# Microcapsules filled with reactive solutions for self-healing materials

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## ARTICLE INFO

## ABSTRACT

Microcapsules containing a solvent and reactive epoxy resin are a critical component for the development of cost-effective, low toxicity, and low flammability self-healing materials. We report a robust *in situ* encapsulation method for protection of a variety of oil soluble solvents and reactive epoxy resins surrounded by a thin, polymeric, urea–formaldehyde (UF) shell. Resin–solvent capsules are produced in high yield with diameters ranging from 10 to 300 μm by controlling agitation rates. These capsules have a continuous inner shell wall and a rough exterior wall that promotes bonding to a polymer matrix. Capsules as small as 300 nm in diameter are achieved through sonication and stabilization procedures. The presence of both the epoxy resin and solvent core components is confirmed by differential scanning calorimetry (DSC) measurements, and the relative amount of epoxy and solvent in the liquid core is determined by thermogravimetric analysis (TGA). The capsules are shown to satisfy the requirements for use in self-healing materials including processing survivability, thermal stability, and efficient *in situ* rupture for delivery of healing agent.

## 1. Introduction

Microencapsulation enables compartmentalization of reactive components in a wide variety of applications ranging from fragrance and cosmetics to nutrient retention and advanced coatings [1–4]. The microencapsulation of active materials including epoxy resins [5,6], hardeners [7–9], and solvents [10,11] is of particular interest for capsular adhesives [8], protection of catalysts [12], and self-healing materials [13–28]. Microcapsules release their contents in response to a stimulus such as mechanical damage or through a controlled release process. A variety of polymerization procedures are available to create liquid-containing microcapsules [13,29–33].

Poly(urea-formaldehyde) (UF) microcapsules prepared by *in situ* polymerization of urea and formaldehyde meet the demanding criteria required for use in self-healing materials [13]. These criteria include excellent bonding to the matrix, sequestration of the healing monomer from the surrounding environment, and rupture and release of the monomer into the crack plane upon matrix damage.

Here we report on UF capsules containing epoxy resins and solvents for use in self-healing materials. Both Epon 828 (DGEBA) and Epon 862 (DGEBF) epoxide resins were encapsulated since they are two of the most common epoxides in commercial use [34]. Not all solvents are suitable as healing agents for self-healing materials. Solvents with dielectric constants ($\varepsilon$) between 5 and 38 are ideal [24,25]. Based on a screening of solvent $\varepsilon$ parameters, boiling points, and flash points (Table 1), the solvent chlorobenzene (ClB) and the less toxic, lower flammability solvents phenylacetate (PA) and ethyl phenylacetate (EPA) were chosen for encapsulation and use in solvent-promoted self-healing materials [25,35]. Using the microcapsules, as prepared in this paper, previous research has shown complete recovery of fracture toughness in an epoxy matrix [25].

## 2. Materials and methods

### 2.1. Microcapsule materials

Core materials used in the encapsulations included three solvents and two different epoxy resins. The solvents chlorobenzene, phenylacetate, and ethyl phenylacetate were obtained from Sigma–Aldrich and used as received. The reactive epoxy resins diglycidyl ether of bisphenol-A (DGEBA Epon 828 resin) and

**Table 1**
Critical parameters for solvents used in microcapsule core solutions.

| Solvent (abbr.) | Dielectric constant, $\varepsilon$ [36] | Boiling point (°C) [37] | Flash point (°C) [37] |
|---|---|---|---|
| Chlorobenzene (ClB) | 5.7 | 132 | 27 |
| Phenylacetate (PA) | 5.4 | 193 | 77 |
| Ethyl phenylacetate (EPA) | 5.3 | 226 | 101 |

diglycidyl ether of bisphenol-F (DGEBF Epon 862 resin) were obtained from Miller–Stephenson. Prior to encapsulation, each resin was diluted with one of the solvents to decrease the viscosity of the mixture. Structures of these core materials are shown in Fig. 1.
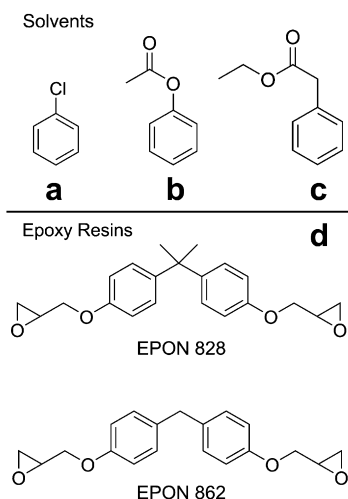
The microcapsule wall-forming materials, urea ($NH_2CONH_2$) and ammonium chloride ($NH_4Cl$), were purchased from Fisher Chemicals. Additional wall-forming materials formalin (37% formaldehyde in water) solution, and resorcinol ($C_6H_4$-1,3-$(OH)_2$) were purchased from Sigma–Aldrich. Ethylene–maleic anhydride copolymer (Zemac-400) powder of average molecular weight ($M_w = 400,000$) was provided by Zeeland Chemicals. As-received EMA powder was mixed overnight with deionized water in a warm bath to obtain a 2.5% (wt/vol) aqueous surfactant solution.
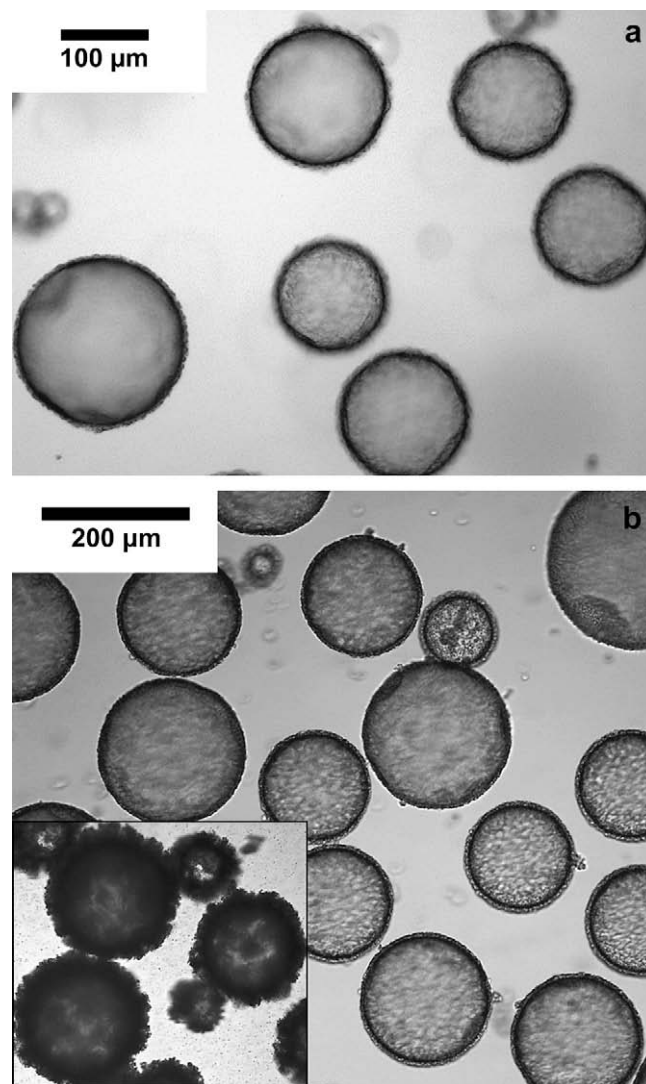
## 2.2. Epoxy matrix materials

