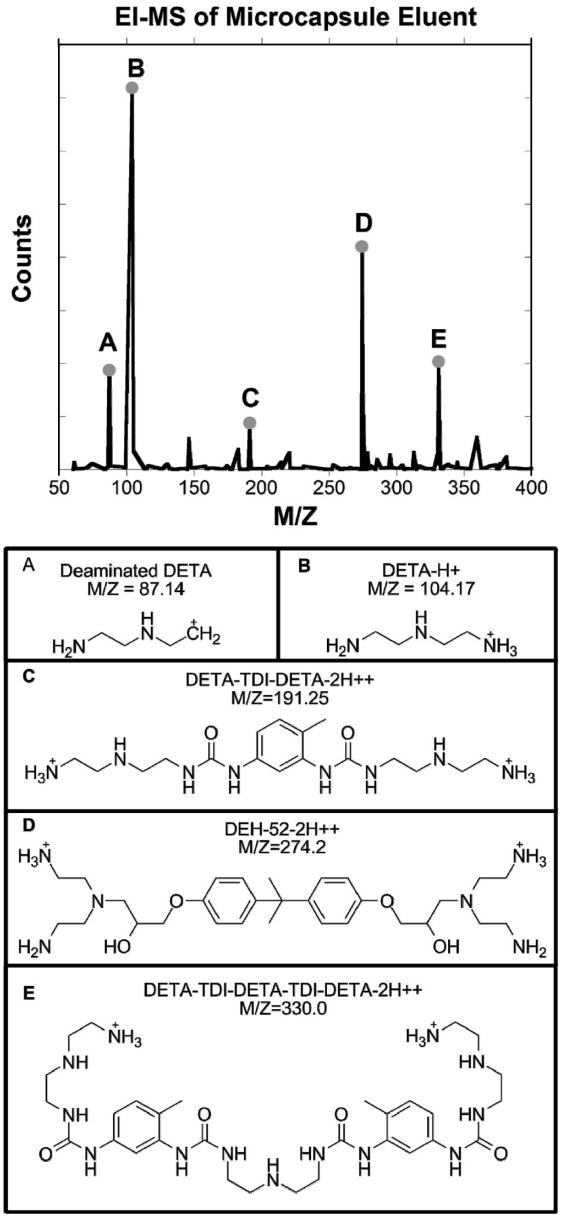

Figure 4. Electrospray mass spectrum with identified peaks.

Mass spectroscopy by electron ionization was performed to determine the contents of the microcapsules (Figure 4). Results indicated the presence of DETA, DEH-52, and TDI-DETA oligomers. These data further indicate that a reaction between DETA and TDI has occurred to create amine-terminated oligomers and that residual DEH-52 and DETA have been incorporated in the core material, with no remaining TDI in the product.

Reactivity of Core Material. Capsules were crushed with a mortar and pestle and were added to neat Epon 828 resin at a 1:1 mass ratio. The resulting slurry was then placed between two glass slides. After resting 72 h at room temperature, the slides could not be manually separated by shear, indicating that a reaction had taken place between ruptured core material and the epoxy resin. In contrast, control slides with only epoxy resin were easily separated and no film was present. Control slides where only amine microcapsules were ruptured under pressure also did not form a solid film.

The slides coated with cured material were separated with a razor blade. Optical microscopy of the film showed no remnant capsules and no discrete fluorescence. A 72 h/100 °C cure cycle was employed to prepare a second film between octadecyltrichlorosilane-treated glass slides (Figure 5) for improved visualization.[34]

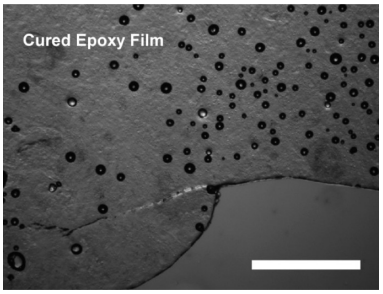

Figure 5. Film of Epon 828 cured by crushed microcapsules. Spherical regions are voids in the film. Scale bar 500 μm.