Epon 828 resin cured with diethylenetriamine (DETA), obtained from Air Products, was chosen as the matrix. DETA and Epon 828 were mixed in the ratio of 12 pph DETA to Epon 828. Microcapsules were then stirred into the epoxy by hand and degassed to remove entrapped air. The matrix resin, containing microcapsules at various weight percentages, was poured into cylindrical molds (dimensions: $h = 16$ mm $d = 8$ mm). After curing for 24 h at room temperature and 24 h at 35 °C, the samples were frozen in liquid nitrogen and fractured with a razor blade to obtain a smooth fracture plane for imaging.

## 2.3. Thermal analysis

Thermogravimetric analysis (TGA) was performed on a Mettler–Toledo TGA851[e] using a nitrogen atmosphere and a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo DSC821[e] using a nitrogen atmosphere to



**Fig. 2.** Optical micrographs of capsules immersed in mineral oil showing (a) Epon 828–ClB capsules prepared at 400 RPM and (b) Epon 828–EPA capsules prepared at 275 RPM using improved solvent encapsulation method. (b – inset) Epon 828–EPA capsules with a thick layer of porous UF on the surface prepared at 275 RPM using standard UF encapsulation method (Table 2a) [13].

measure heat flow (positive exothermal) from 25 to 400 °C at a heating rate of 10 °C/min.

For core analysis, dried and sieved capsules were placed in a syringe filter (Millipore Millex®GP) attached to the end of a syringe. The syringe was depressed to crush the capsules, and the liquid contents of the microcapsules were collected in a vial and analyzed using TGA and DSC.

To obtain thermal stability curves, a mass of dried microcapsules (mean diameter ca. 180 µm) was measured in an alumina crucible. The sample mass was recorded during a heating cycle over the temperature range of 25–600 °C, with a 2 h isotherm at one of the specified temperatures of 100, 150, 180, and 210 °C. Sample mass loss was defined as the difference between the original mass of the sample and the mass after the isotherm.

## 2.4. Size distributions

Size distributions for capsules prepared using mechanical agitation were obtained from multiple optical images of dried



**Fig. 1.** Chemical structures of the solvents (a) chlorobenzene, (b) phenylacetate, (c) ethyl phenylacetate and the epoxy resins (d) Epon 828 DGEBA and Epon 862 DGEBF.

**Table 2**
(a) *In situ* UF microencapsulation techniques for encapsulation of DCPD compared to
(b) the technique used in this work for encapsulation of resin–solvent mixtures and
(c) for preparation of submicron capsules.

| Technique | Aqueous phase | Urea (g) | NH$_4$Cl (g) | Resorcinol (g) | Formalin (g) | pH |
|---|---|---|---|---|---|---|
| (a) Standard UF encapsulation [13] | 200 mL H$_2$0, 50 mL 2.5% EMA, 60 mL core | 5.0 | 0.5 | 0.5 | 12.7 | 3.5 |
| (b) Resin–solvent UF encapsulation (this research: 10–300 μm diameter microcapsule) | 100 mL H$_2$0, 25 mL 2.5% EMA, 60 mL core (epoxy + solvent) | 2.5 | 0.25 | 0.25 | 6.3 | 3.5 |
| (c) Resin–solvent UF submicron encapsulation (this research: 0.3–2 μm diameter capsules) | 10 mL H$_2$0, 20 mL 5.0% EMA, 5.45 mL core (epoxy + solvent + co-stabilizer) | 0.45 | 0.10 | 0.045 | 1.3 | ~2.3 |

capsules taken using a USAF 1951 calibrated camera (QImaging Micropublisher 3.3). Images of dried submicron capsules were taken using a SEM (FEI/Philips XL30 ESEM-FEG). Capsule diameter measurements were then obtained from the micrographs using ImageJ analysis software. A minimum of 50 measurements was made for each analysis.

## 2.5. Encapsulation procedure

Microcapsules containing a mixture of resin and solvent were prepared by an *in situ* urea–formaldehyde microencapsulation procedure. The encapsulation method was adapted from that of Brown et al. [13]. Without modification, the method of Brown et al. produced capsules with a thick layer of porous UF on the surface (Fig. 2b – inset). This thick layer of UF caused agglomerations in solution and after filtration when the core material was a solution of resin and solvent. The encapsulation shell wall materials and aqueous phase were then each decreased by half. This proportional decrease maintained the concentrations of the shell wall-forming materials in the aqueous solution while decreasing the overall mass of shell wall-forming materials in the solution. The two methods are compared in Table 2a,b.

For encapsulation of solvents, 100 mL of deionized H$_2$O at room temperature was placed in a 600 mL beaker, along with 25 mL of 2.5% (wt/vol) EMA as a surfactant. To the aqueous solution was added the solid wall-forming materials of 2.50 g urea, 0.25 g ammonium chloride, and 0.25 g resorcinol. After addition of the solid wall-forming materials, the pH was adjusted by addition of NaOH solution from approximately 2.7 to 3.5. The beaker was then placed in a temperature controlled water bath equipped with a mechanical stirring blade (40 mm diameter). The encapsulated phase was measured as 60 mL (epoxy resin + solvent), and dispersed in the beaker at a desired agitation rate for 10 min. After 10 min, 6.33 g of formalin solution was added, and the temperature was increased at a rate of 10 °C/min to 55 °C. The reaction proceeded under continuous agitation with the temperature held at 55 °C for 4 h. The fully formed microcapsules were recovered by filtration and subsequent air-drying after allowing the bath to cool for at least 6 h after completion of the reaction.

To prepare resin–solvent capsules smaller than 10 μm in diameter, sonication and other stabilization procedures, such as the addition of a co-stabilizer, were used to prepare a mini-emulsion of the resin–solvent core material [14,39,40]. A core solution of Epon 828, EPA, and optionally hexadecane was slowly added to an aqueous solution of water, EMA surfactant, urea, resorcinol and ammonium chloride as presented in Table 2c. The mixture was stirred at 800 RPM and the emulsion was allowed to equilibrate for 10 min before sonication. The tapered 1/8″ tip sonication horn of a 750-W ultrasonic homogenizer (Cole–Parmer) was placed in the solution for 3 min at 40% intensity with continuous mixing at 800 RPM. Formalin was then added to the aqueous phase. The temperature control bath was slowly heated and held constant for 4 h of reaction. At the completion of the reaction, the mechanical agitation and heating were stopped, and the pH was adjusted to 3.50 with sodium hydroxide. Further characterization of capsules prepared using this procedure, and a thorough description of the encapsulation procedure is available in a previous publication [14].

## 3. Results and discussion

Microcapsules were prepared using the resin–solvent encapsulation technique presented in Table 2a,b. In Fig. 2, optical micrographs of 15 pph Epon 828–ClB capsules prepared at 400 RPM are compared to 15 pph Epon 828–EPA capsules prepared
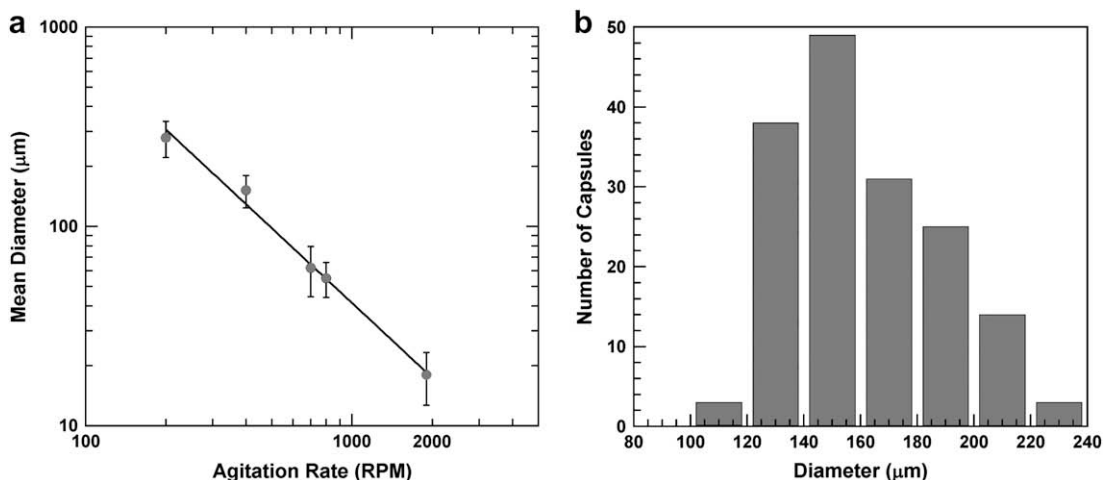