In a second experiment, the capsules were allowed to osmotically rupture by suspension in water for 1 week, eluting the core material into the aqueous layer since both DETA and DEH-52 are soluble in water. The solution was then filtered and titrated with acid to determine an amine equivalent weight (AEW) of 254 g capsules/mol NH_2. This result indicates a capsule fill ratio of 35 wt %, which is lower than that measured by TGA, suggesting that some residual DEH may have remained in the capsules or had been inadvertently protonated during the digestion, and therefore the actual AEW may be slightly lower than that determined by this process. We note that digestion in acid and back-titration against a base is undesirable due to the potential hydrolysis of the polyurea shell, resulting in a lower AEW than is actually present.

To further determine capsule loading fraction of the core mixture, dynamic DSC was employed to measure the degree of cure ($\alpha = \Delta H/\Delta H_{tot}$)[35] of an epoxy sample loaded with microcapsules. The neat DEH-52/DETA mixture used as core material was used as a control (40 pph in Epon 828, 100% cure at 250 °C). Microcapsules were ground with a mortar and pestle, then delivered into Epon 828 at 40 pph, and evaluated immediately by DSC. The degree of cure as measured by heat evolution was 20.8 ± 5.3%, indicating that the microcapsules are 20% efficient at curing epoxy compared to the neat core material. Refer to Supporting Information for curves.

While DETA and DEH-52 compounds are intended to be used at 12 parts per hundred resin (phr)[36] and 25 phr,[37] respectively, with AEWs of 34 g/mol NH_2 and 90 g/mol NH_2, the AEW measured of our microcapsules is substantially higher. By extrapolating the AEWs of DETA and DEH-52 and applying them to published cure cycles,[36,37] we determine that a nearly 1:1 capsule:resin ratio is required for the optimum stoichiometry of the cured material. Successive generations of this encapsulation strategy will focus on decreasing the AEW of the encapsulated system to improve efficiency and decrease required microcapsule loading levels for effective self-healing.

Conclusions

A method for preparation of microcapsules containing reactive amines has been developed. This method relies on physical stabilization of emulsion droplets for wall formation and utilizes the rapid condensation of isocyanate with amine to form a stable shell wall. A reverse-phase emulsion was employed to create discrete amine droplets and interfacial polymerization occurred at the droplet−oil interface. Capsules were determined to contain amine by titration, TGA, and qualitative curing of epoxy resin. Cured adhesive films were formed from the reaction of microcapsules with epoxy resin. Studies are underway to employ these

capsules for application in self-healing systems for epoxy composites.