**Fig. 3.** (a) Mean diameter of 15 pph Epon 828–EPA microcapsules obtained by optical measurement as a function of stir rate. Vertical error bars represent one standard deviation. (b) Representative microcapsule diameter histogram showing the size distribution for 15 pph Epon 828–EPA capsules made at 400 RPM ($n = 163$).
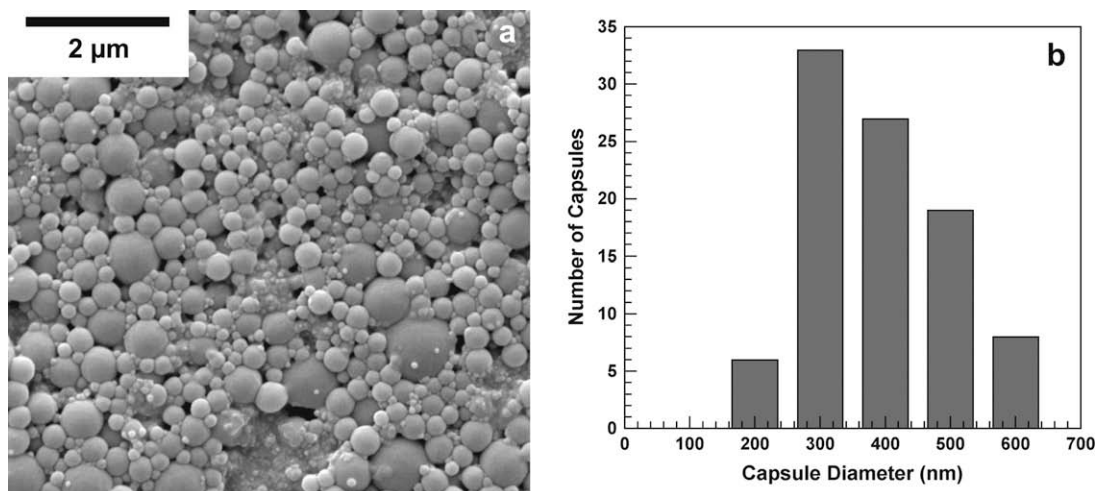
**Fig. 4.** (a) Submicron capsules of 15 pph Epon 828–EPA prepared using 5% hexadecane co-stabilizer using the procedure presented in Table 2c [14] (b) Representative histogram of capsule diameter for 15 pph Epon 828–EPA submicron capsules prepared using 5% hexadecane co-stabilizer.

at 275 RPM using the optimized solvent encapsulation technique (Table 2b) and the standard encapsulation technique (Table 2a). When using the optimized solvent encapsulation technique, microcapsule quality and surface morphology were consistent between the different resin–solvent combinations, and for varying stirring rates.

### 3.1. Microcapsule size and size distribution

Microcapsule size dependence on stir rate was investigated. Varying stir rates were used, and 15 pph epoxy concentration in the solvent was chosen in an effort to be consistent with the concentrations used by Caruso et al. in prior self-healing work [25]. As expected, the microcapsule size decreased with agitation rate, following a power law relationship as shown in Fig. 3a. This power law relationship reflects the dependence of droplet size on shear rate described previously by Taylor [38]. The size distribution of

capsules (Fig. 3b) exhibits the same asymmetric shift towards smaller capsule diameters caused by turbulent regions in the flow as noted by Brown et al. [13]. A representative size distribution for capsules with a core of 15 pph Epon 828–EPA prepared at a stir rate of 400 RPM is shown in Fig. 3b.

To obtain resin–solvent capsules below 10 μm, the sonication encapsulation technique described in Table 2c was used [14]. Using this method, submicron capsules with an average diameter of 295 (±140) nm were prepared using 5% hexadecane co-stabilizer and are shown in Fig. 4a. A representative diameter histogram of the capsules is shown in Fig. 4b.

### 3.2. Yield analysis

The yield was determined for multiple batches of each type of microcapsule. Microcapsule yield, shown in Fig. 5, was measured by the mass of capsules able to pass through a 500 μm sieve compared to the mass of solids used in the encapsulation (i.e. urea, resorcinol, $NH_4Cl$, formaldehyde, core weight). Microcapsule yield ranged from a low of 67.0% for 828-PA to a high of 98.6% for 862-EPA. The calculated yields and mean diameters of capsules containing different resin–solvent combinations are listed in Table 3.

### 3.3. Core and thermal analysis

Control of microcapsule core composition is critical for self-healing applications [25]. In particular, healing efficiency for solvent-based systems is a function of both the epoxy and the solvent delivered to the crack plane [25]. The presence of both
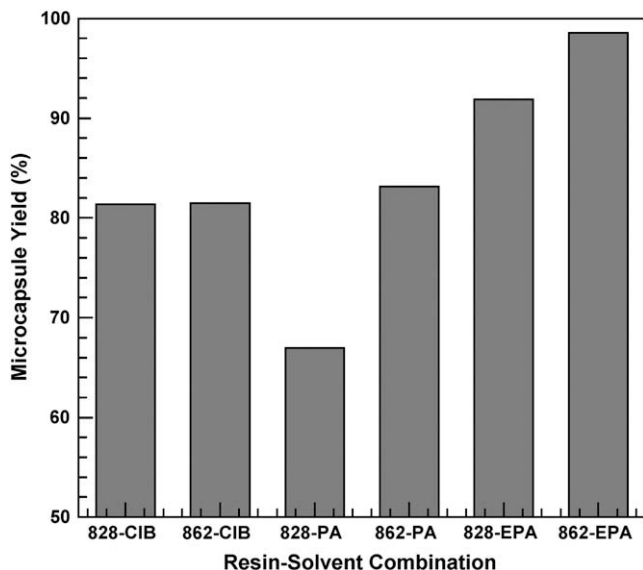


**Fig. 5.** Microcapsule yields for each resin–solvent combination for 15 pph resin core stirred at 300 RPM.

**Table 3**
Yield and mean diameter for each resin–solvent combination prepared with 15 pph resin and at an agitation rate of 300 RPM.

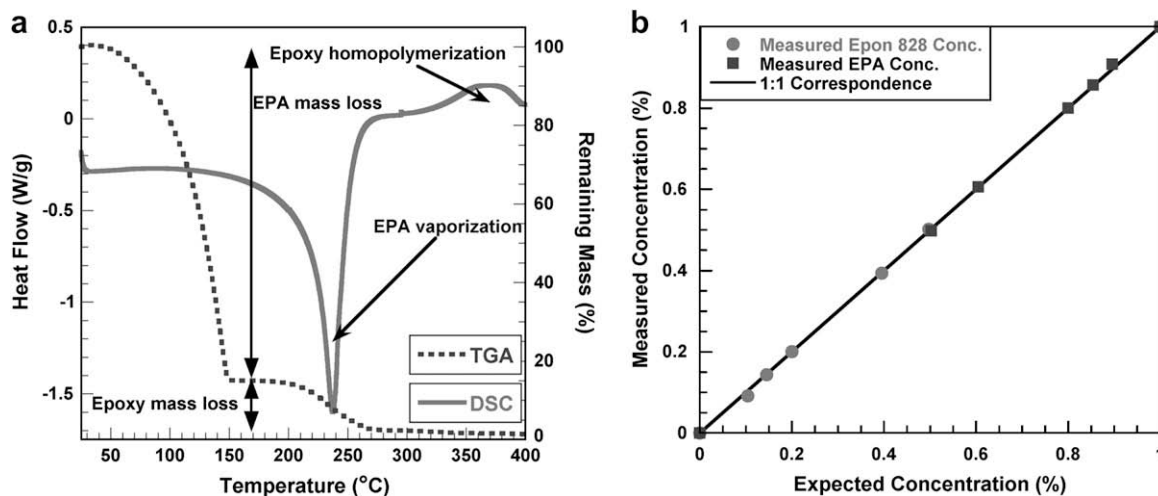| Capsule type Resin–solvent | Microcapsule yield (%) | Mean diameter (μm) ± standard deviation |
|---|---|---|
| Epon 828–ClB | 81.4 | 177 ± 61 |
| Epon 862–ClB | 81.5 | 142 ± 65 |
| Epon 828–PA | 67.0 | 161 ± 76 |
| Epon 862–PA | 83.2 | 127 ± 58 |
| Epon 828–EPA | 91.9 | 143 ± 82 |
| Epon 862–EPA | 98.6 | 112 ± 63 |

**Fig. 6.** (a) Representative DSC and TGA curves for 15 pph Epon 828–EPA extracted microcapsule core solution. (b) TGA determination of EPA and Epon 828 concentration in microcapsules as a function of expected concentrations.

components within the microcapsules was confirmed through examination by DSC, and the relative amounts of epoxy and solvent in the liquid core of these capsules were determined by TGA.

Representative DSC and TGA scans of the extracted microcapsule core are shown in Fig. 6a[1]. In the DSC experiments, we observed two distinct transitions which were characteristic of the epoxy resin and the solvent in the core of the microcapsules. The DSC plots contained an endothermic peak representing the evaporation of EPA (minimum ca. 240 °C) and an exothermic peak representing the homopolymerization of Epon 828 (maximum ca. 370 °C) [41]. To confirm that the epoxy to solvent ratio remained constant once the solutions were encapsulated, the relative mass ratios of epoxy resin to solvent were characterized by TGA. A series of capsule batches at different resin–solvent ratios were prepared and analyzed (Fig. 6b). Excellent agreement was obtained between the expected microcapsule core concentrations and the concentrations measured by TGA.

### 3.4. Thermal stability analysis

Thermal stability of the capsules was investigated by tracking the mass loss of a microcapsule sample during a 2 h isotherm at a given temperature. All capsules contained a combination of 15 pph Epon 828 resin and a solvent. Fig. 7 shows that capsules with chlorobenzene as the core solvent (Epon 828–ClB) exhibited a minimal mass loss during a 2 h isotherm at 100 °C, but lost over 40% of its core material during a 2 h isotherm at 150 °C. Capsules with phenylacetate as the core solvent (Epon 828–PA) were more temperature stable, showing a mass loss of less than 5% during a 2 h isotherm at 150 °C. The highest level of thermal stability for the resin–solvent combinations investigated was reported using capsules with ethyl phenylacetate as the core solvent (Epon 828–EPA), showing a mass loss of less than 20% during a 2 h isotherm at 180 °C. Only during an isotherm at the elevated temperature of 210 °C was more than 50% of the core material lost for Epon 828–EPA capsules.
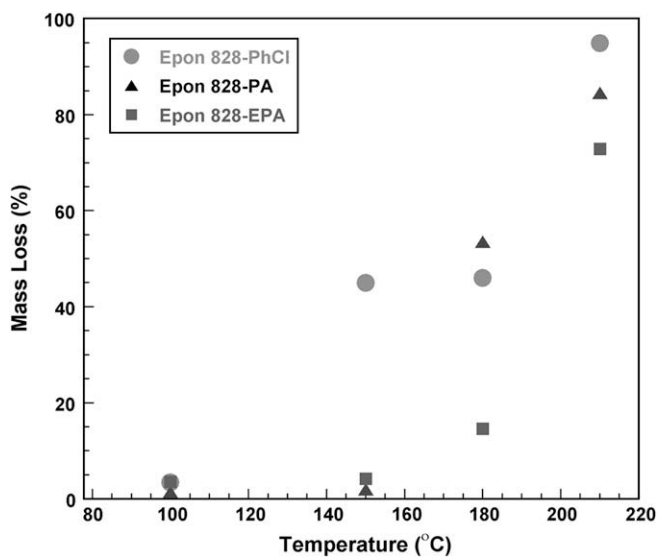