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Supporting Information Available: Synthesis solution rheology, emulsion preparation flowchart, summary of experiments performed, and representative DSC thermograms. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Blaiszik, B. J.; Sottos, N. R.; White, S. R. *Compos. Sci. Technol.* **2008**, *68* (3−4), 978–986.
(2) Caruso, M. M.; Blaiszik, B. J.; White, S. R.; Sottos, N. R.; Moore, J. S. *Adv. Funct. Mater.* **2008**, *18* (13), 1898–1904.
(3) Keller, M. W.; White, S. R.; Sottos, N. R. *Adv. Funct. Mater.* **2007**, *17*, 2399–2404.
(4) Kessler, M. R.; Sottos, N. R.; White, S. R. *Composites Part A* **2003**, *34* (8), 743–753.
(5) Sottos, N.; White, S.; Bond, I. *J. R. Soc. Interface* **2007**, *4* (13), 347–348.
(6) Toohey, K. S.; Hansen, C. J.; Lewis, J. A.; White, S. R.; Sottos, N. R. *Adv. Funct. Mater.* **2009**, *19* (9), 1399–1405.
(7) Toohey, K. S.; Sottos, N. R.; Lewis, J. A.; Moore, J. S.; White, S. R. *Nat. Mater.* **2007**, *6*, 581–585.
(8) White, S. R.; Caruso, M. M.; Moore, J. S. *MRS Bull.* **2008**, *33* (8), 766–769.
(9) Wilson, G. O.; Moore, J. S.; White, S. R.; Sottos, N. R.; Andersson, H. M. *Adv. Funct. Mater.* **2008**, *18* (1), 44–52.
(10) Yin, T.; Rong, M. Z.; Zhang, M. Q.; Yang, G. C. *Compos. Sci. Technol.* **2007**, *67* (2), 201–212.
(11) Yuan, Y. C.; Rong, M. Z.; Zhang, M. Q. *Polymer* **2008**, *49* (10), 2531–2541.
(12) Yuan, Y. C.; Rong, M. Z.; Zhang, M. Q. *Acta Polym. Sin.* **2008**, *5*, 472–480.
(13) 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* (6822), 794–797.
(14) Hoshi, Y. M. Hiroharu US 4,221,710. 4221710, Sep 9, 1980.
(15) Hiestand, E. N. US Pat. 3,539,465. 3,539,465, Nov 10, 1970.
(16) Vassilades, A. E. US 3,418,656. 3,418,656, **1965**.
(17) Rong, M. Z.; Zhang, M. Q.; Zhang, W. *Adv. Compos. Lett.* **2007**, *16* (5), 167–172.
(18) Yuan, L.; Gu, A. J.; Liang, G. Z. *Mater. Chem. Phys.* **2008**, *110* (2−3), 417–425.
(19) Yuan, L.; Liang, G. Z.; Xie, J. Q.; Li, L.; Guo, J. *J. Mater. Sci.* **2007**, *42* (12), 4390–4397.
(20) Cosco, S.; Ambrogi, V.; Musto, P.; Carfagna, C. *J. Appl. Polym. Sci.* **2007**, *105* (3), 1400–1411.
(21) Blaiszik, B. J.; Caruso, M. M.; McIlroy, D. A.; Moore, J. S.; White, S. R.; Sottos, N. R. *Polymer* **2009**, *50* (4), 990–997.
(22) Rosenbauer, E.-M.; Landfester, K.; Musyanovych, A. *Langmuir* **2009**.
(23) Keller, M. W.; Sottos, N. R. *Exp. Mech.* **2006**, *46* (6), 725–733.
(24) Trask, R. S.; Williams, G. J.; Bond, I. P. *J. R. Soc. Interface* **2007**, *4* (13), 363–371.
(25) Trask, R. S.; Williams, H. R.; Bond, I. P. *Bioinspiration Biomimetics* **2007**, *2* (1), P1–P9.
(26) Trask, R. S.; Bond, I. P. *Smart Mater. Struct.* **2006**, *15* (3), 704–710.
(27) Pang, J. W. C.; Bond, I. P. *Compos. Sci. Technol.* **2005**, *65* (11−12), 1791–1799.
(28) Yuan, Y. C.; Rong, M. Z.; Zhang, M. Q.; Chen, J.; Yang, G. C.; Li, X. M. *Macromolecules* **2008**, *41* (14), 5197–5202.
(29) Kobaslija, M.; McQuade, D. T. *Macromolecules* **2006**, *39* (19), 6371–6375.
(30) Voorn, D. J.; Ming, W.; van Herk, A. M. *Macromolecules* **2006**, *39* (6), 2137–2143.
(31) Lu, Q. W.; Hoye, T. R.; Macosko, C. W. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (14), 2310–2328.
(32) Brown, E. N.; Kessler, M. R.; Sottos, N. R.; White, S. R. *J. Microencapsulation* **2003**, *20* (6), 719–730.
(33) Thomasin, C.; Merkle, H. P.; Gander, B. *J. Pharm. Sci.* **1998**, *87* (3), 269–275.
(34) Sha, Y.; Hui, C. Y.; Kramer, E. J.; Hahn, S. F.; Berglund, C. A. *Macromolecules* **1996**, *29* (13), 4728–4736.
(35) Kessler, M. R.; White, S. R. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (14), 2373–2383.
(36) Hexion Epon Resin 828 Technical Bulletin, Sept **2005**.
(37) Dow DEH-52 Technical Bulletin, 296-01539.