**Fig. 7.** Mass loss reported for epoxy resin–solvent microcapsules during isothermal TGA experiments at the specified temperatures. The mass loss percentages shown were recorded at the end of a 2 h isotherm.
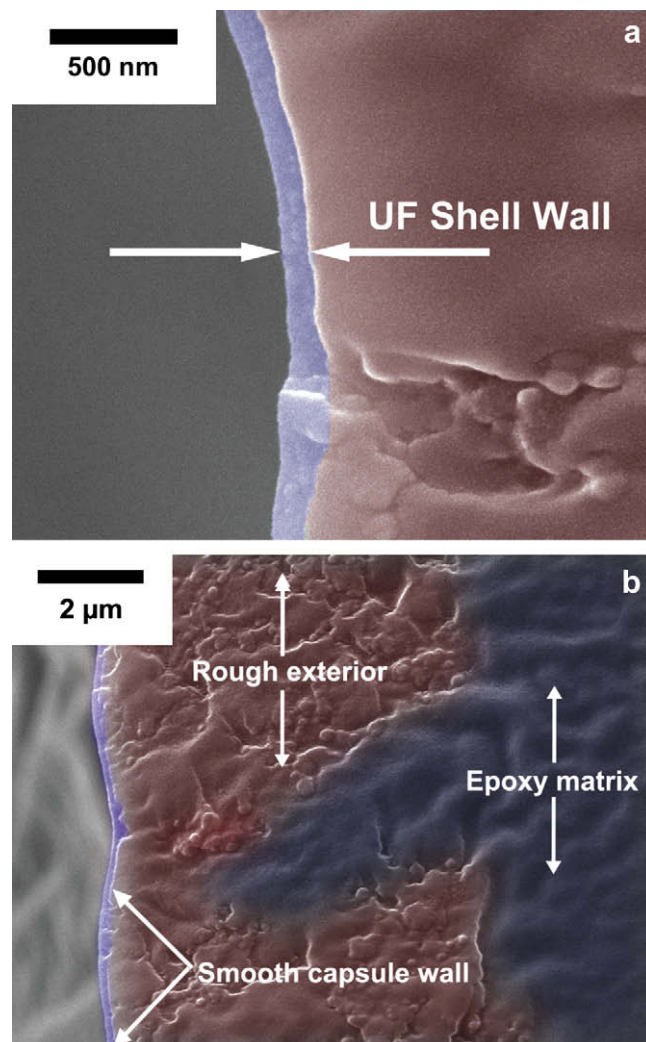
### 3.5. Shell wall morphology

Scanning electron microscopy was performed to analyze capsule surface morphology and shell wall thickness. A dried powder of sieved microcapsules was placed on a conductive carbon tape attached to a mounting piece for imaging. Fig. 8a and b shows resin–solvent filled microcapsules and their rough exterior shell walls. Some microcapsules were ruptured with a razor blade to allow for viewing of the inner shell wall morphology. Fig. 8c shows the smooth inner shell wall membrane with the rough exterior visible in the background.

In the case of resin–solvent microcapsules, the capsule shell wall is comprised of two distinct regions that include a thin continuous inner shell wall, and a thicker rough exterior shell wall. The thin continuous interior shell wall was measured to be 160 (±25) nm thick (Fig. 9a). This continuous membrane is formed as urea and formaldehyde react in the aqueous phase resulting in

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[1] Additional TGA and DSC results are available in the electronic supplementary material.
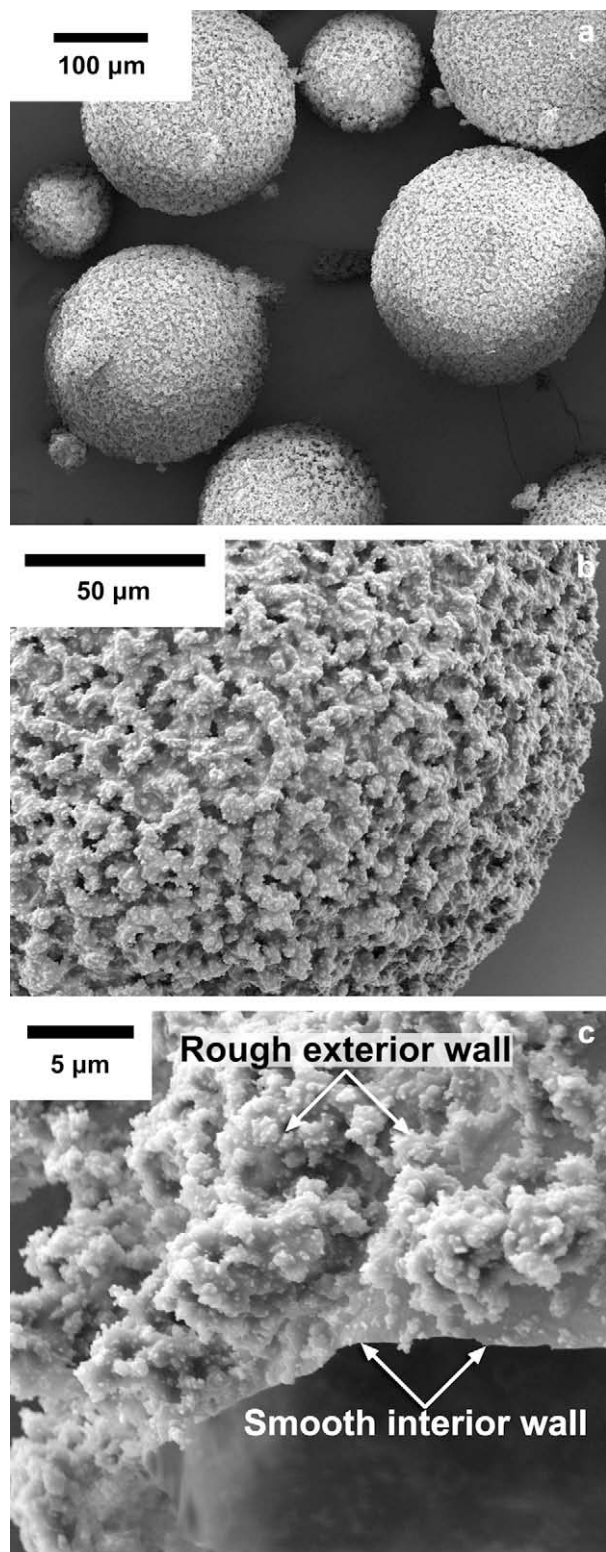
Fig. 8. SEM images of Epon 828–EPA microcapsules showing (a) the spherical capsules produced, (b) the rough exterior shell wall, and (c) a view of the interior of a ruptured microcapsule showing the smooth interior wall and the rough exterior of the wall.



Fig. 9. SEM images of Epon 828–EPA microcapsules in false color showing (a) the shell wall (light blue) of a ruptured microcapsule and (b) the three-part interphase region comprised of smooth shell wall (light blue), rough exterior (red), and epoxy matrix (dark blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### 3.6. Incorporation into an epoxy matrix

When the capsules are incorporated into an epoxy matrix, the rough exterior shell wall of the capsules leads to the formation of a three-part interphase region (Fig. 9b) comprised of the smooth shell wall, the rough exterior shell wall infiltrated by matrix epoxy, and the epoxy matrix. The ability of the exterior epoxy matrix to partially penetrate the rough exterior wall of the capsules is advantageous for promoting bonding to the surrounding polymer material, increasing the probability of capsule fracture, and therefore increasing healing agent delivery. Even after extended capsule shelf time, the capsules retained their core integrity and fractured in a brittle manner when incorporated in an epoxy matrix.

When the microcapsules containing the resin–solvent combination are ruptured, the reactive contents are delivered to the crack plane. Fig. 10a shows ruptured microcapsules and regions of deposited epoxy film. The buckled regions (Fig. 10b) were shown to be epoxy material deposited from the capsules in a prior publication [25].

a low molecular weight polymer that deposits at the oil–water interface. As the UF reaction progresses, the rough exterior is formed as colloidal UF particles coalesce, and deposit along the interface [13].
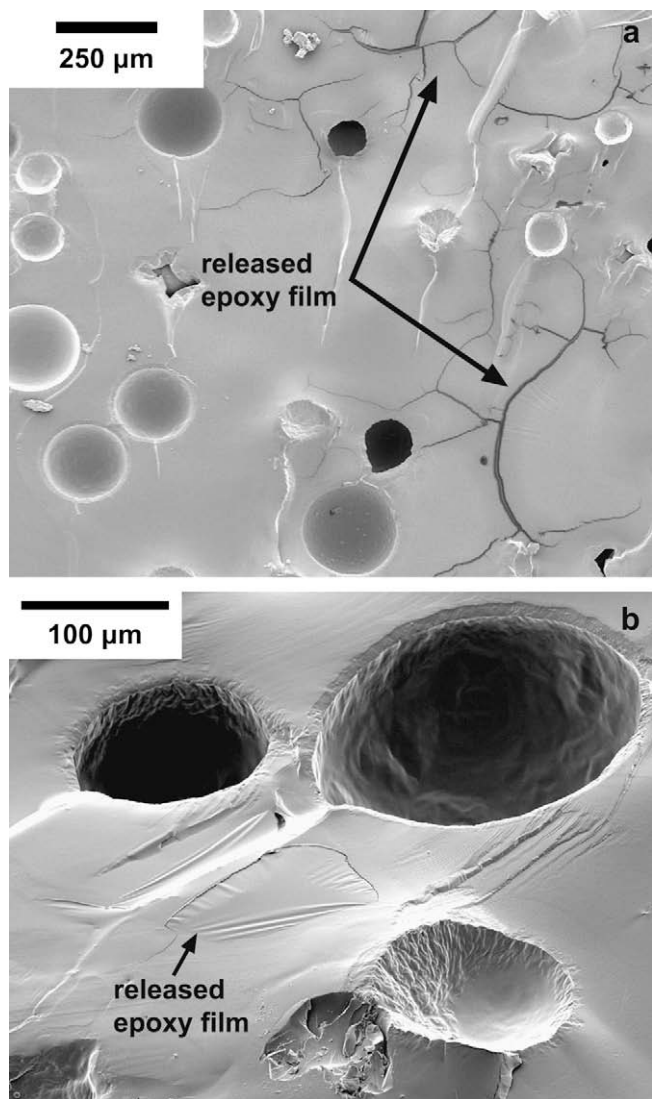
**Fig. 10.** Images of the crack plane showing (a) ruptured Epon 828–EPA microcapsules and regions of deposited epoxy film and (b) a titled view of the crack plane showing the buckled epoxy film.

## 4. Conclusions

A robust method for the preparation of microcapsules containing reactive resin and solvent as the core material was developed. The resulting capsules were comprised of a thin continuous shell wall (160 nm) and a rough exterior shell wall, allowing for better adhesion to an epoxy matrix in self-healing polymers. Capsules were prepared using this method for sizes ranging from 300 nm to over 300 μm.

DSC analysis confirmed that the capsules contained both reactive epoxy resin and solvent. The relative resin–solvent ratio in the microcapsules matched the expected encapsulation core, and that the resin–solvent mixture is best maintained using the epoxy–EPA combination at elevated temperatures.

The resin–solvent capsules were successfully incorporated into an epoxy matrix and ruptured by a propagating crack. The crack plane contained many of the same features seen in previous self-healing studies such as crack tails and regions of healed material. An epoxy film was visible on the crack plane, providing evidence that the reactive epoxy resin was delivered to the damage location,

and that capsules prepared by this method are suitable for use in self-healing materials.

## Appendix. Supplementary information

Supplementary information associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.12.040.

## References

[1] Benita S, editor. Microencapsulation: methods and industrial applications. 2nd ed. Informa Healthcare; 2005.
[2] Ghosh SK, editor. Functional coatings: by polymer microencapsulation. Wiley-VCH; 2006.
[3] Kondo A. Microcapsule processing and technology. Marcel Dekker; 1979.
[4] Pothakamury UR, Barbosa-Canovas GV. Trends in Food Science and Technology 1995;6(12):397–406.
[5] Cosco S, Ambrogi V, Musto P, Carfagna C. Journal of Applied Polymer Science 2007;105(3):1400–11.
[6] Yuan L, Liang GZ, Xie JQ, Li L, Guo J. Polymer 2006;47(15):5338–49.
[7] Yuan YC, Rong MZ, Zhang MQ, Chen J, Yang GC, Li XM. Polymer 2008;49(10):2531–41.
[8] Peters GH, Schaab CK, Hilbelink RD, Davis TR. Development of Multipurpose Capsular Adhesive Systems. United States: NTIS; 1971.
[9] Bank M, Bayless R, Botham R, Shank P. Modern Plastics 1973;50(11):84–6.
[10] Shulkin A, Stover HDH. Journal of Membrane Science 2002;209(2):421–32.
[11] Tobitsuka K, Miura M, Kobayashi S. Journal of Agricultural and Food Chemistry 2006;54(14):5069–76.
[12] Rule JD, Brown EN, Sottos NR, White SR, Moore JS. Advanced Materials 2005;17(2):205–8.
[13] Brown EN, Kessler MR, White SR, Sottos NR. Journal of Microencapsulation 2003;20(6):719–30.
[14] Blaiszik BJ, Sottos NR, White SR. Composites Science and Technology 2008;68(3–4):978–86.
[15] Yuan L, Liang GZ, Xie JQ, He SB. Colloid and Polymer Science 2007;285(7):781–91.
[16] Liu X, Sheng X, Lee JK, Kessler MR. Proceedings of the SPIE 2007;6423:642337–9.
[17] Brown EN, Sottos NR, White SR. Experimental Mechanics 2002;42(4):372–9.
[18] Cho SH, Andersson HM, White SR, Sottos NR, Braun PV. Advanced Materials 2006;18(8):997–1000.
[19] Keller MW, White SR, Sottos NR. Advanced Functional Materials 2007;17(14):2399–404.
[20] Rule JD, White SR, Sottos NR. Polymer 2007;48(12):3520–9.
[21] White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. Nature 2001;409(6822):794–7.
[22] Kamphaus JM, Rule JD, Moore JS, Sottos NR, White SR. Journal of the Royal Society Interface 2008;5(18):95–103.
[23] Wilson GO, Moore JS, White SR, Sottos NR, Andersson HM. Advanced Functional Materials 2008;18(1):44–52.
[24] Caruso MM, Delafuente DA, Ho V, Moore JS, Sottos NR, White SR. Macromolecules 2007;40(25):8830–2.
[25] Caruso MM, Blaiszik BJ, White SR, Sottos NR, Moore JS. Advanced Functional Materials 2008;18(13):1898–904.
[26] Van Der Zwaag S. Plastics Engineering 2008;64(4):36–41.
[27] Wool RP. Soft Matter 2008;4(3):400–18.
[28] Keller MW, Blaiszik BJ, White SR, Sottos NR. In: Wagg D, Bond IP, editors. Wiley; 2007. p. 314.
[29] Bocanegra R, Gaonkar AG, Barrero A, Loscertales IG, Pechack D. Journal of Food Science 2005;70(8):492–7.
[30] Kobaslija M, McQuade DT. Macromolecules 2006;39(19):6371–5.
[31] Mathiowitz E, Cohen MD. Journal of Membrane Science 1989;40(1):55–65.
[32] Soto-Portas ML, Argillier JF, Mechin F, Zydowicz N. Polymer International 2003;52(4):522–7.
[33] Taguchi Y, Yokoyama H, Kado H, Tanaka M. Colloids and Surfaces A 2007;301(1–3):41–7.
[34] Petrie EM. Epoxy adhesive formulations. New York: McGraw-Hill; 2006.

[35] Nelson WM. Green solvents for chemistry: perspectives and practice. Oxford University Press; 2003.
[36] Lide DR, Frederikse HPR. CRC handbook of chemistry and physics. CRC Press; 1996.
[37] Chlorobenzene MSDS No. 284513, v.1. 10; Phenyl acetate MSDS No. W395803, v.1. 4; Ethyl phenylacetate MSDS No. W245208, v.1. 3; Sigma–Aldrich: St. Louis, MO, November 18, 2008.
[38] Taylor GI. Proceedings of the Royal Society of London 1932;138:41–8.
[39] Ramírez LP, Landfester K. Macromolecular Chemistry and Physics 2003;204(1):22–31.
[40] Tiarks F, Landfester K, Antonietti M. Langmuir 2001;17(3):908–18.
[41] Peloux J, Tighzert L, Pascault JP, Malinge J, Sillion B. Polymer Bulletin (Berlin) 1988;20(2):207–13.